QUANTITATIVE OPTICAL DIAGNOSTICS OF PLASMAS

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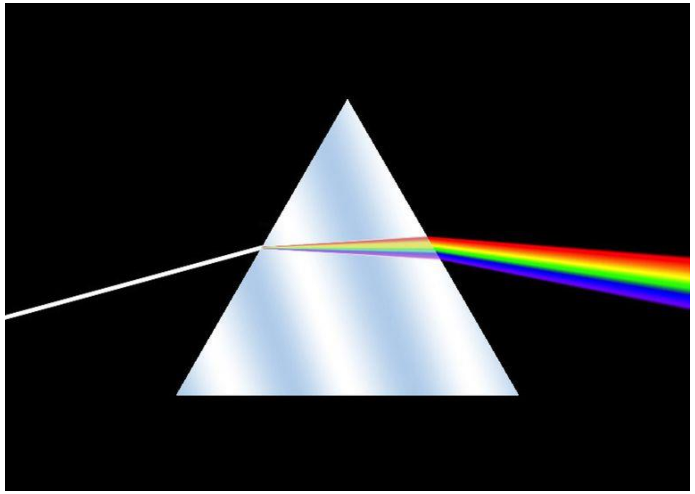
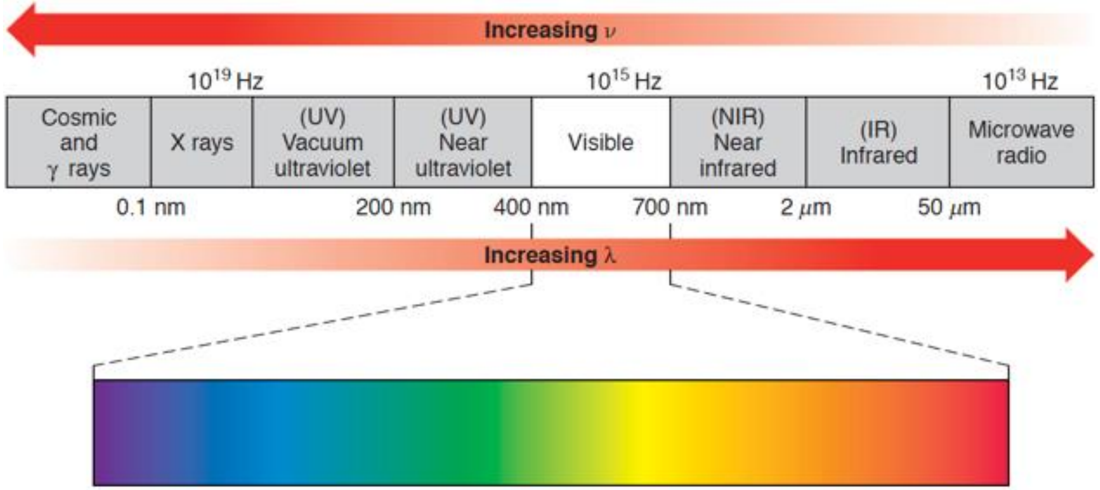
Course Overview

Underlying science: atomic and molecular spectroscopy

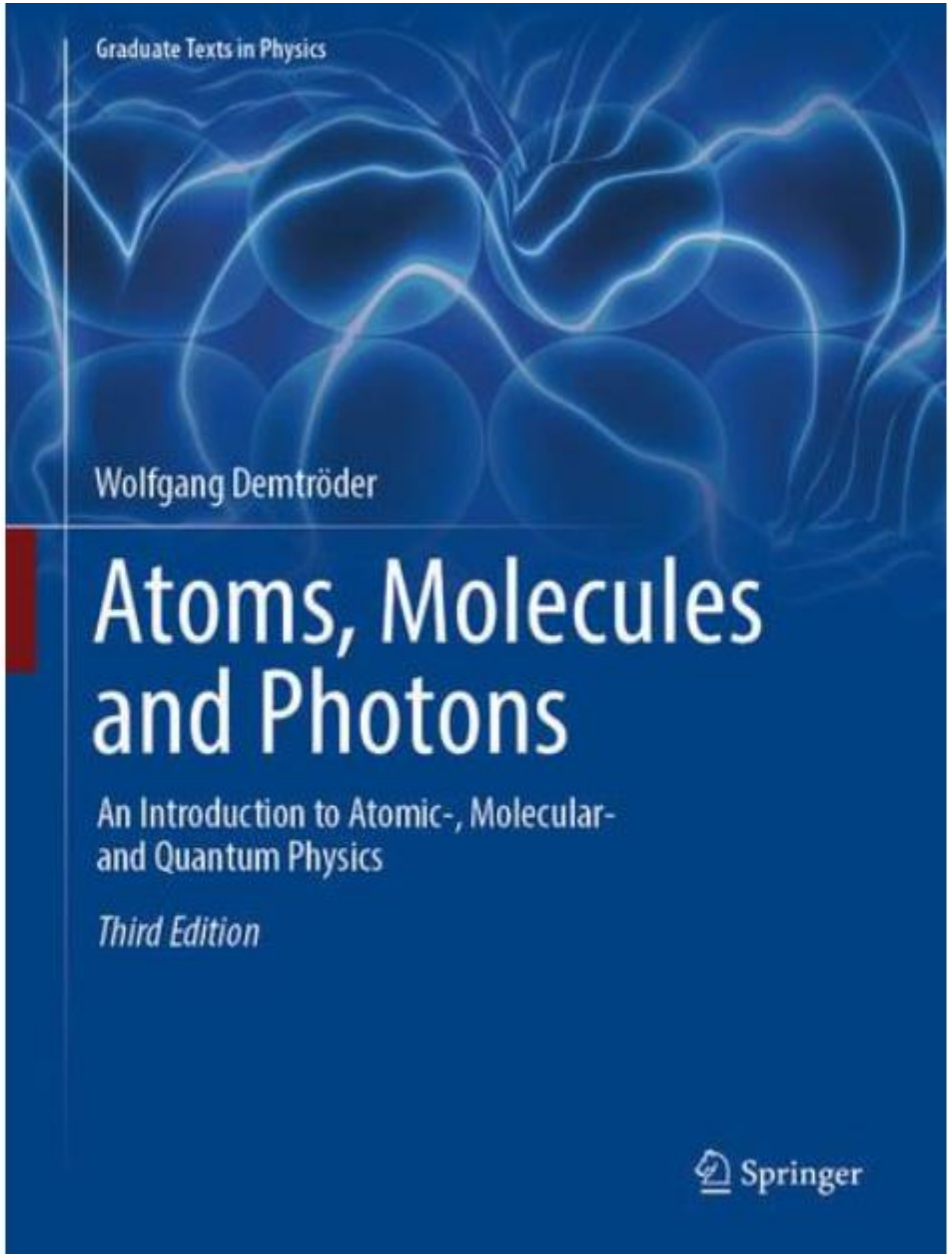




- **Introduction to fundamentals of atomic and molecular spectroscopy**
- **Quantitative emission and absorption spectroscopy**
- **Laser induced fluorescence (LIF) and Two-photon Absorption laser induced fluorescence (TALIF)**
- **Laser Scattering techniques (Rayleigh, Raman, Thomson)**
- **Non-linear techniques (CARS, E-CARS, E-FISH)**

Fundamentals of Atomic and Molecular Spectroscopy

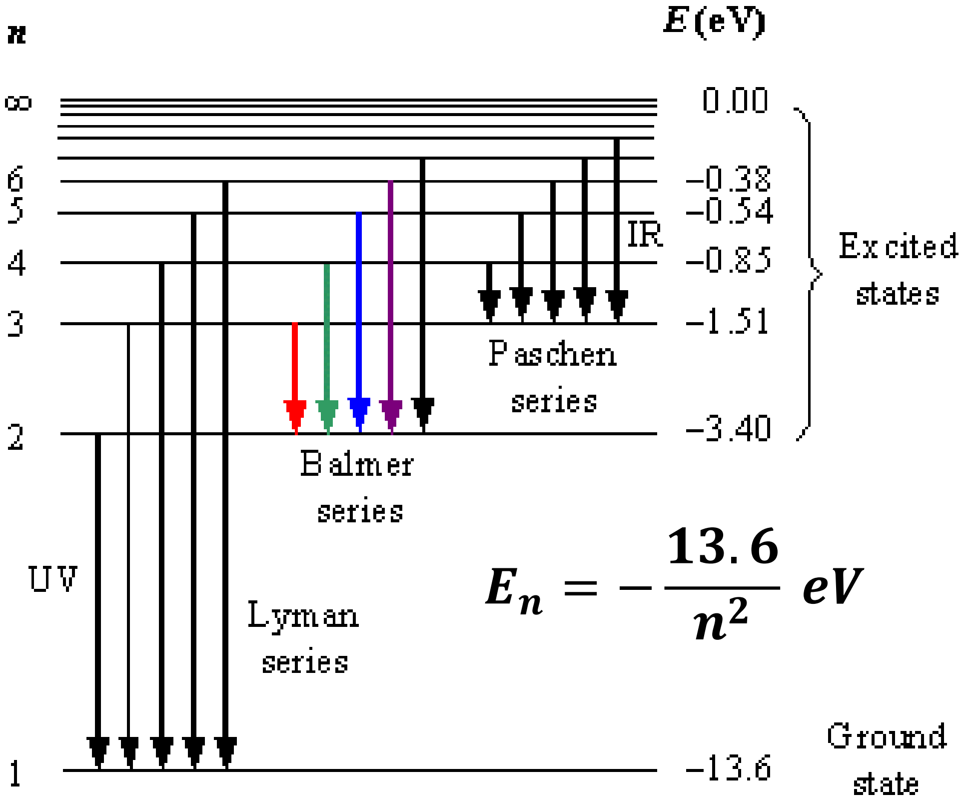
Additional Information



Slides are not complete, a few textbooks can be useful

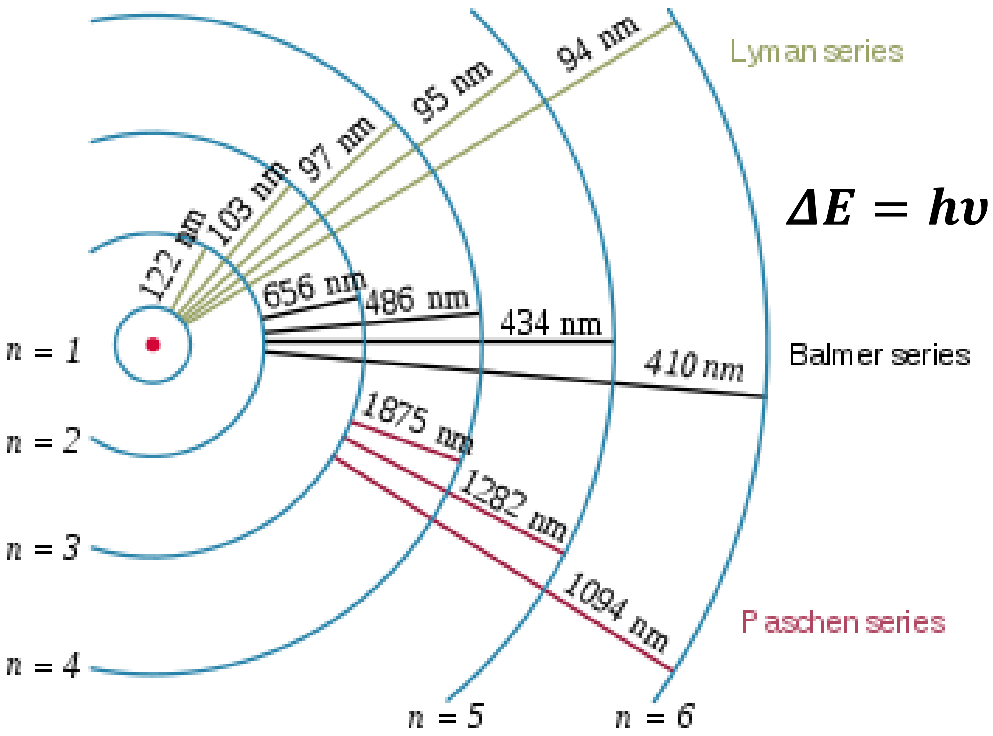
Electronic Transitions of the Hydrogen Atom

Hydrogen atom energy levels



$$E_n = -\frac{13.6}{n^2}\ eV$$

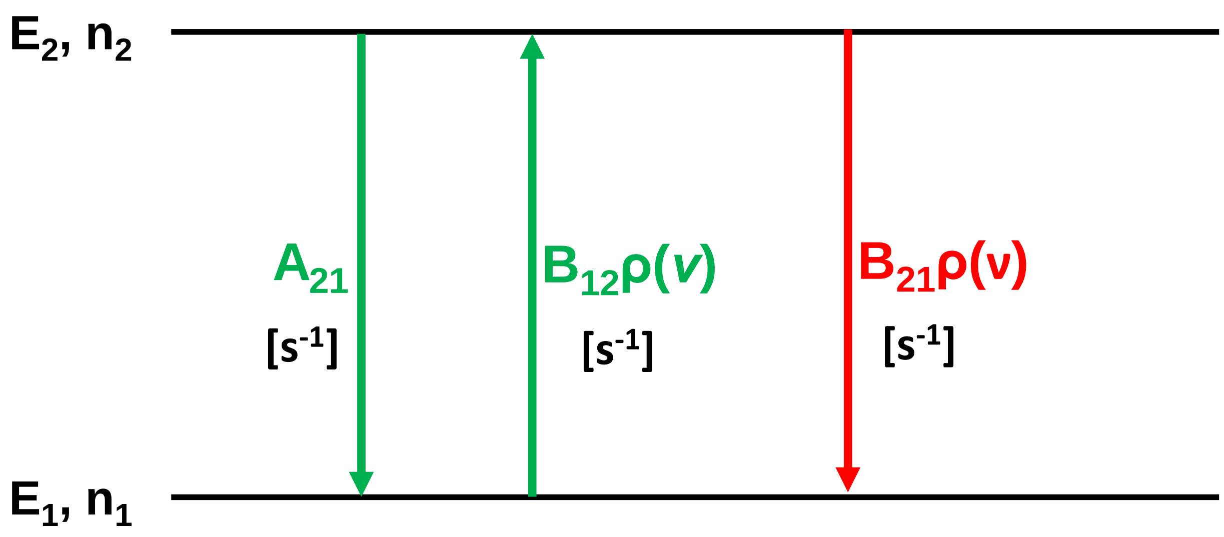
Bohr model of the hydrogen atom



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

Hydrogen atom emission spectrum in the visible spectral region

Two-level System: Optical Transitions



$$\Delta E = E_2 - E_1 = h\nu_{21} = h\frac{c}{\lambda_{21}}$$

E_i: energy of level I

n_i: population of level *i*

A_{21}: Einstein coefficient for spontaneous emission (transition probability)

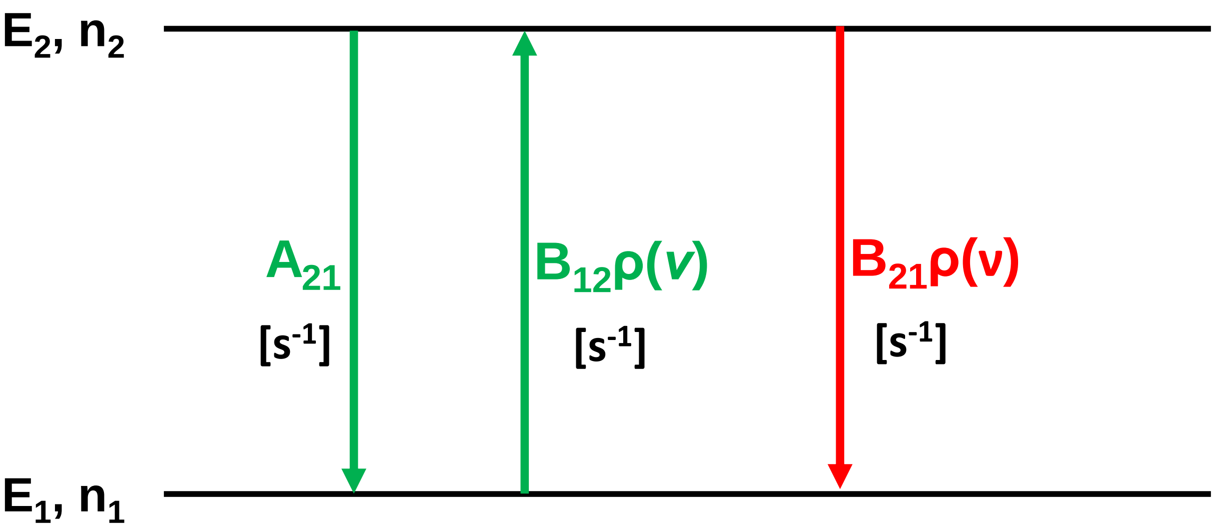
$B_{12}\rho(v)$, $B_{21}\rho(v)$: transition probability for absorption, stimulated emission

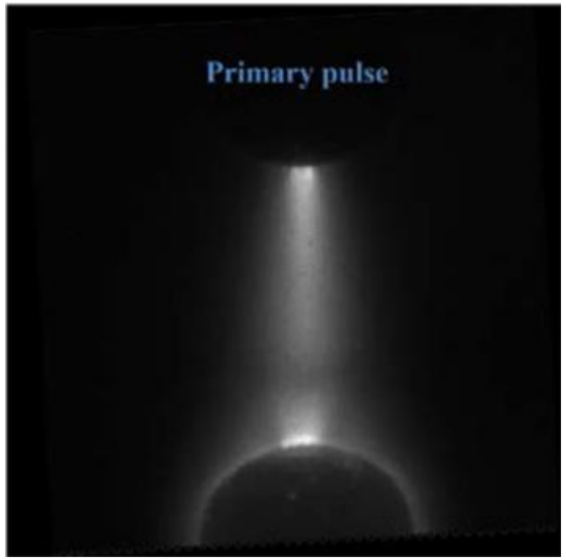
$\rho(v)$: spectral density function

$$\left(\frac{dn_2}{dt}\right)_{spontaneous} = -A_{21}n_2$$

$$\left(\frac{dn_1}{dt}\right)_{absorption} = -B_{12}\varrho(\nu)n_1$$

Emission Intensity





Roettgen *et al*, Plasma Sources Sci. Technol. 25 (2016) 055009

Local emissivity

$$e_\lambda = \frac{1}{4\pi} h\nu A_{21} N_2 \phi(\lambda)$$

Wavelength-dependent measured intensity

$$I_\lambda = \int_l e_\lambda(l)\,\mathrm{d}l = \frac{1}{4\pi} L h\nu A_{21} N_2 \phi(\lambda).$$

Uniform volumetric absorbing medium

***Φ*(v): spectral line profile**

- **Information about excited states can be accessed**
- ***Φ*(v) cannot be Dirac's function because of Heisenberg's uncertainty principle→ Natural broadening**

Line Broadening

Atomic line broadening due to:

- **Doppler broadening** (thermal broadening, temperature effect)

$$\Delta\lambda_{Doppler} \propto \sqrt{T_g}$$

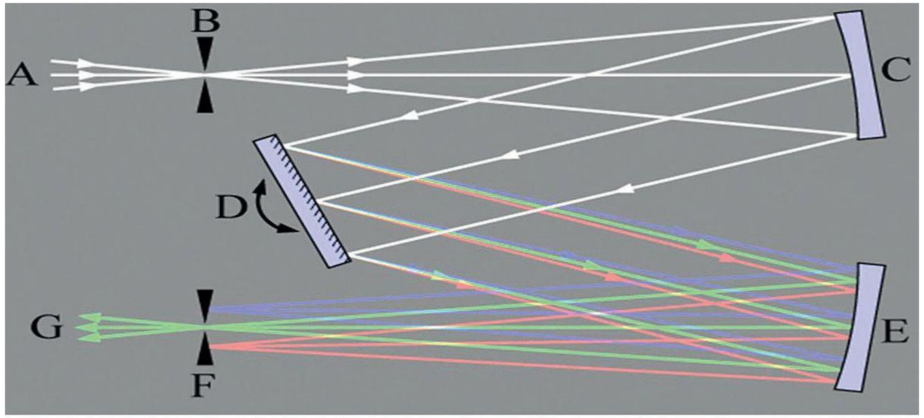
- **Van der Waals broadening** (emitter perturbed by atoms and molecules)

$$\boxed{\Delta\lambda_{vdW} \propto \frac{p}{T_g^{\ 0.7}}}$$

- **Stark broadening**
- **Instrumental broadening / apparatus function** (finite resolution of the spectrometer)

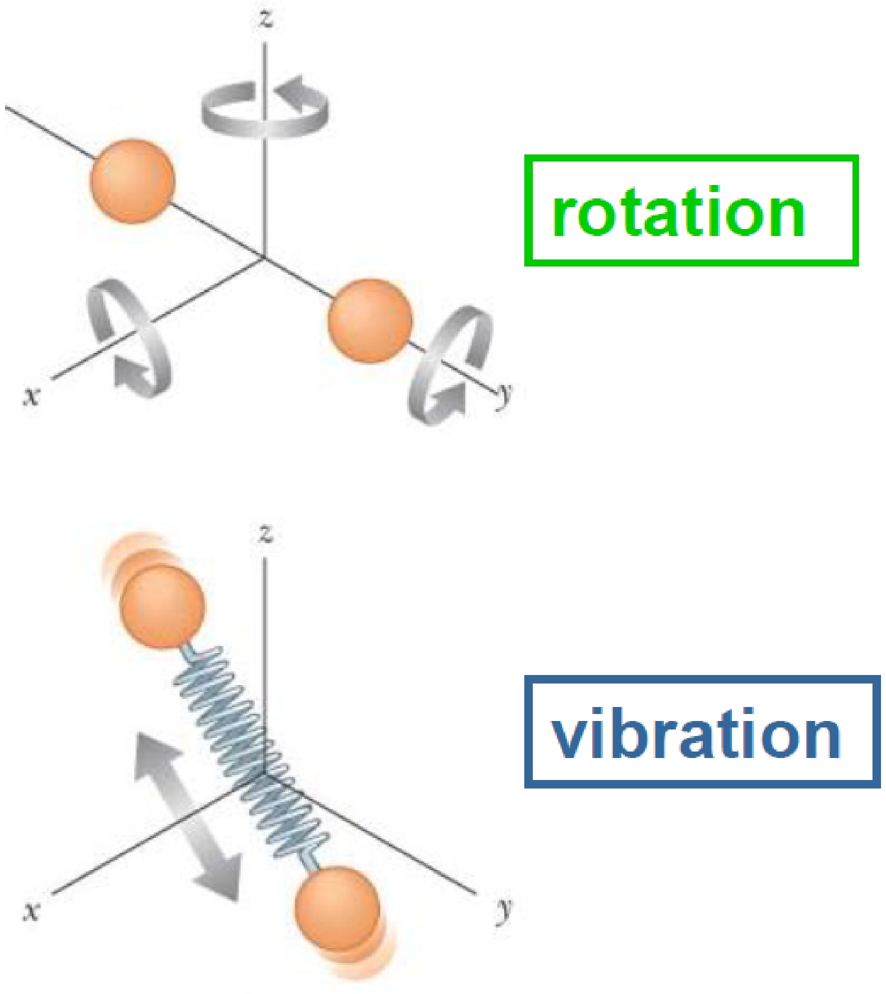
for high resolution spectrometer, width of spectral lines provides information on gas temperatures!

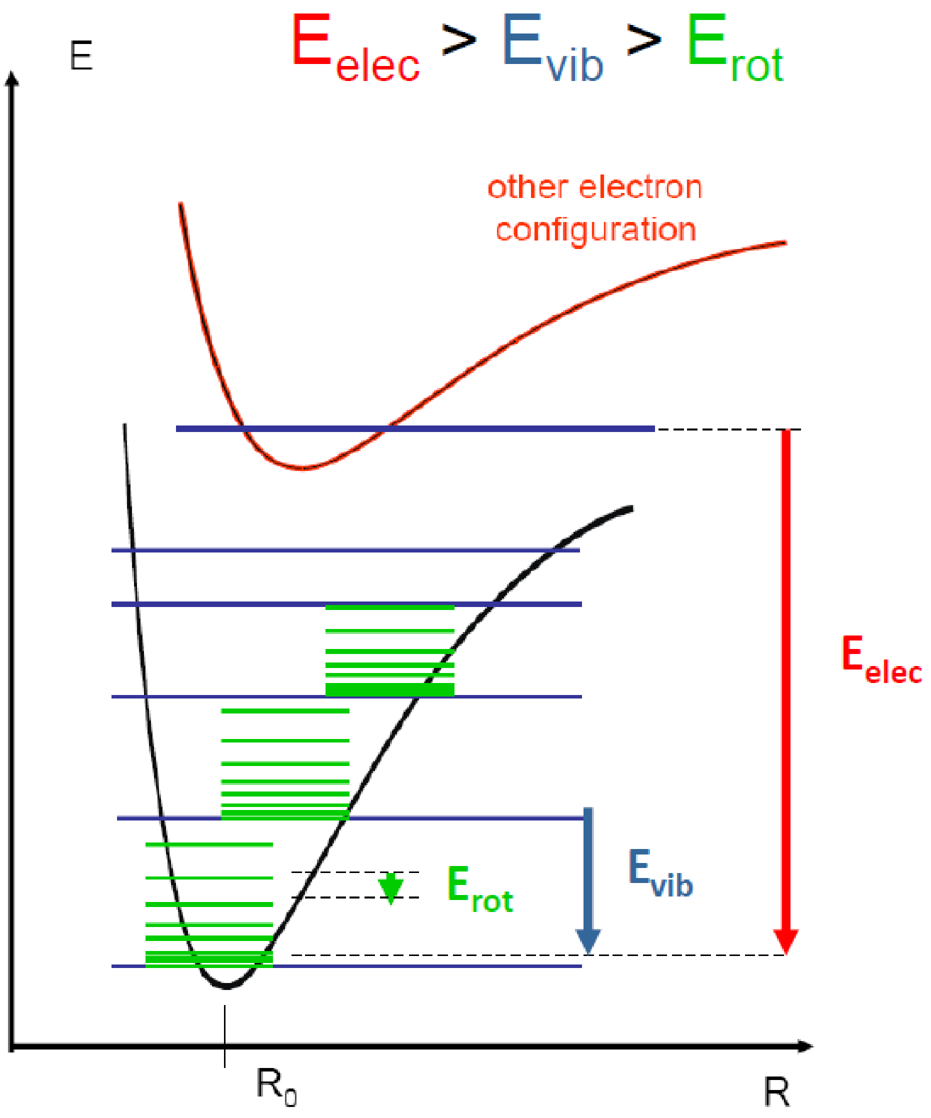
Czerny-Turner spectrometer



A. Incoming light source
B. Entrance slit
C. Collimating mirror
D. Grating on turret
E. Focusing mirror
F. Exit slit
G. Single channel detector

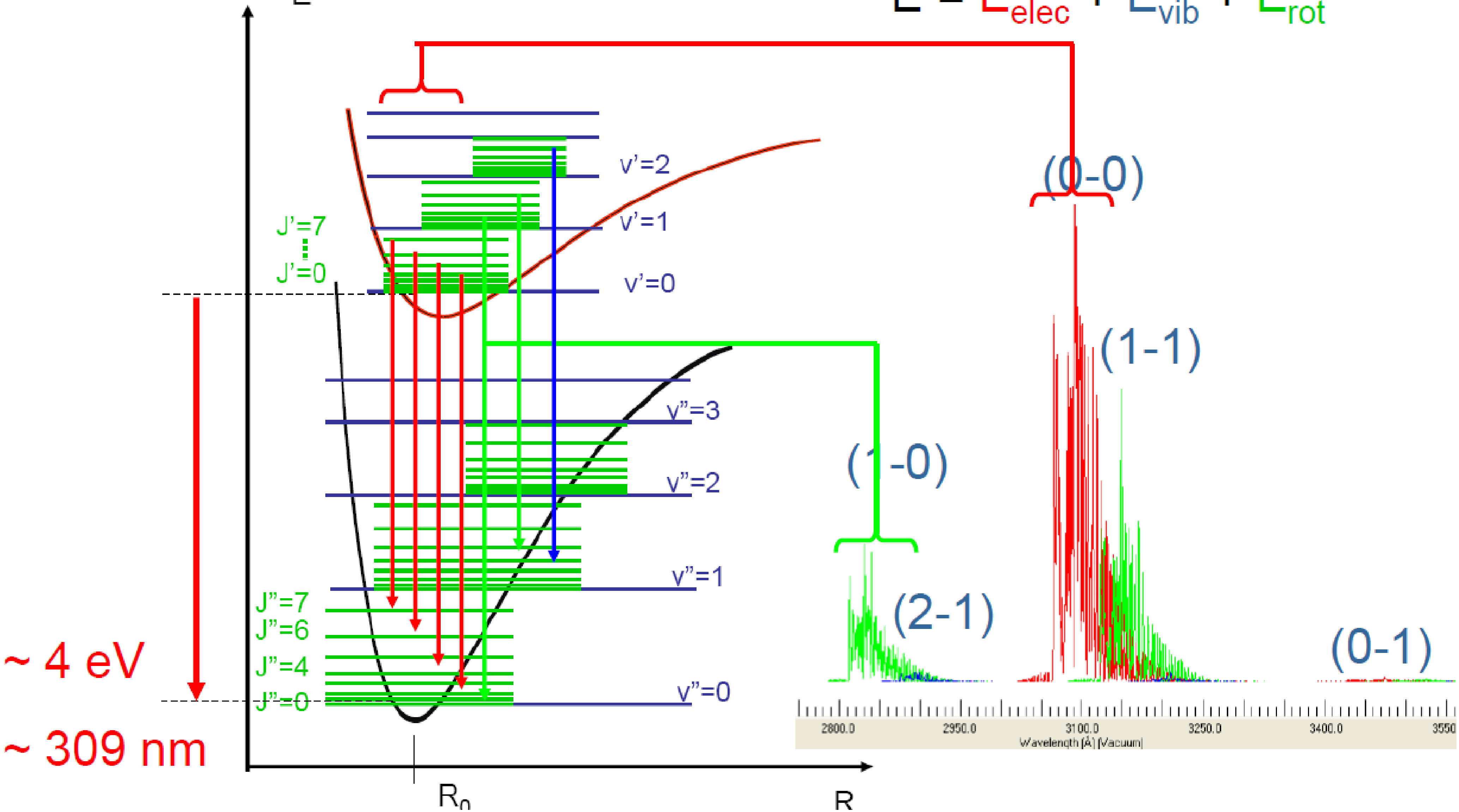
Diatomic Molecules



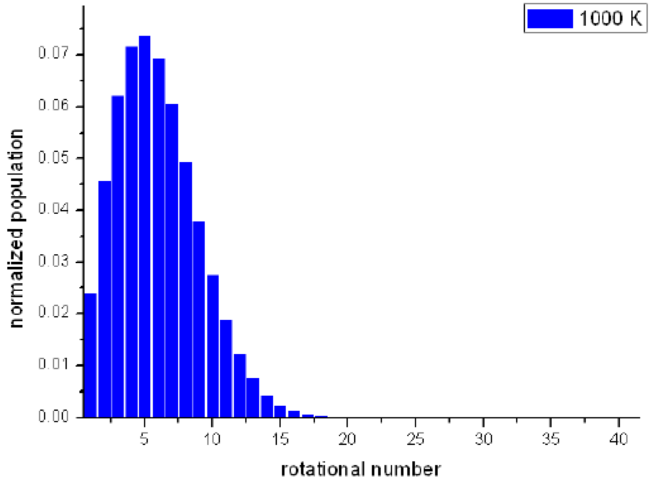


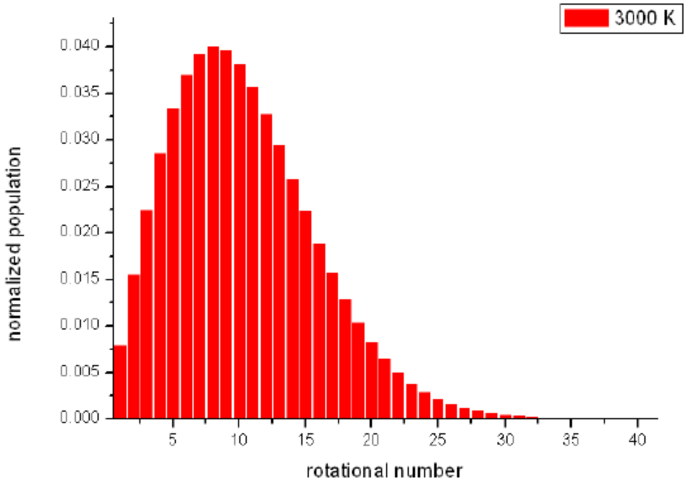
Molecular Spectra

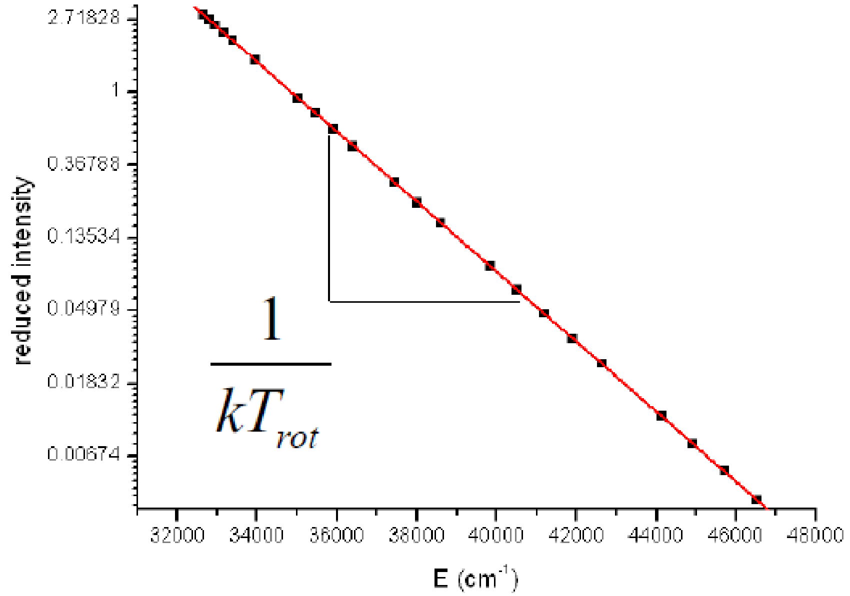
$E = E_{elec} + E_{vib} + E_{rot}$



Rotational Temperature Effects







Higher rotational states occupied for higher temperatures !!!

(radiative) transition probability

rotational energy

literature

$$population_J \propto I_{JJ'} \propto (2J+1) A_{JJ'} \nu \exp\left(\frac{-E_J}{kT_{rot}}\right)$$

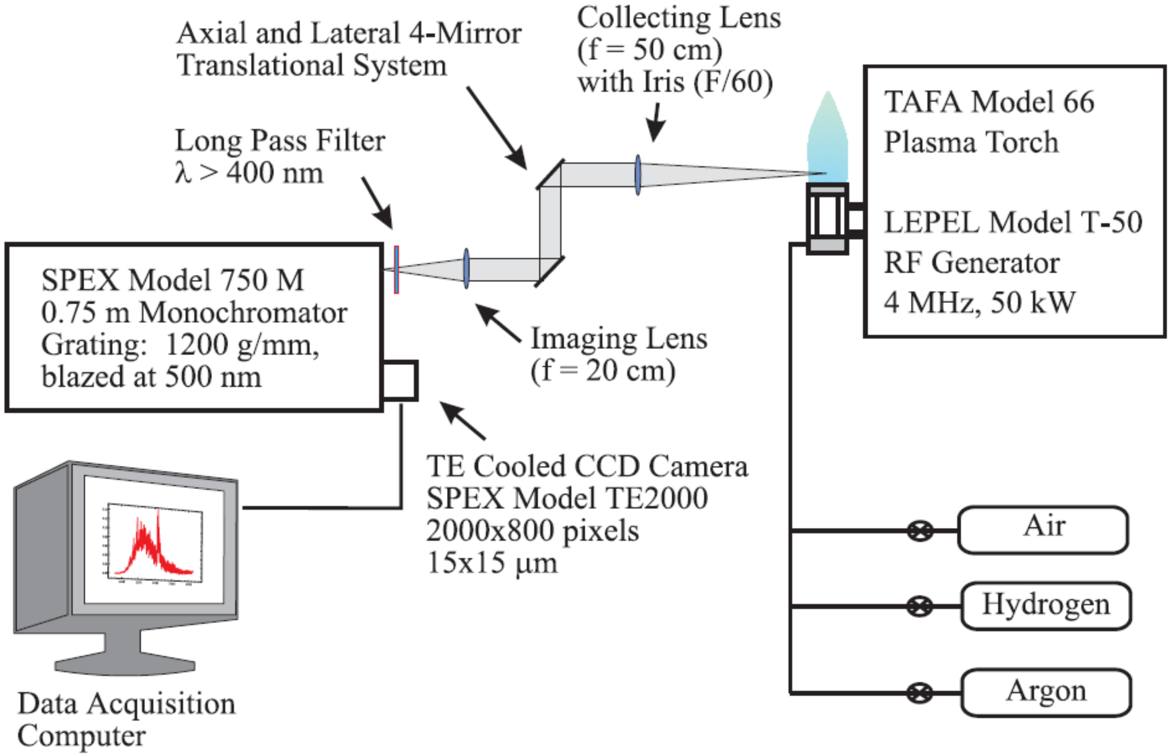
measured intensity

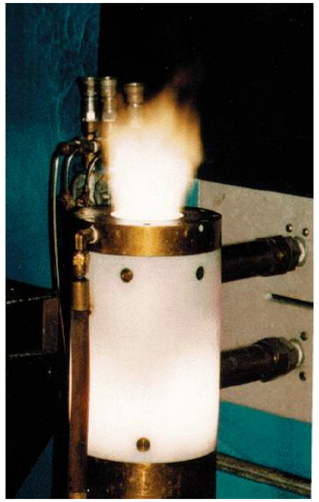
needed !

$$I_{JJ'} \propto (2J+1) A_{JJ'} \nu \exp\left(\frac{-E_J}{kT_{rot}}\right) \quad \longrightarrow \quad \ln\left(\frac{I}{(2J+1) A_{JJ'} \nu}\right) = \left(\frac{-E_J}{kT_{rot}}\right) + cst$$

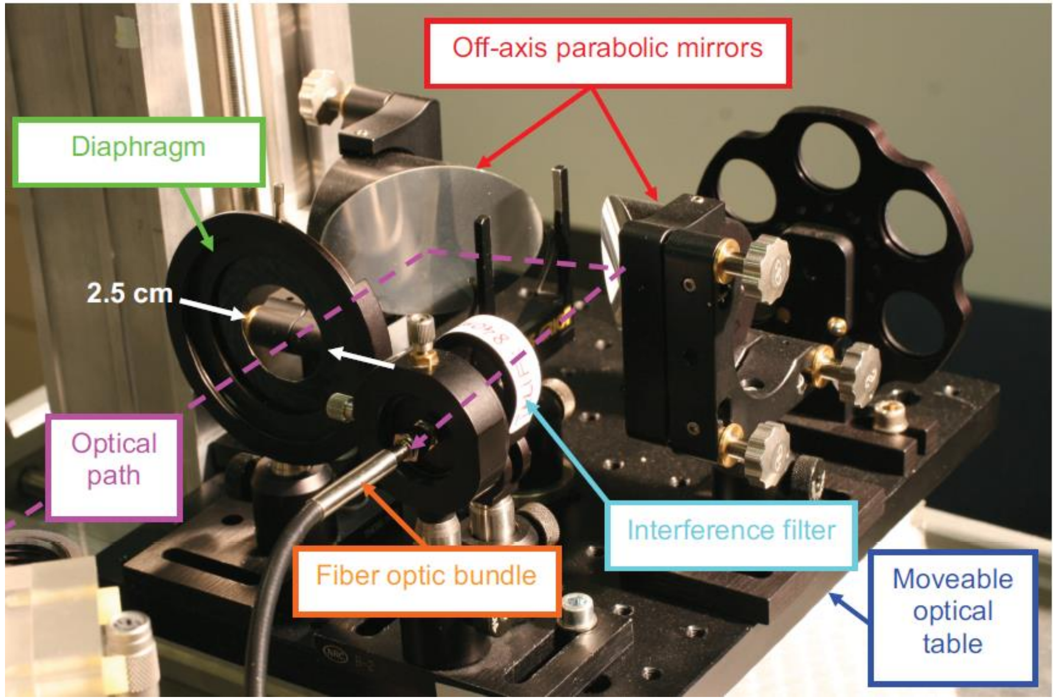
Quantitative Emission and Absorption Spectroscopy

Optical Emission Spectroscopy (OES)





Laux *et al*, Plasma Sources Sci. Technol. 12 (2003) 125–138

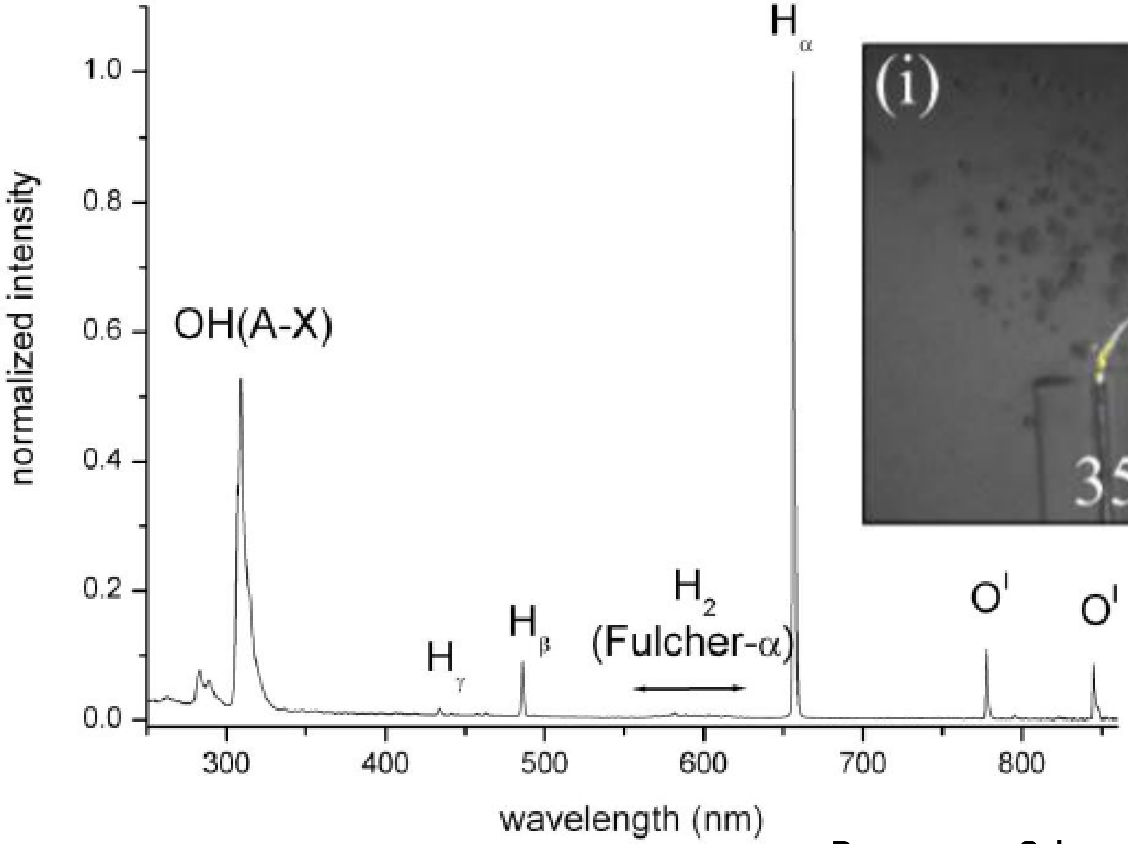


David Pai, PhD Thesis Ecole Centrale Paris (2008)

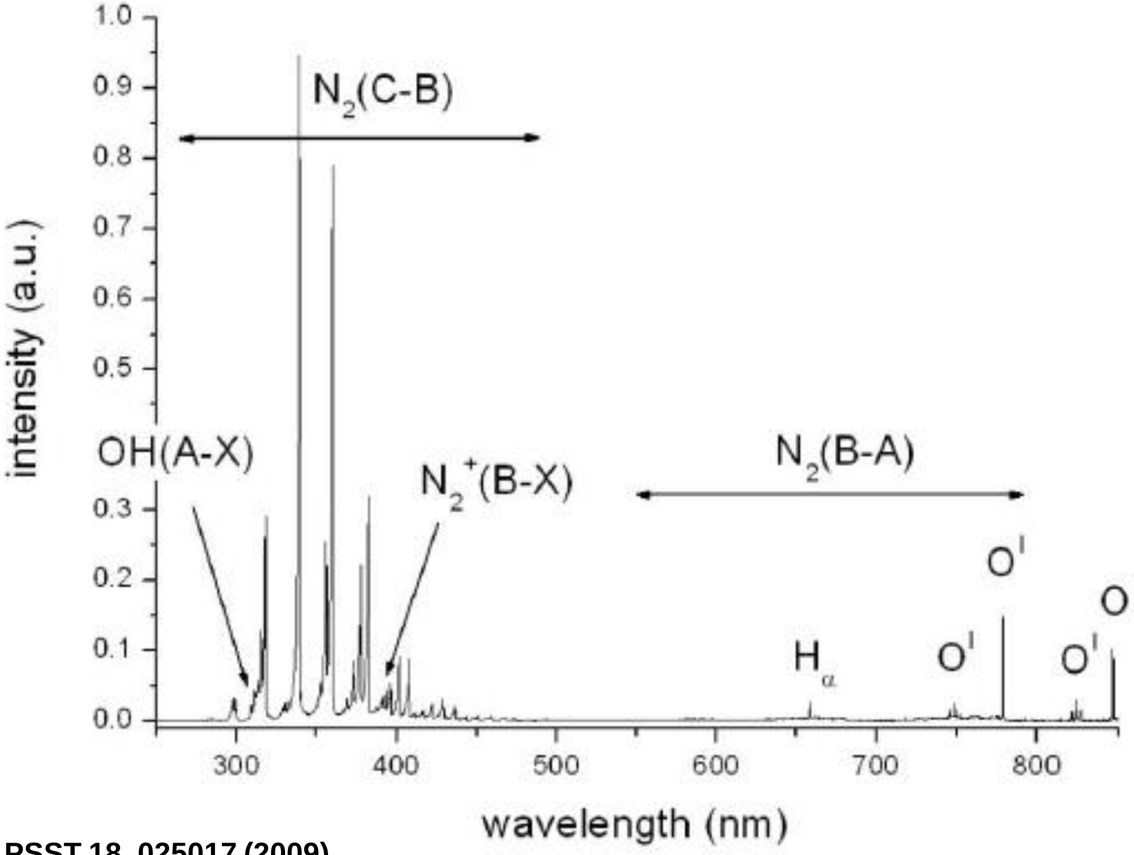
- **Passive diagnostic**
- **Line-of-sight integrated**
- **High temporal resolution and 1D measurements achievable**
- **Primarily gives information about species in their excited states**
- **Can be used to measure: temperatures, neutral species densities, electron densities and electric field vectors**

Typical Emission Spectra in Plasmas

Direct discharge in water



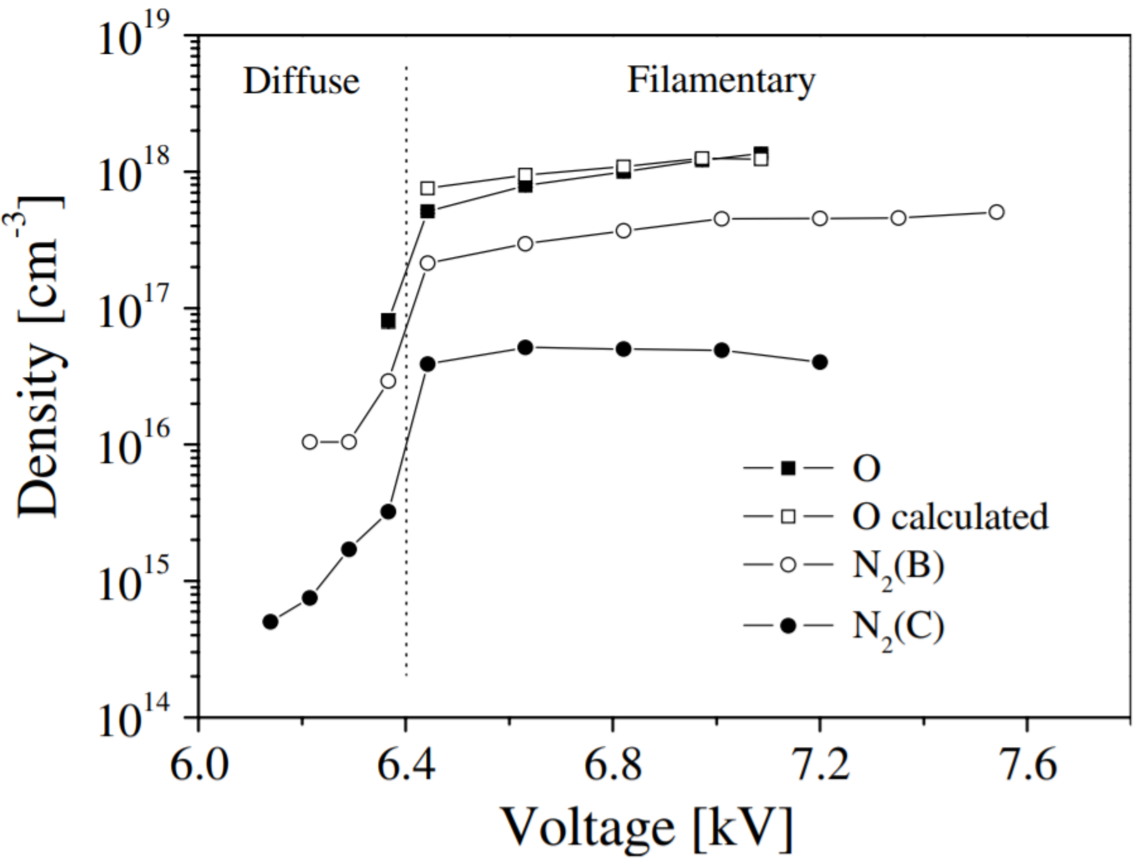
Discharge in humid air



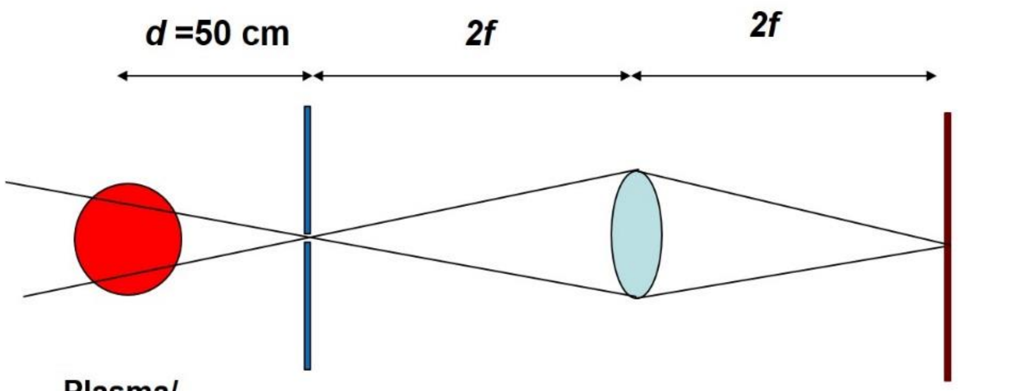
Bruggeman , Schram , Gonzalez et al PSST 18, 025017 (2009)

- N_2(C-B), OH(A-X), N_2^+(B-X) → Rotational temperatures measurements → Gas temperatures measurements
- Atomic hydrogen lines → Stark broadening → Electron densities measurements
- Atomic hydrogen lines → Stark shifting → Electric field vector measurements

Excited States Absolute Densities Measurements

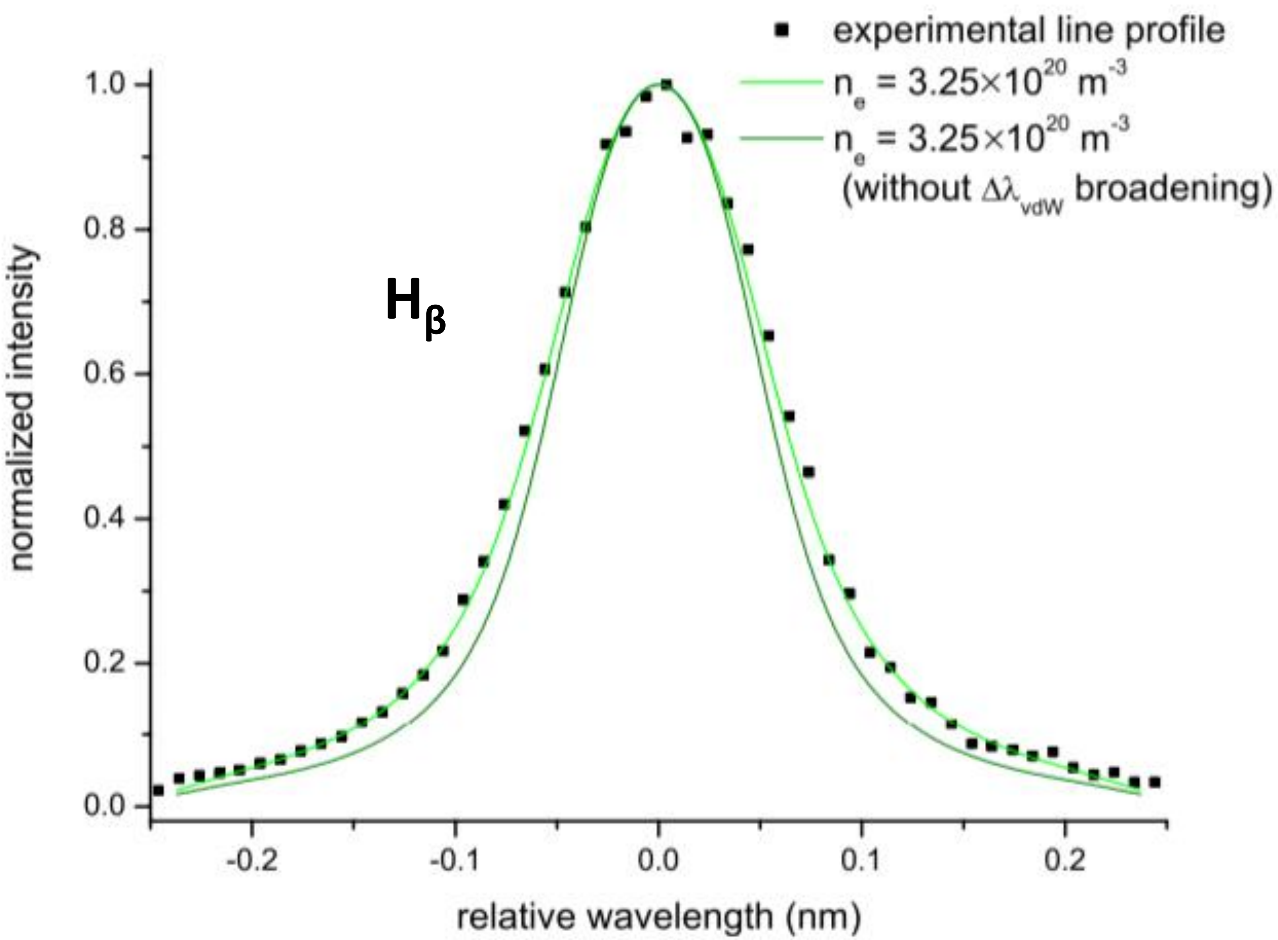


Stancu et al J. Phys. D: Appl. Phys. 43 (2010) 124002



- **Densities of $N_2(B)$ and $N_2(C)$ were obtained from $N_2(B-C)$ and $N_2(B-A)$ spectra**
- **Absolute densities obtained using standard quartz tungsten halogen (QTH) lamps**

Electron Density Measurements



$\Delta\lambda_{Doppler} \sim (T_g)^{1/2}$

$\Delta\lambda_{Stark} \sim (n_e)^{2/3}$

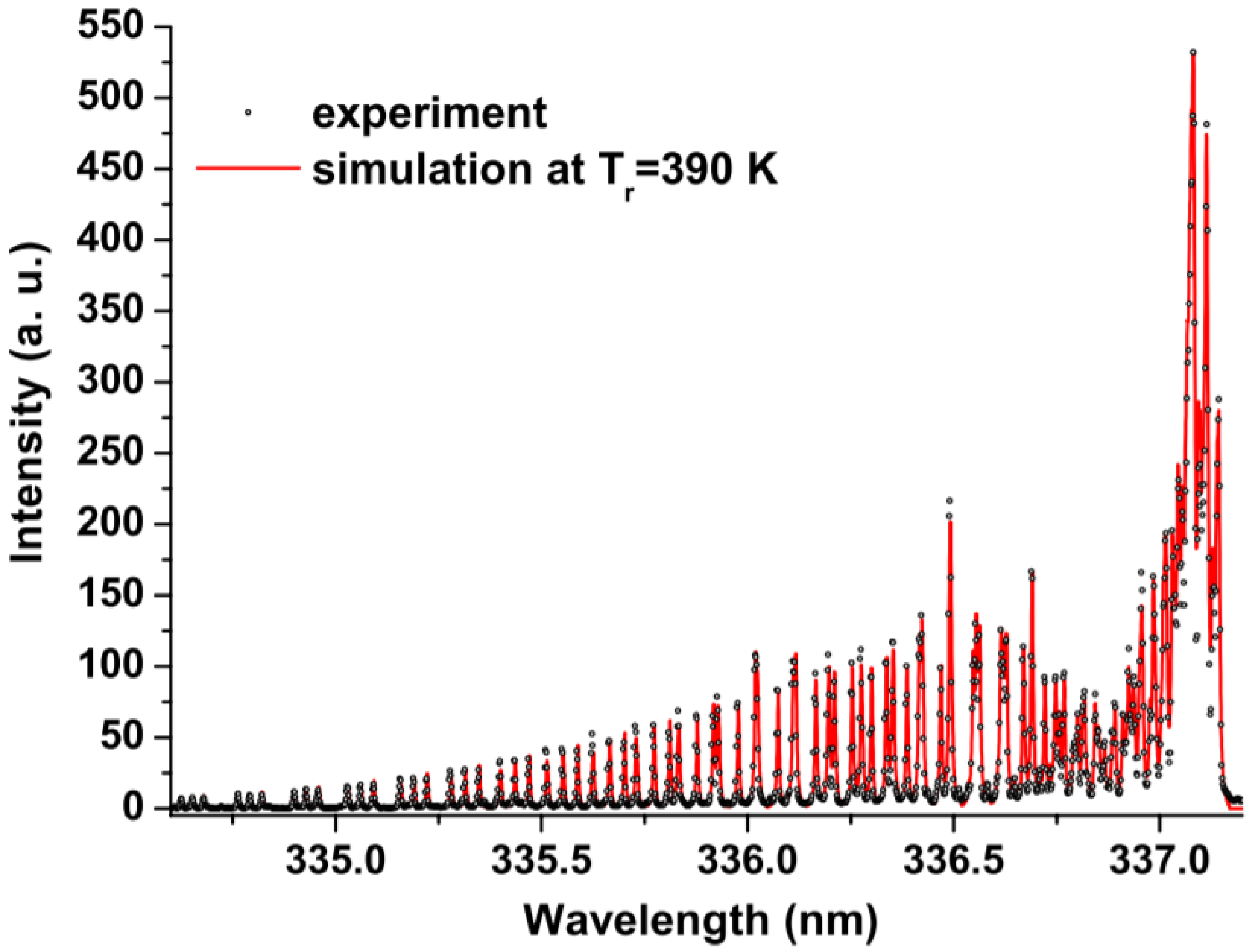
$\Delta\lambda_{vdw} \sim P/(T_g^{0.7})$

Instrument function measured experimentally

Bruggeman , Schram , Gonzalez et al PSST 18, 025017 (2009)

- **Balmer β line is very reliable for n_e measurements as its FWHM is only weakly dependent on T_e and on ions dynamics**
- **A deconvolution is necessary to extract the part of the broadening due to Stark broadening**

Rotational/Gas Temperature Measurements using N_2(C-B)



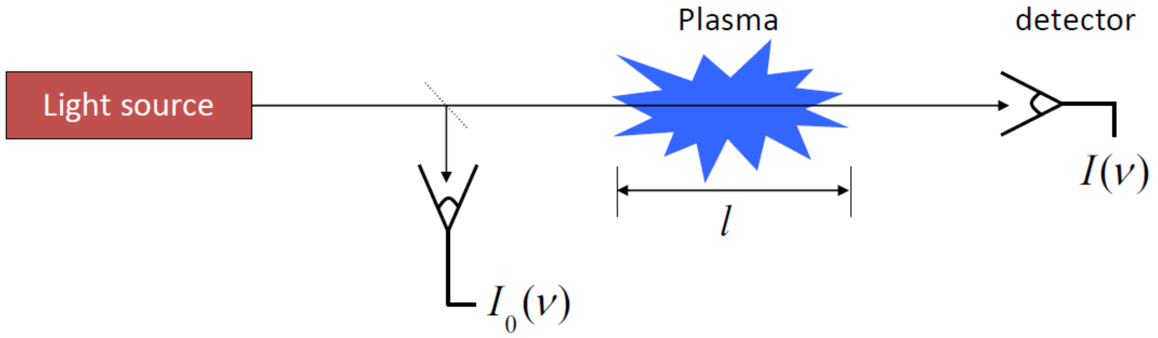
Bruggeman et al, Plasma Sources Sci. Technol. 21 (2012) 035019)

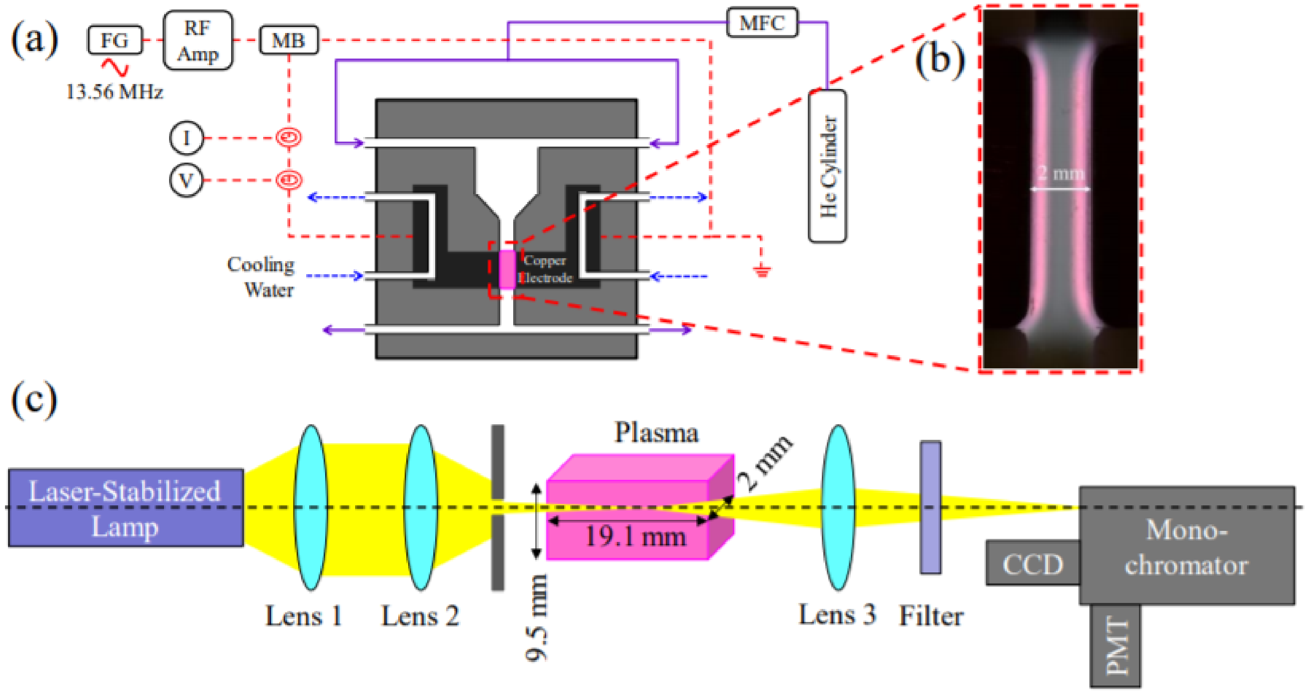
2-m focal length spectrometer from McPherson

CCD detector from Andor Technologies

- **High resolution (4 pm) rotational spectrum of the N_2 (C-B; 0-0) vibrational band in a glow discharge**
- **The 4 pm spectral resolution is obtained using a 2-m focal length spectrometer**

Absorption Spectroscopy





Beer-Lambert: $I(\nu)=I_0(\nu)\exp[-K_\nu L]$

Absorption Coef: $K_\nu = n_i\sigma_i(\nu) = n_{tot} f_B(T)\sigma_i(\nu)$

Nayak et al, al 2019 Plasma Sources Sci. Technol. 28 125006

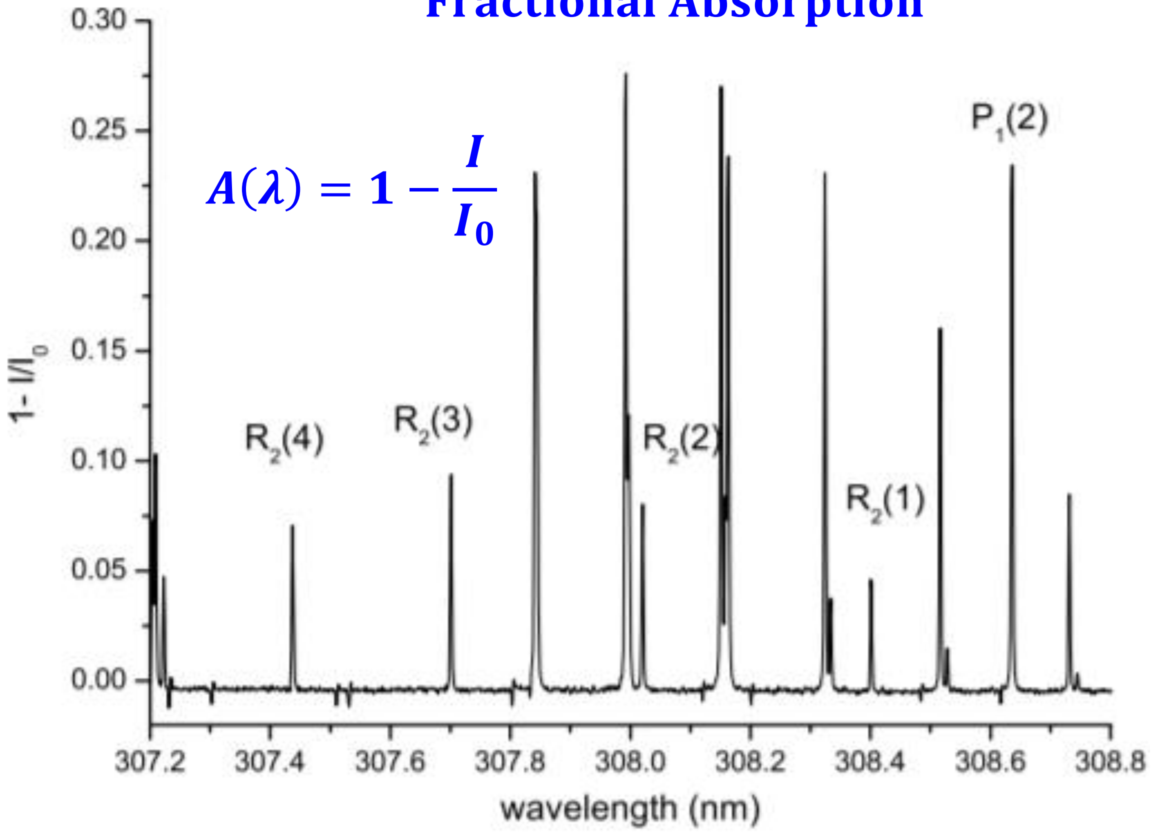
Stable light sources required

Light sources in the UV/Vis and Mid-IR region are of great interest!

- **Active diagnostic**
- **Line-of-sight integrated**
- **High temporal resolution**
- **Primarily gives information about species in their ground state**
- **Can be used to measure: temperatures and neutral species densities**

Absolute Densities Measurements

Fractional Absorption

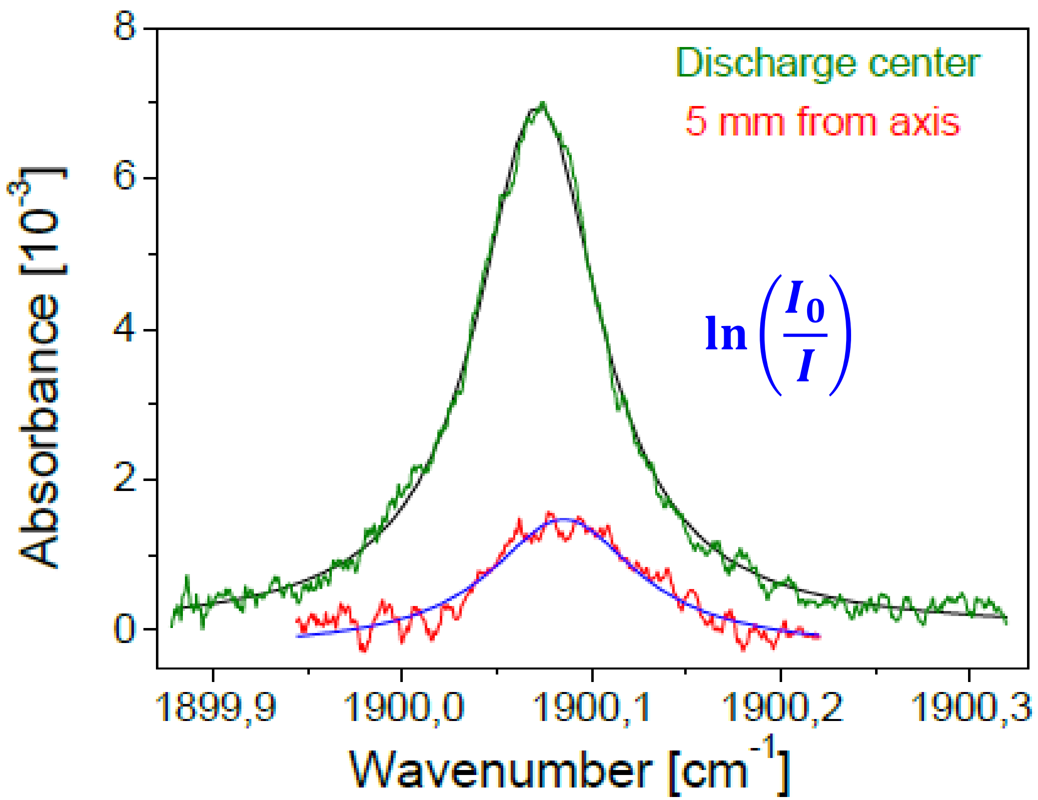


OH(X) broadband absorption

$$W = \int A(\lambda)\,\mathrm{d}\lambda = \int 1 - \exp\left(-h\lambda B\phi(\lambda)n_i L\right)\mathrm{d}\lambda$$

$n_i = n_{tot}\, f_B(T)$

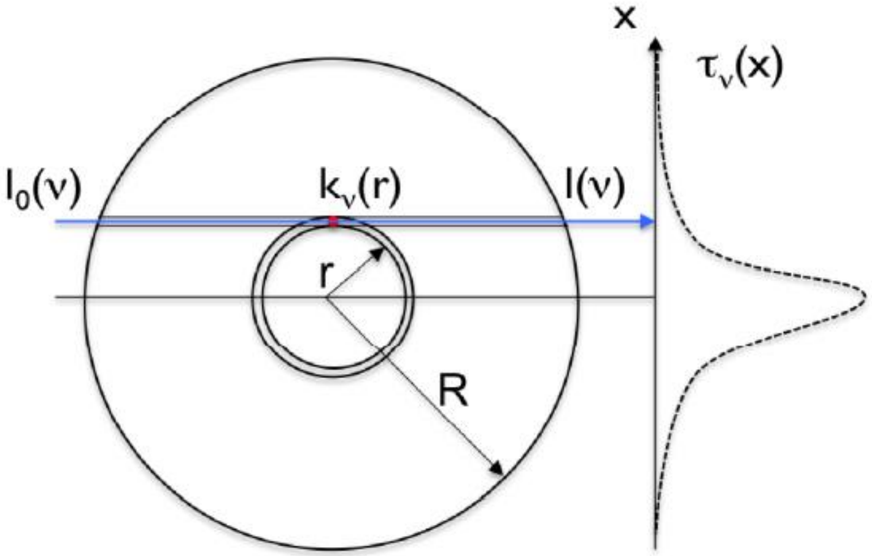
Absorbance



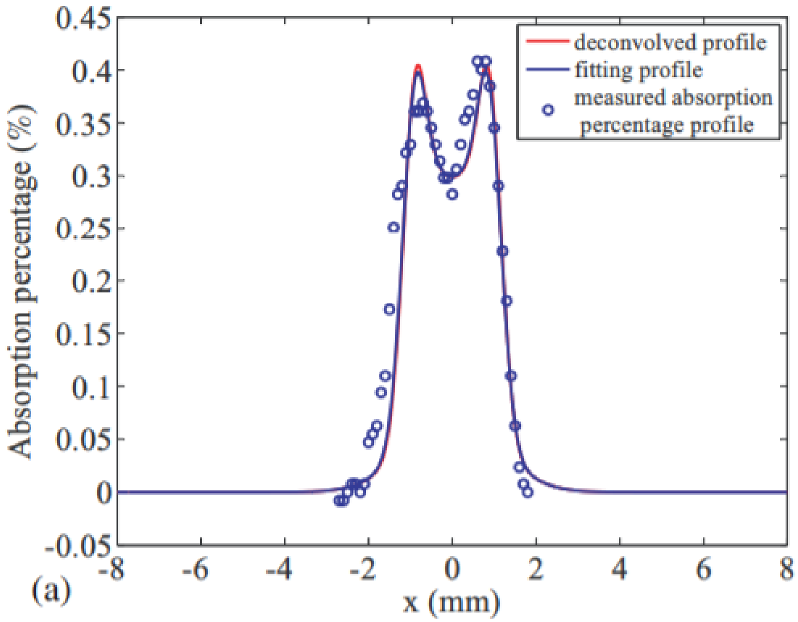
NO(X) Mid-IR absorption

$$N = \frac{\int_\nu \ln\left(\frac{I_0}{I}\right) d\nu}{S(T)L}$$

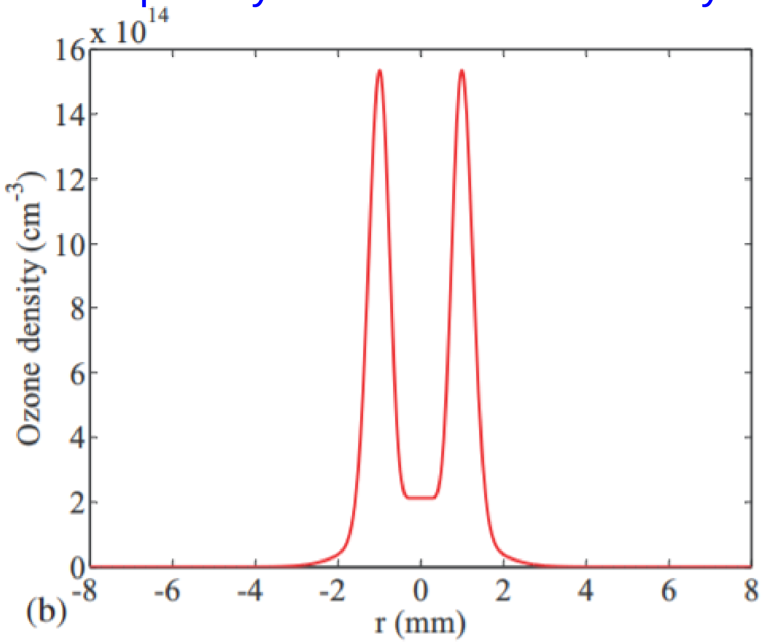
Radial Quantities Determination: Abel Inversion



Line-integrated measurements



Spatially-resolved ozone density



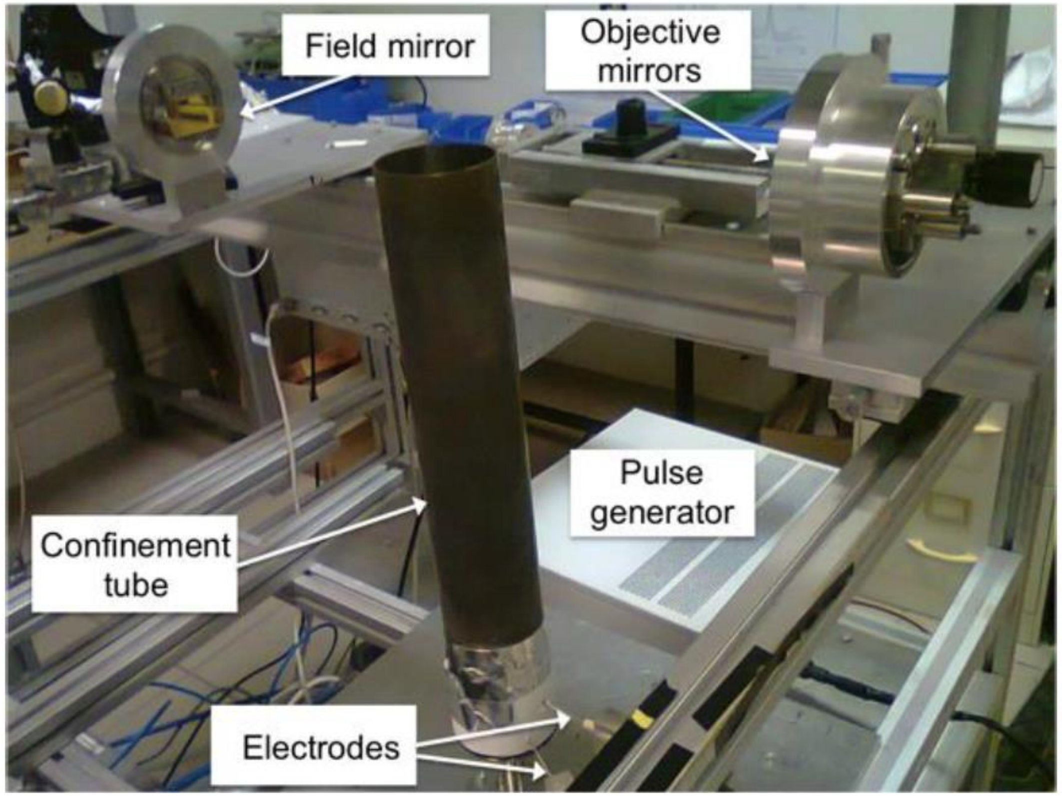
Zhang et al, J. Phys. D: Appl. Phys. 46 (2013) 205202

$$k_\nu(r) = -\frac{1}{\pi}\int_r^R \frac{\tau_\nu'(x)}{\sqrt{x^2 - r^2}}\mathrm{d}x$$

- **Requires an axisymmetric and optical thin absorbing medium**
- **Radial quantities can be obtained**

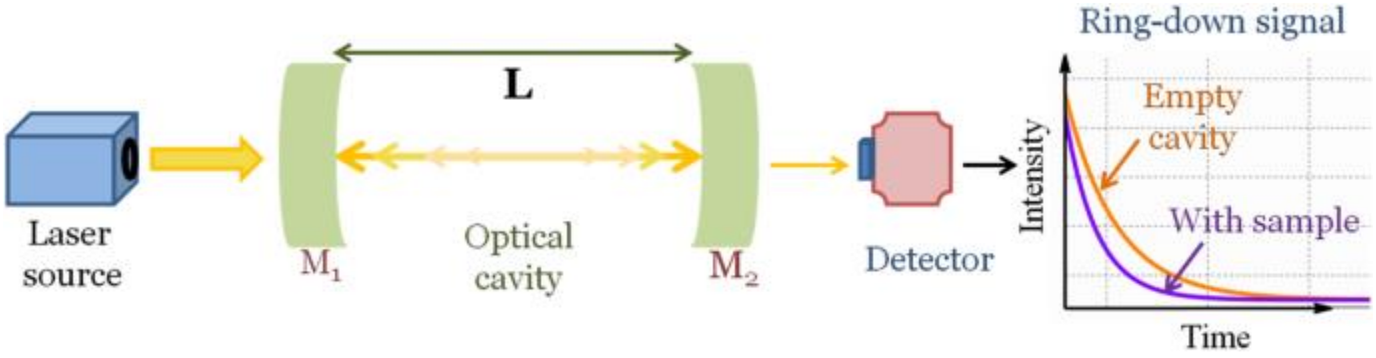
Absolute Measurements of Low Density Species

White multi-pass cell

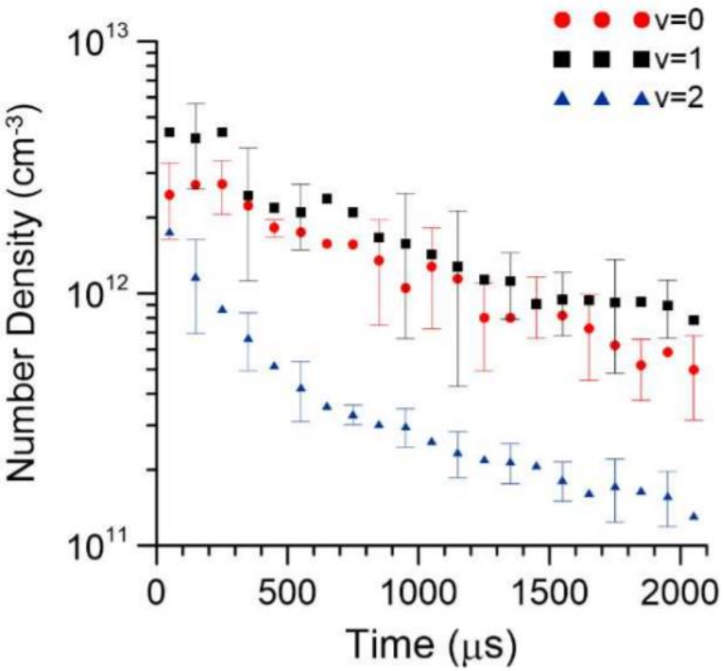


Marien Simeni, PhD Thesis Ecole Centrale Paris (2015)

Cavity Ring-down Spectroscopy



Maithani, S. and Pradhan J., Chem Sci 132, 114 (2020)



$N_2(A)$ measurements at 22 Torr

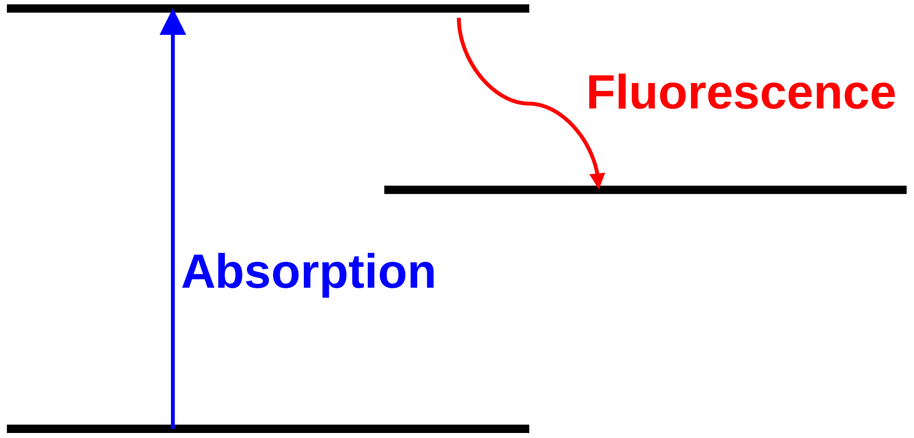
Jans, Frederickson, Miller and Adamovich, J. Mol. Spectrosc (2019)

- **Long absorption lengths: tens of meters to kilomet**
- **Ultrasensitive measurements: trace species densities measurements down to parts per billion**

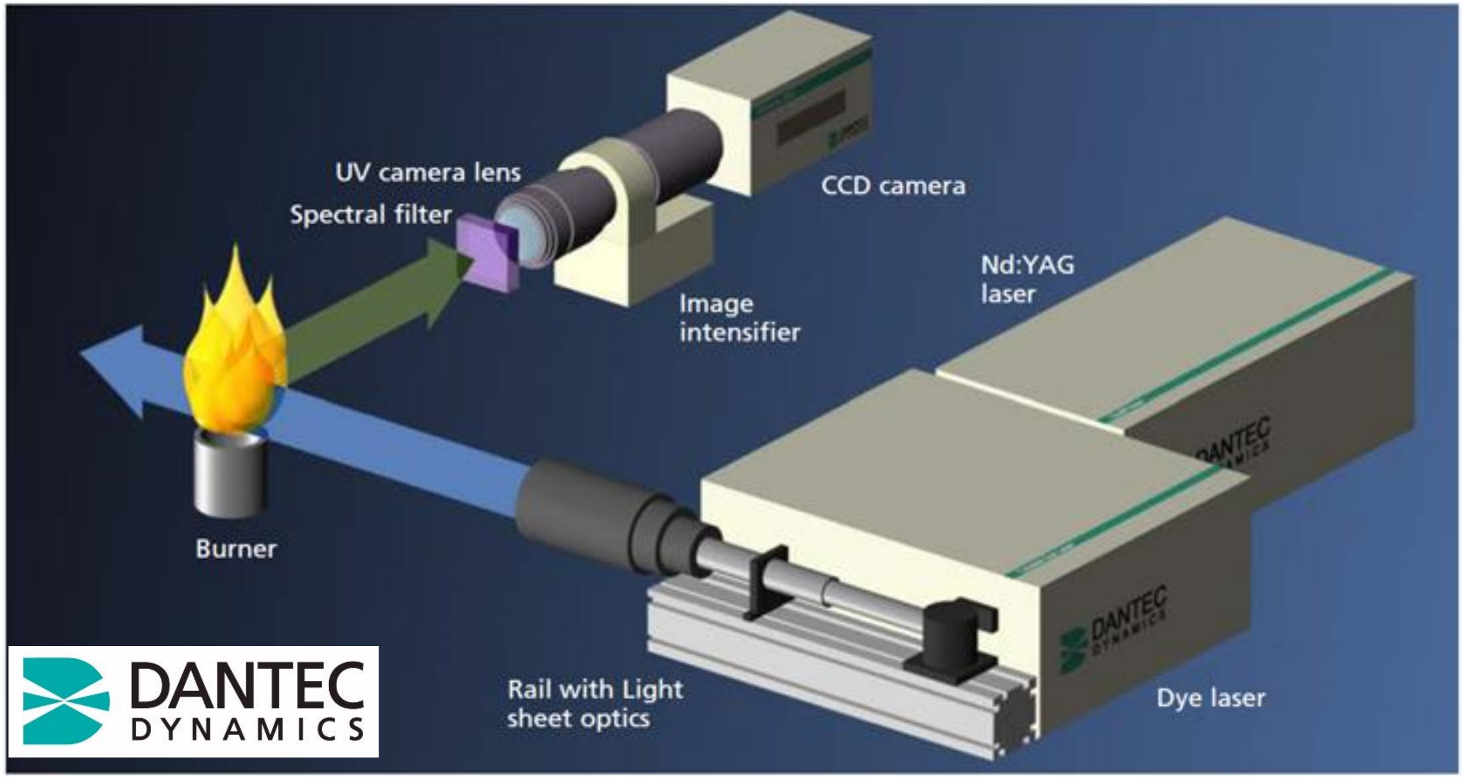
Laser Induced Fluorescence Diagnostics

Laser-induced Fluorescence (LIF)

Principle



Planar LIF system for combustion

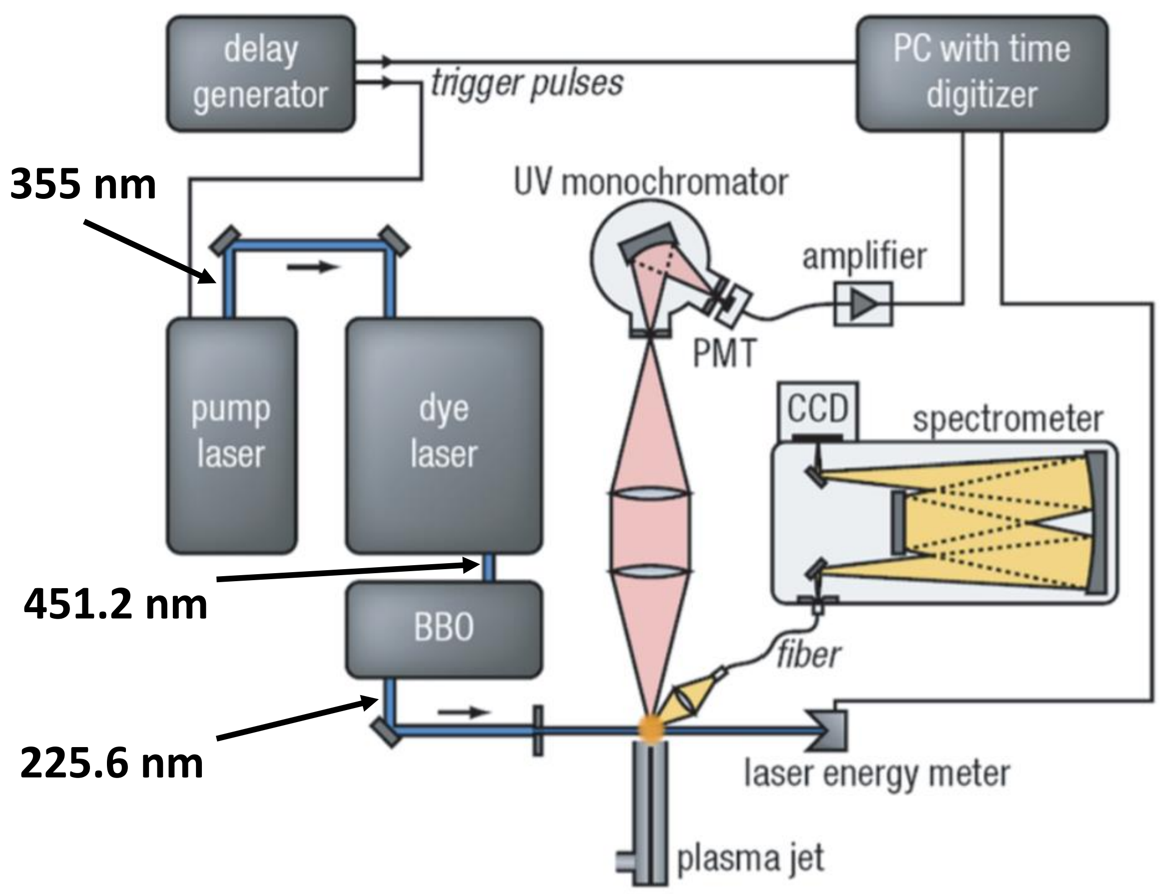


- **Active diagnostic**
- **High Sensitivity/selectivity**
- **2D imaging capabilities**
- **Enable measurements of temperatures and densities**
- **Spontaneous technique**

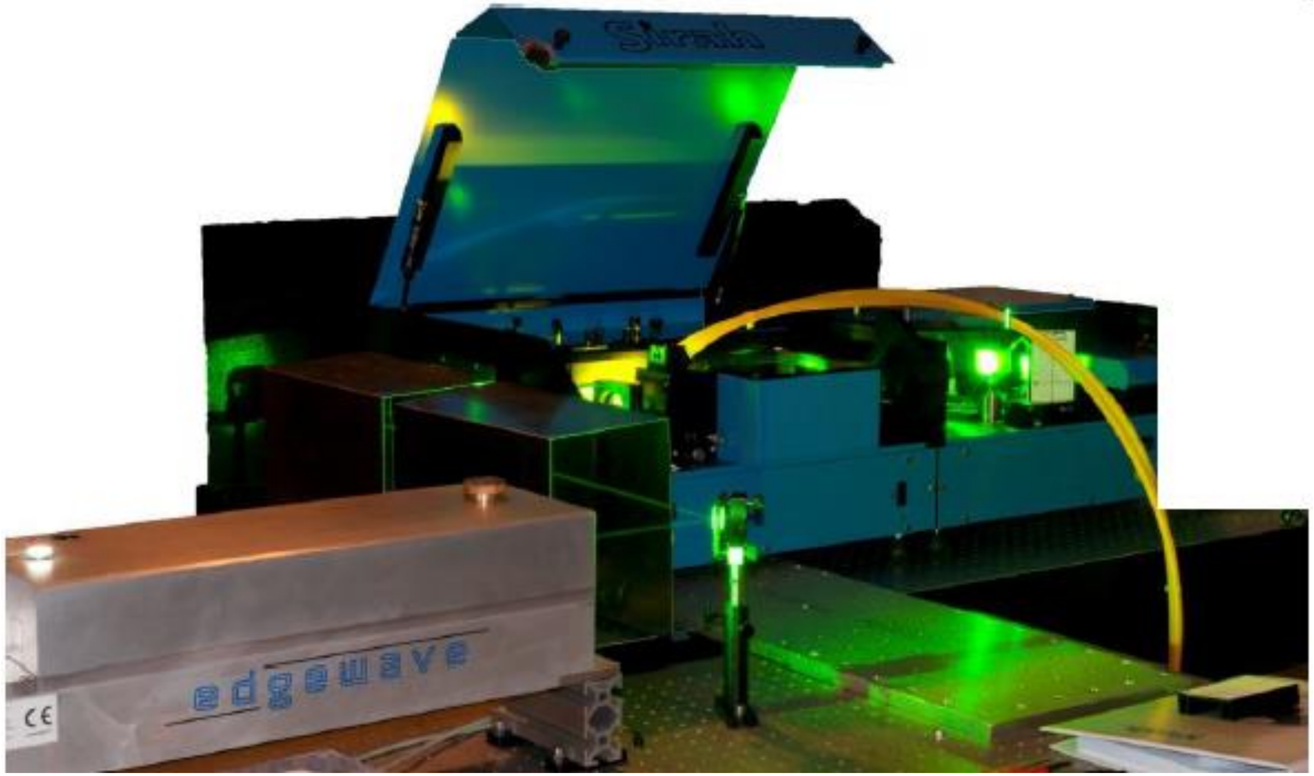
Molecular species: NO, OH, CH, CN, O_2, C_2

Atomic species: N, O, H

NO LIF Setup

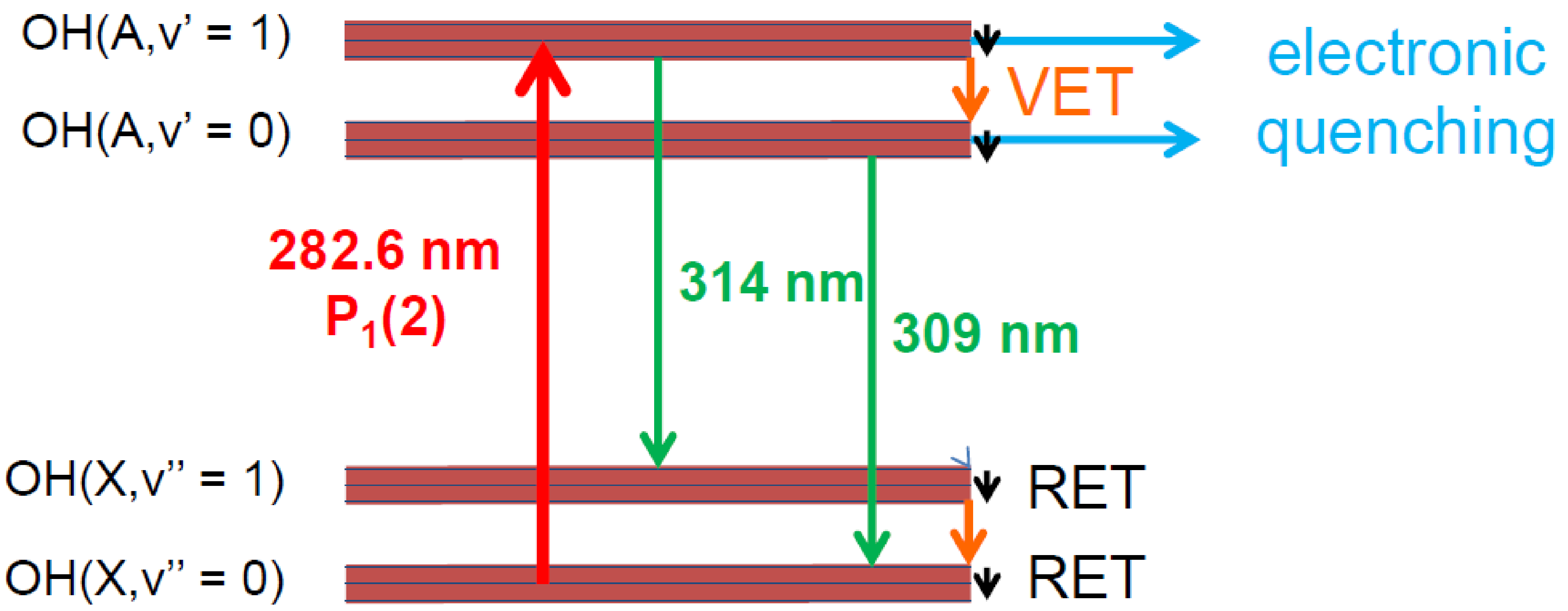


Van Gessel et al J. Phys. D: Appl. Phys. 46 (2013) 095201



- **Pump laser (harmonics of Nd:YAG)**
- **Dye laser**
- **Harmonic crystal**

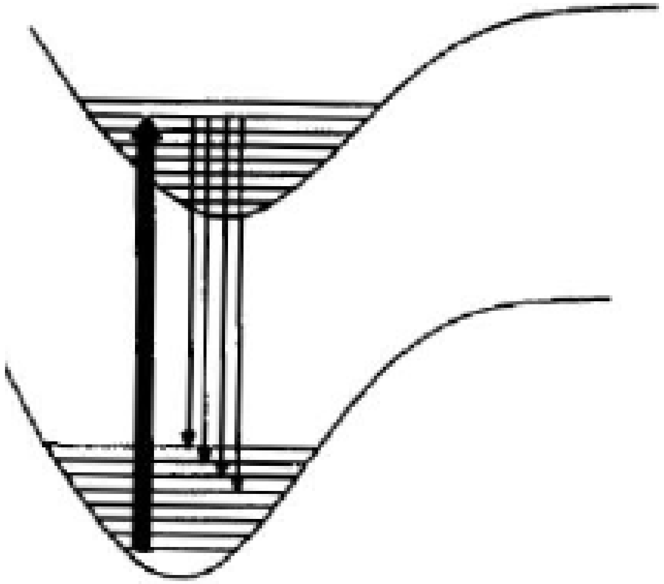
OH LIF



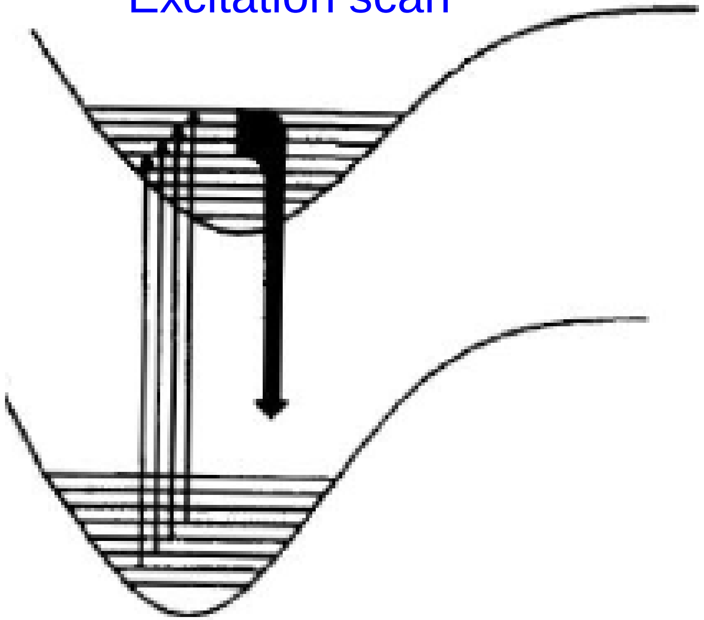
rotational and vibrational energy transfer (RET, VET) and electronic quenching

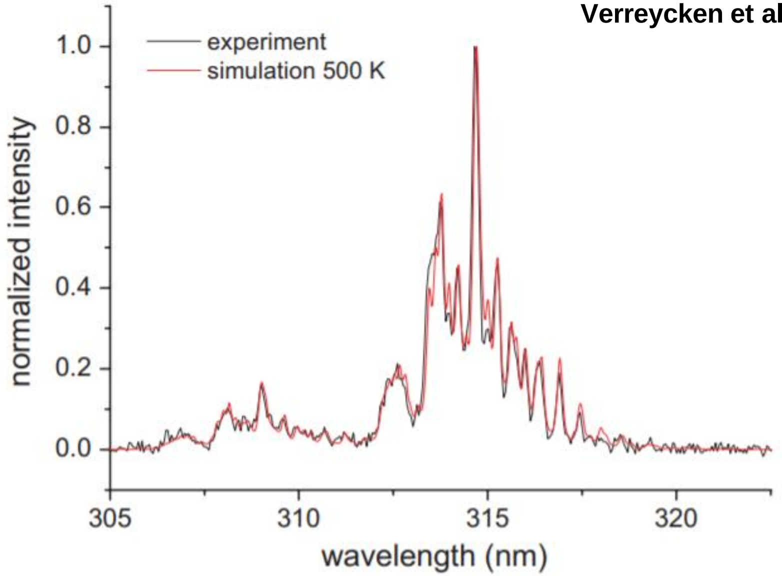
Temperature Measurements: Two LIF Approaches

Fluorescence spectrum

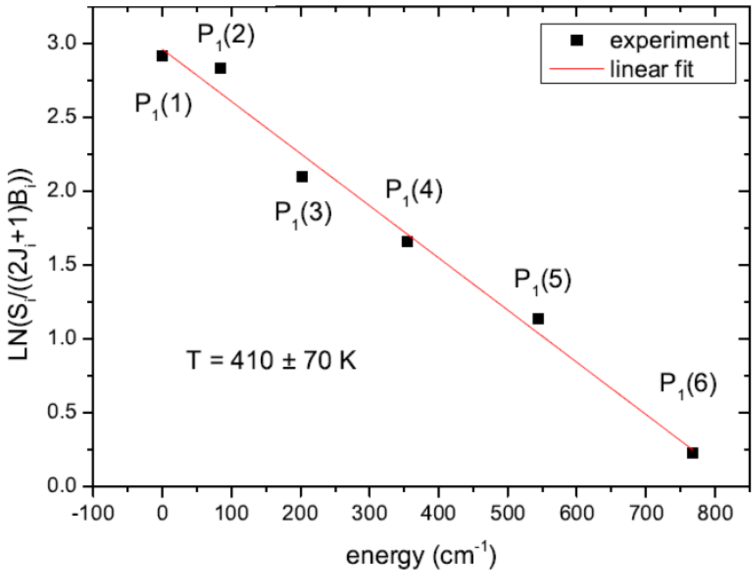


Excitation scan

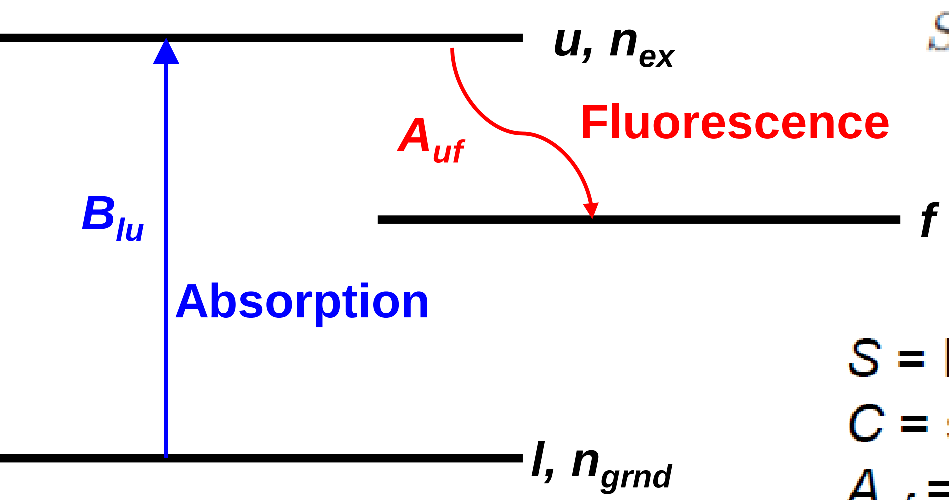




Verreycken et al, J. Phys. D: Appl. Phys. 45 (2012) 045205



Absolute Densities Measurements: 2-level LIF



$$S(\lambda) = \int C A_{uf} n_{ex}(t) \Gamma(\lambda) dt$$

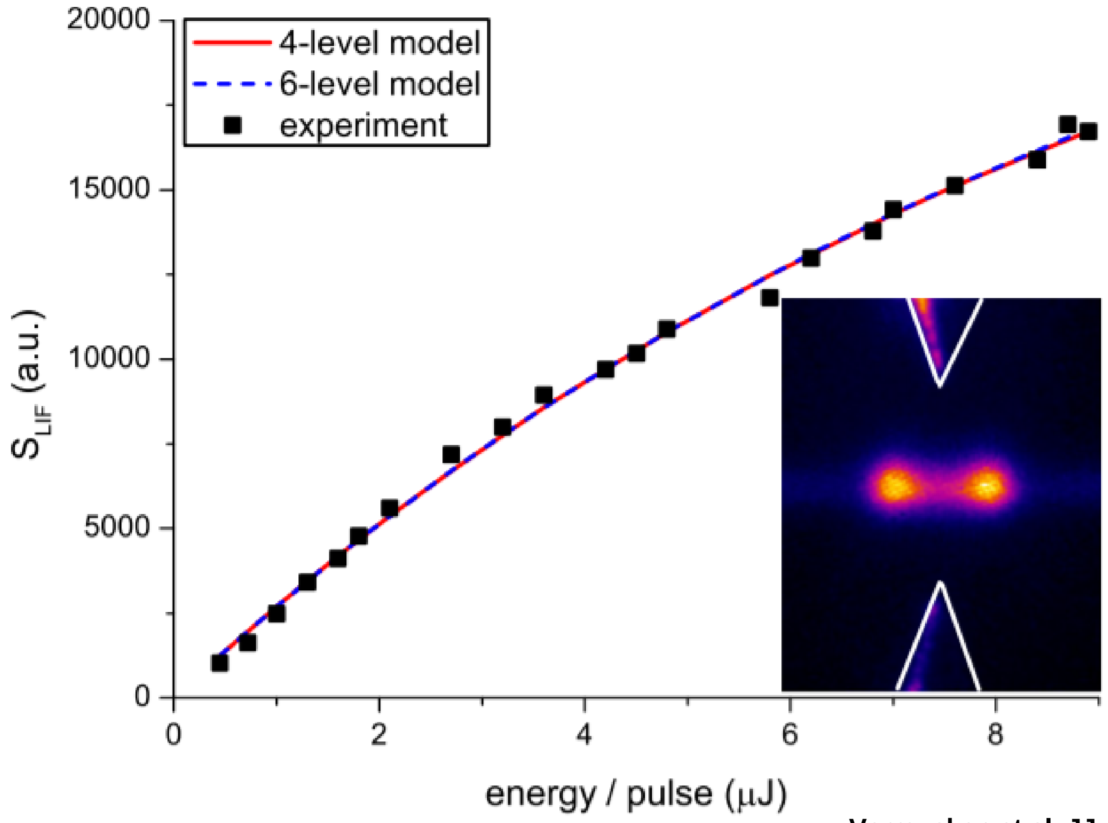
$$\frac{dn_{ex}(t)}{dt} = B_{lu} f_B n_{gnd} I(t) - \frac{n_{ex}(t)}{\tau_{eff}}$$

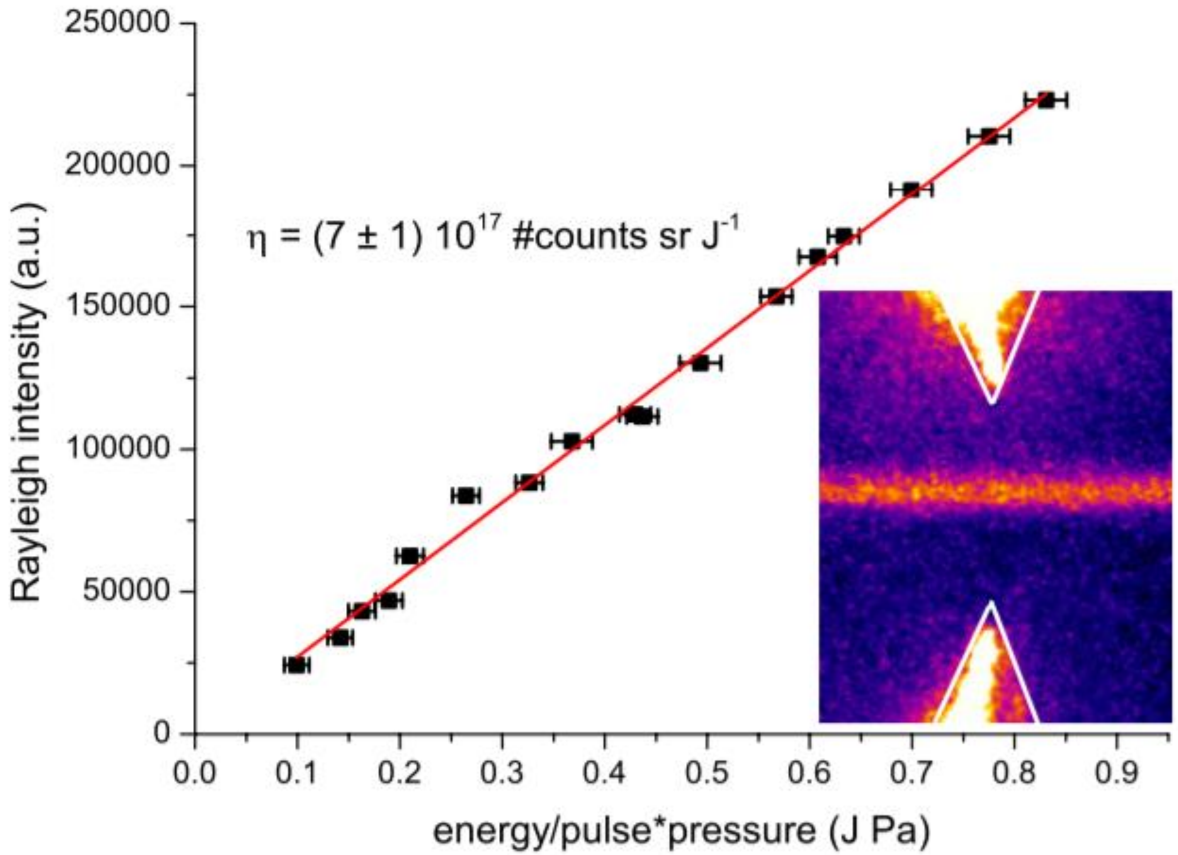
S = LIF intensity
C = setup dependent constant
A_{uf} = Einstein emission coeff.
N_{ex} = excited state density
Γ = line profile

B_{lu} = Einstein absorption coeff.
f_B = Boltzmann factor
n_{gnd} = ground state density
I = laser intensity
T_{eff} = *effective lifetime excited state*

- **A model is required to relate the measure LIF signal to the ground state density**
- **The model contains multiple parameters that are not available for all molecules (RET, VET,…)**
- **A calibration is needed to determine the setup dependent constant**

Absolute Calibration

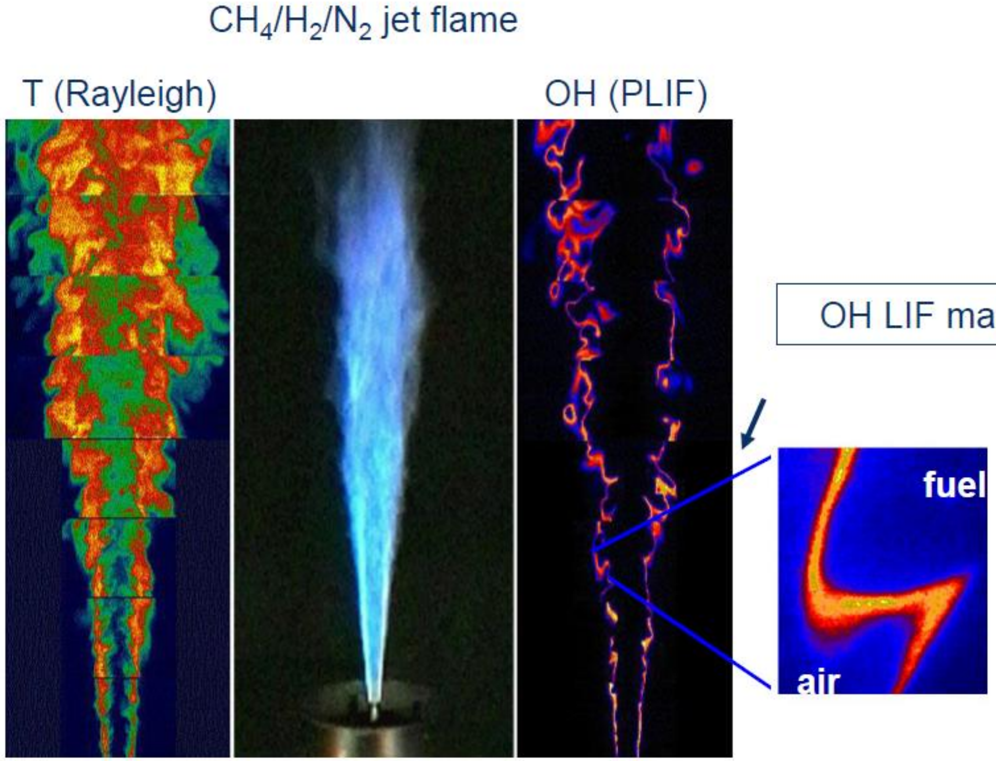




Verreycken et al, JJ. Phys. D: Appl. Phys. 46 (2013) 464004

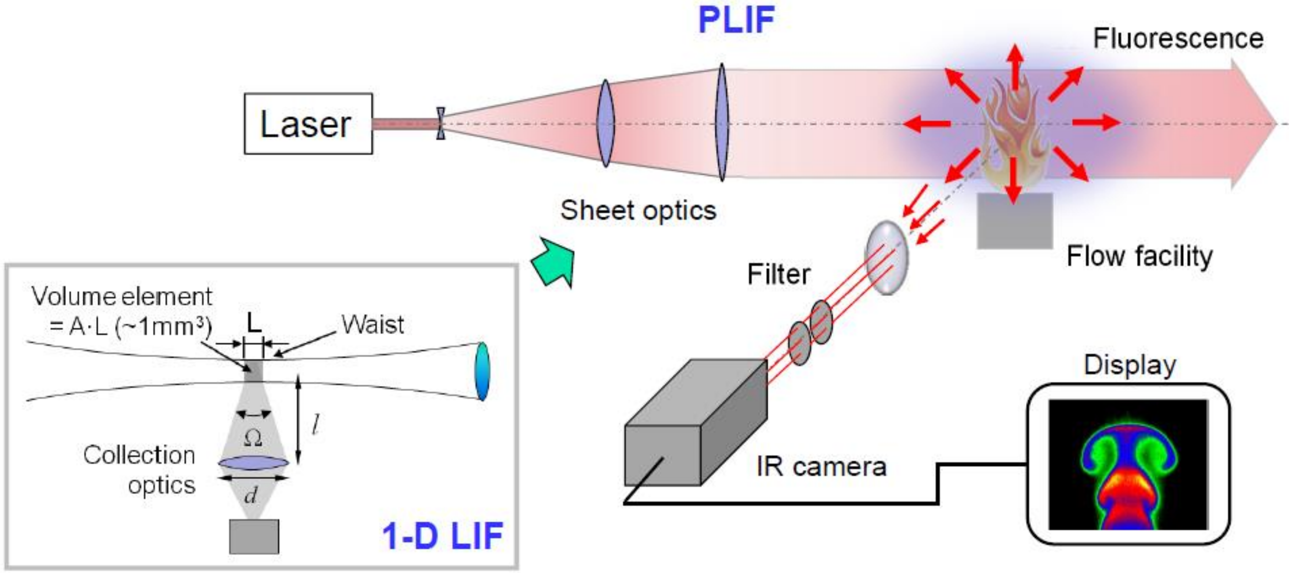
- **Known concentration (density) of the gas: NO**
- **A different species exhibiting a very similar pattern: O and H (Xe and Kr)**
- **Rayleigh/Raman scattering**
- **Absorption spectroscopy**

Planar LIF (PLIF)



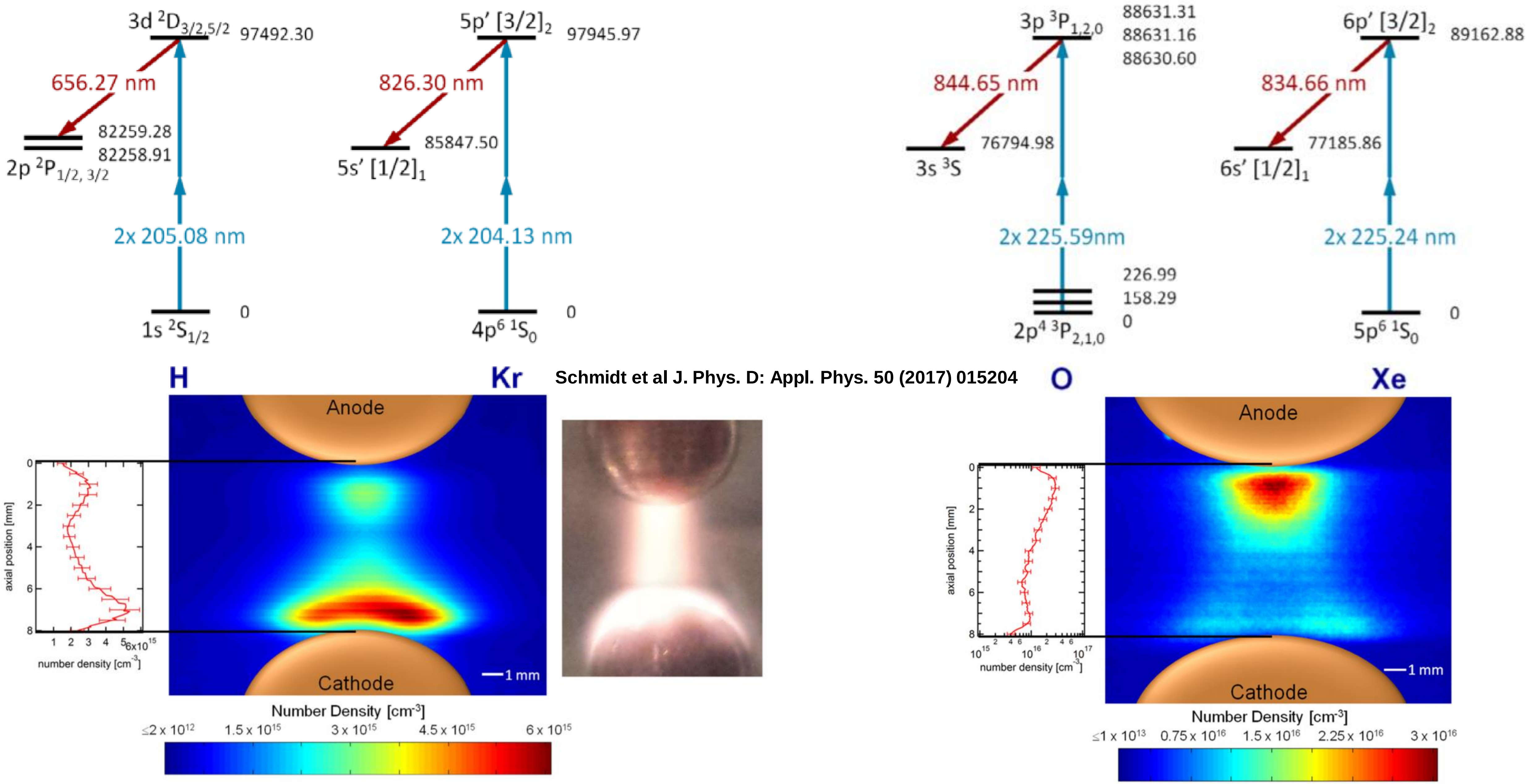
Bergmann et al. *Appl. Phys. B* (1998)

OH LIF marks reaction zone



Hanson, CEFRC, 2015

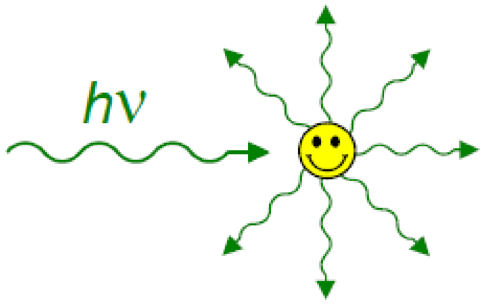
Two-Photon Laser-Induced Fluorescence (TALIF)



Schmidt et al J. Phys. D: Appl. Phys. 50 (2017) 015204

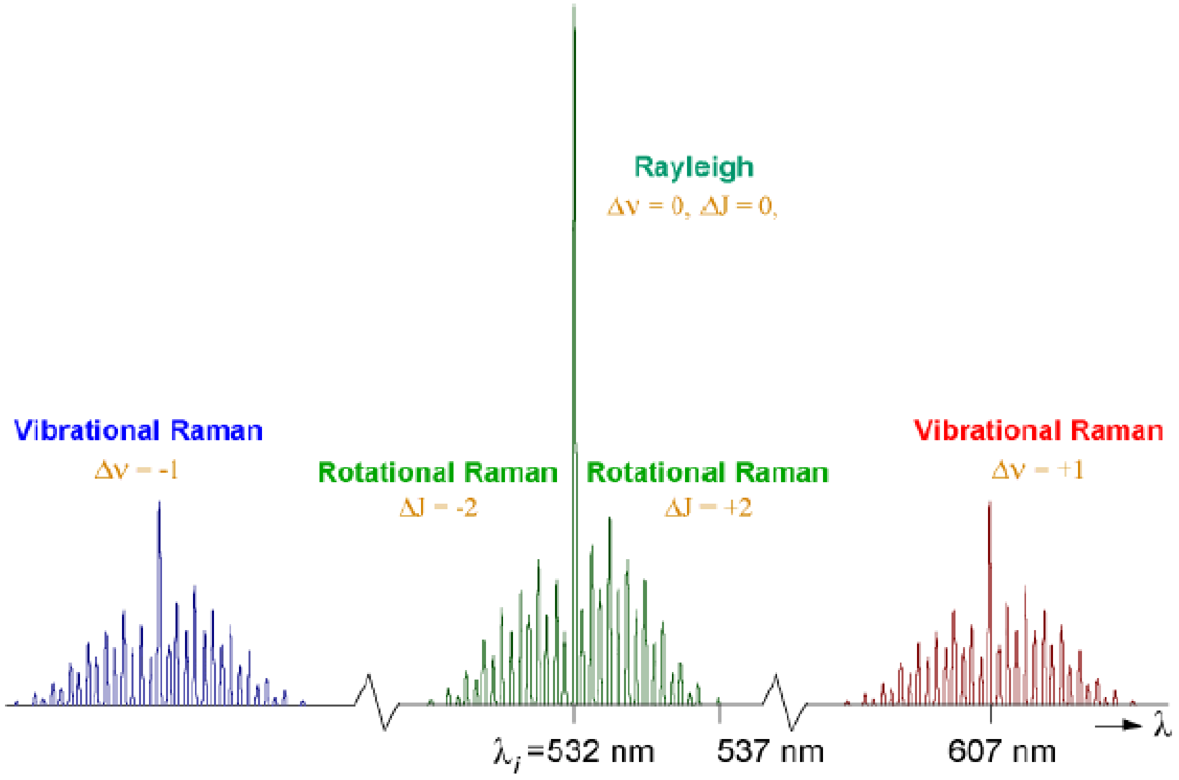
Laser Scattering Techniques

Laser Scattering (1)



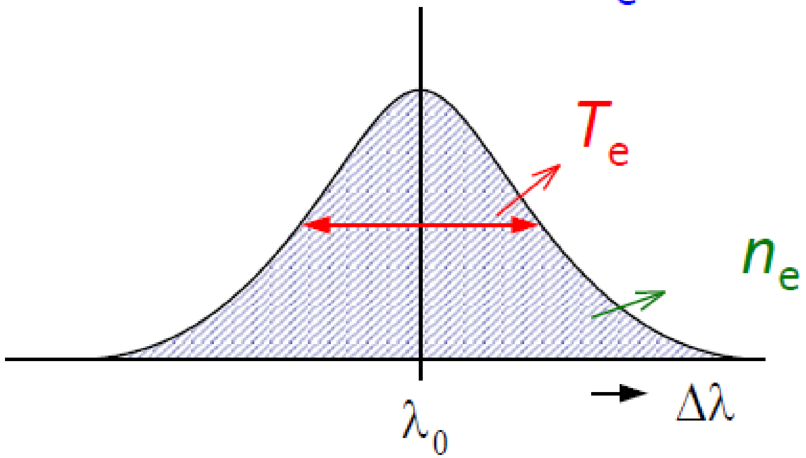
<u>Scattering:</u>

- Thomson: elastic, free electrons
- Rayleigh: elastic, neutrals
- Raman: inelastic, molecular

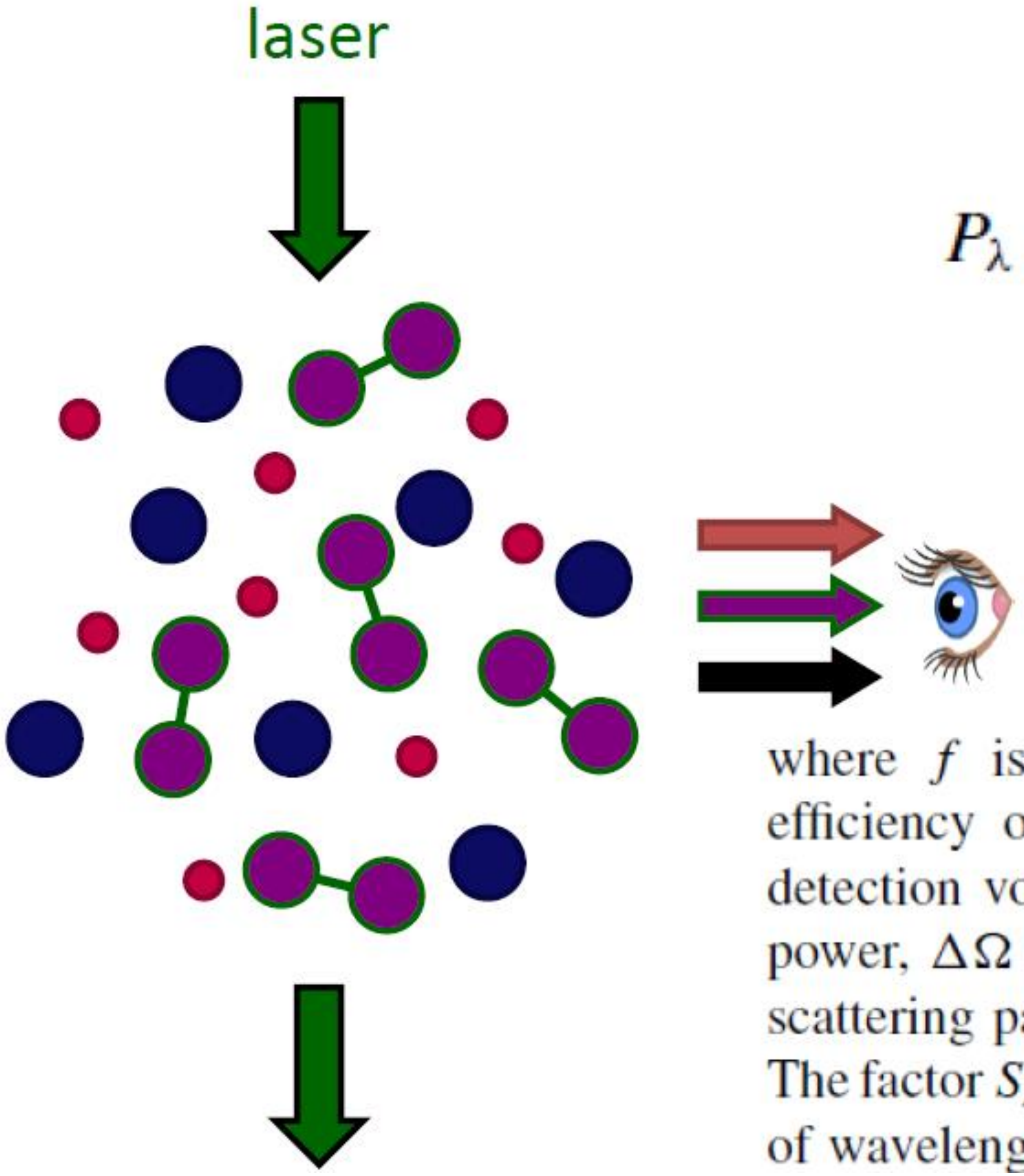


Scattering intensity → n_e

Doppler broadening → T_e



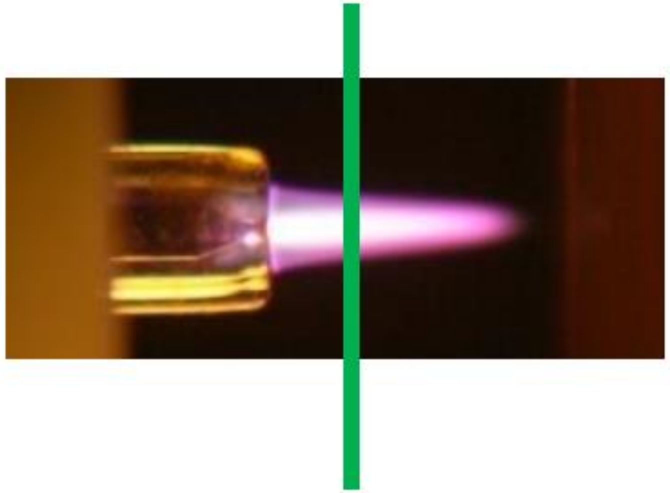
Laser Scattering (2)



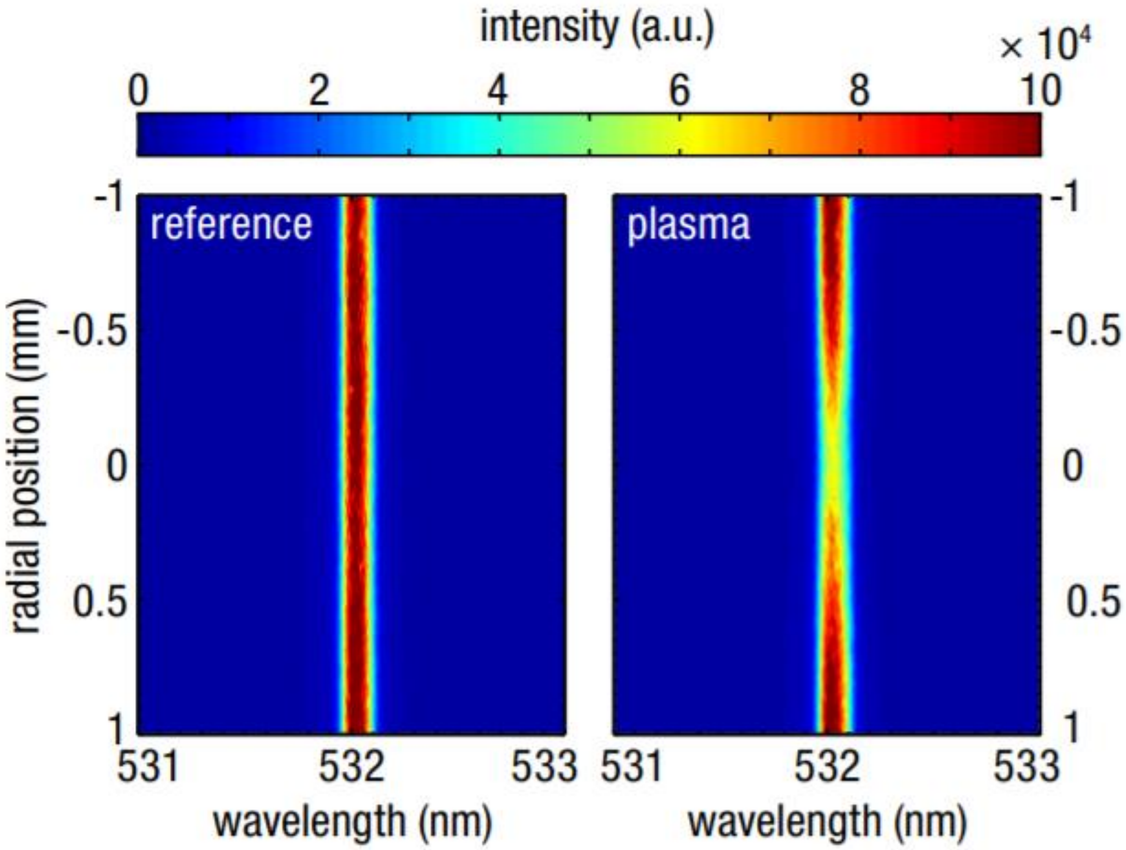
$$P_\lambda = f\, L\, P_i\, \Delta\Omega \cdot n \cdot \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \cdot S_\lambda(\lambda)$$

where f is a constant factor that takes into account the efficiency of the optics and camera, L the length of the detection volume along the laser path, P_i the incident laser power, $\Delta\Omega$ the solid angle of detection, n the density of the scattering particle, and $\mathrm{d}\sigma/\mathrm{d}\Omega$ the differential cross section. The factor $S_\lambda(\lambda)$ includes the spectral distribution as a function of wavelength,

Rayleigh Scattering



$$T_g = \frac{P_{ref}}{P_{Plas}} T_{ref}$$



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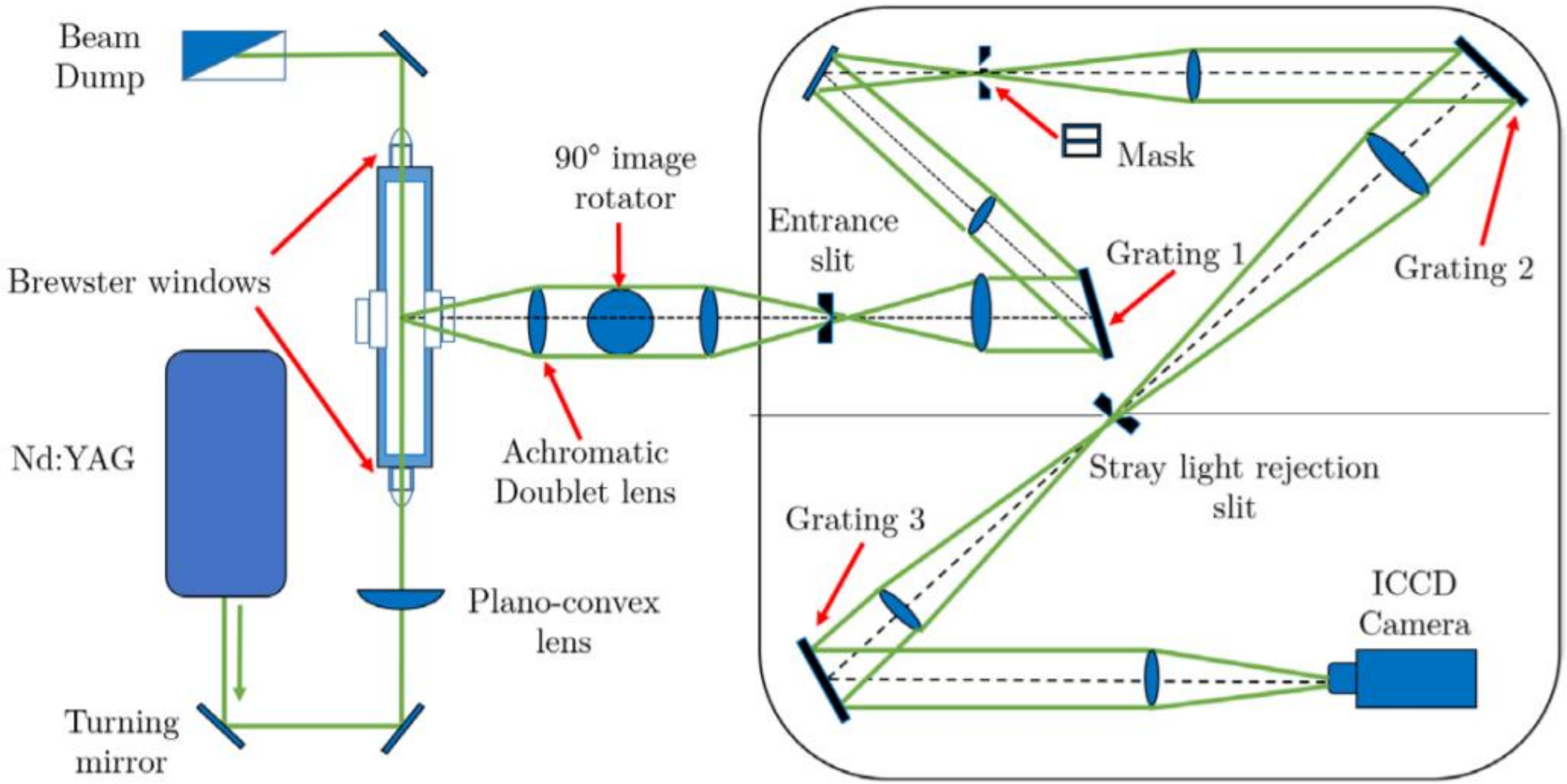
- **Rayleigh scattering cross sections are species dependent!**
- **Scatter off optics and dust particles produce strong unwanted signal**

Laser Scattering Setup



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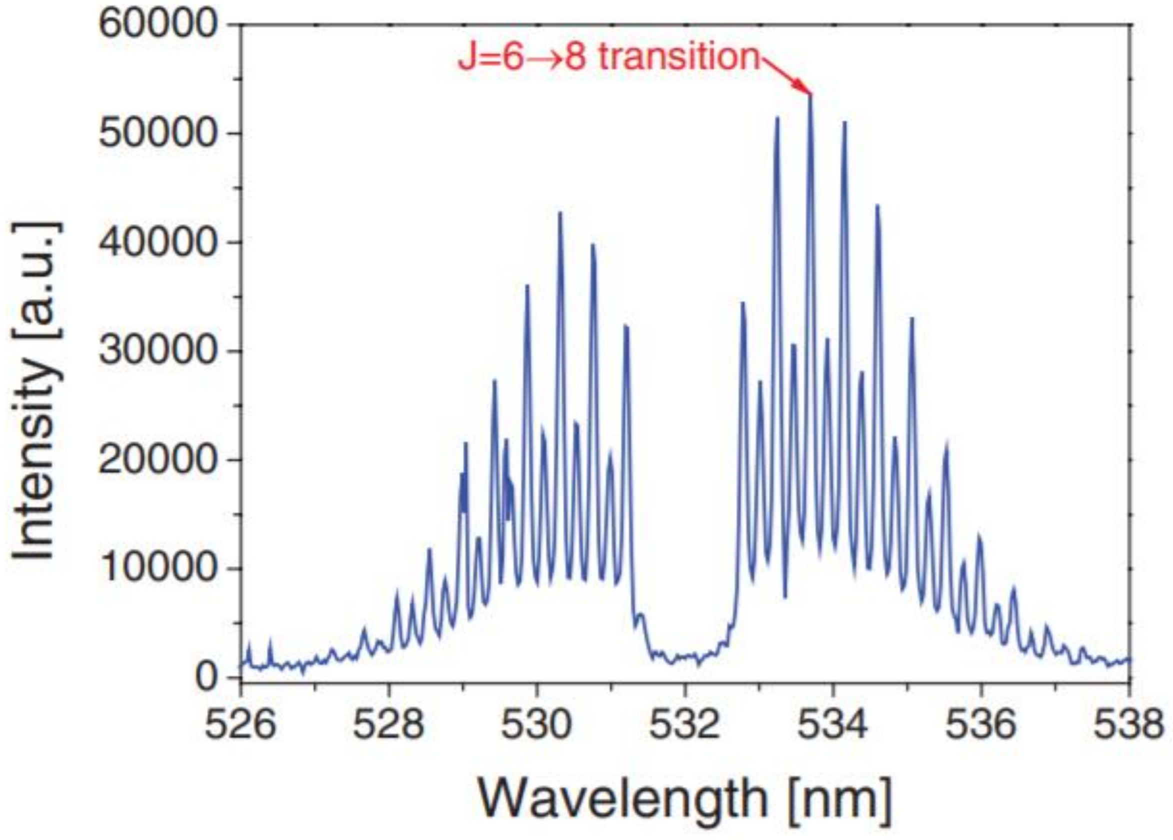
- **Triple grating spectrometer = filter to remove Rayleigh signal**

Rotational Raman Spectrum

N_2 at 100 Torr



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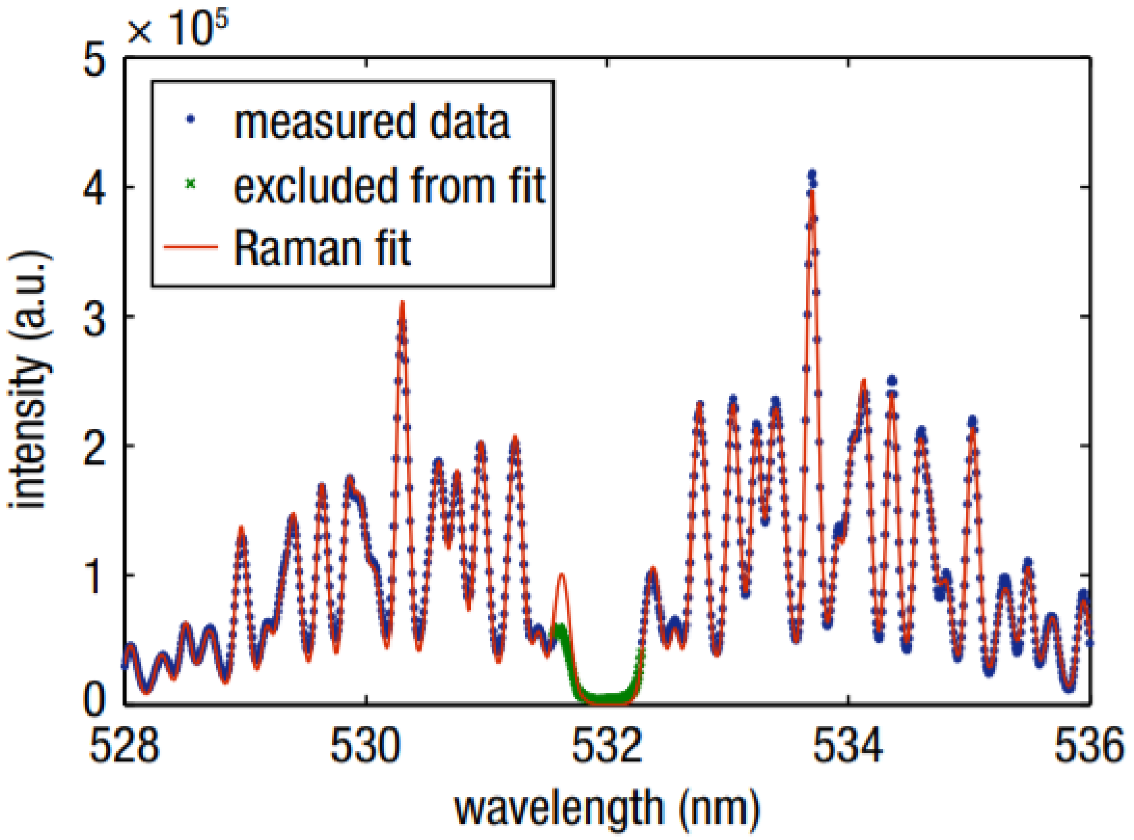
Air at 760 Torr



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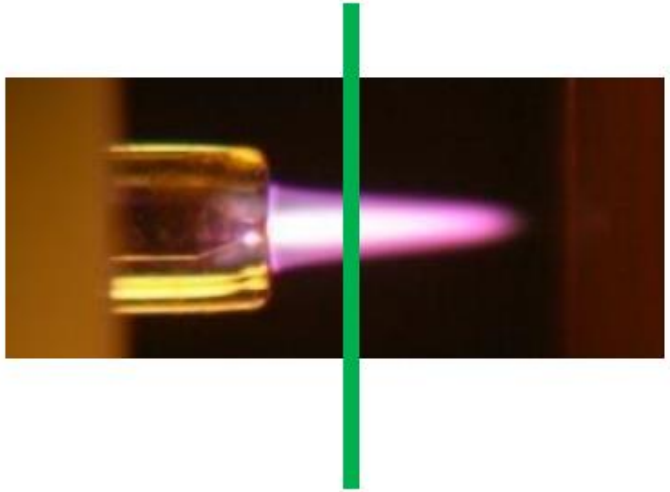
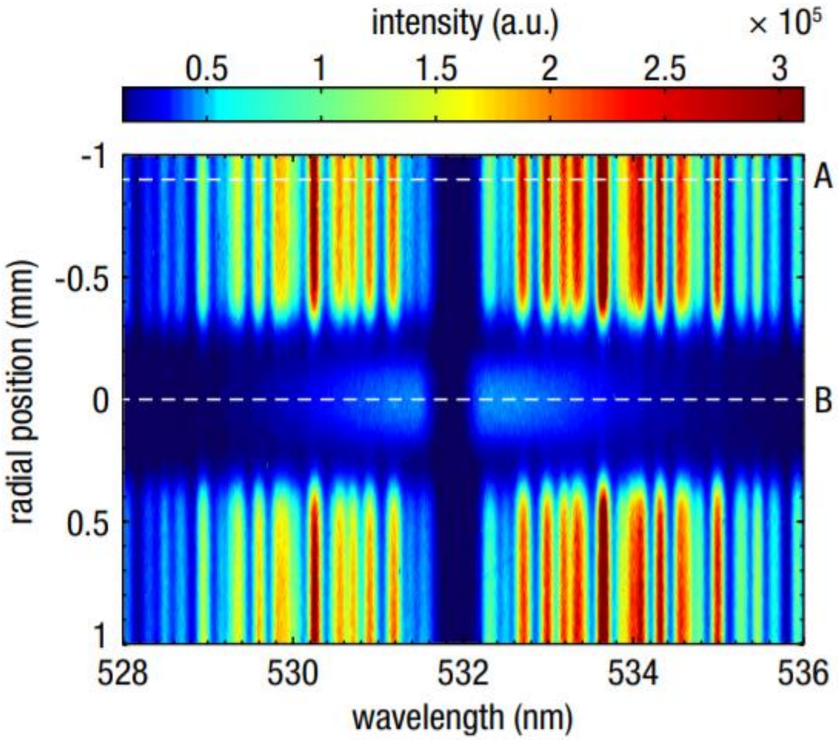
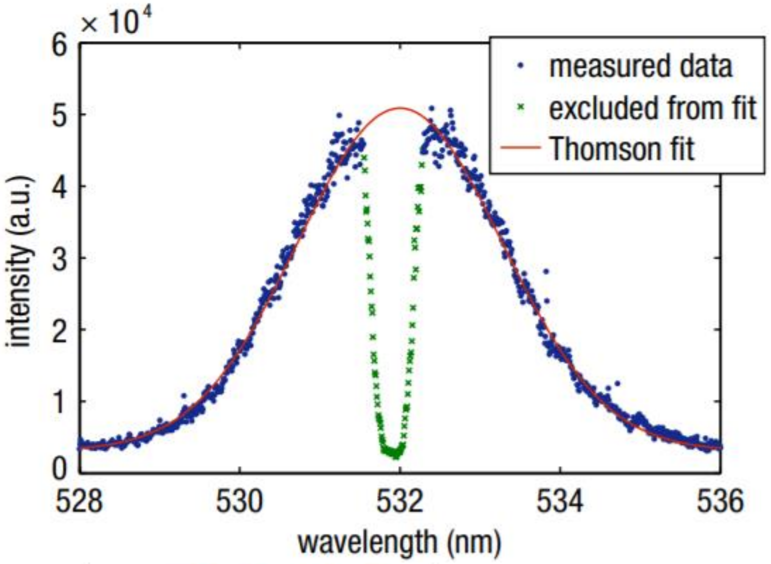
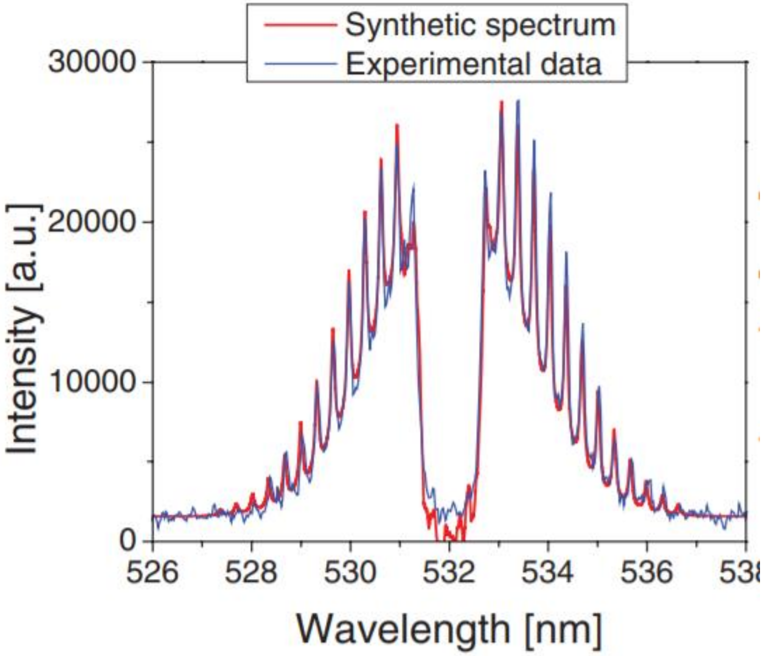
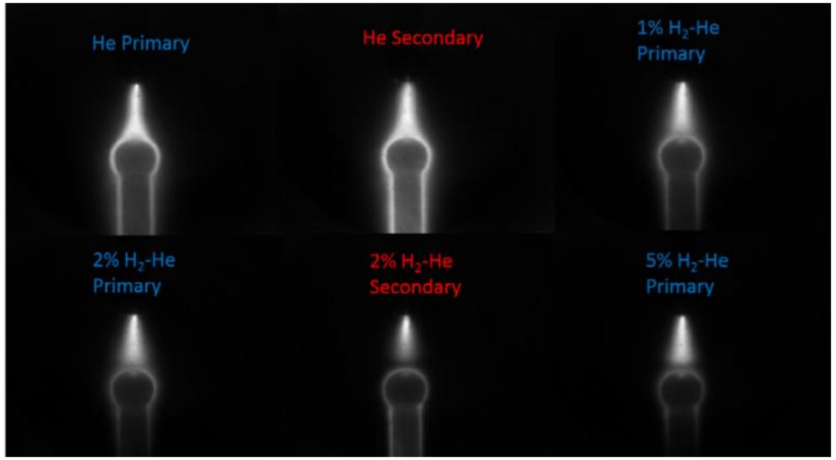
Thomson Scattering

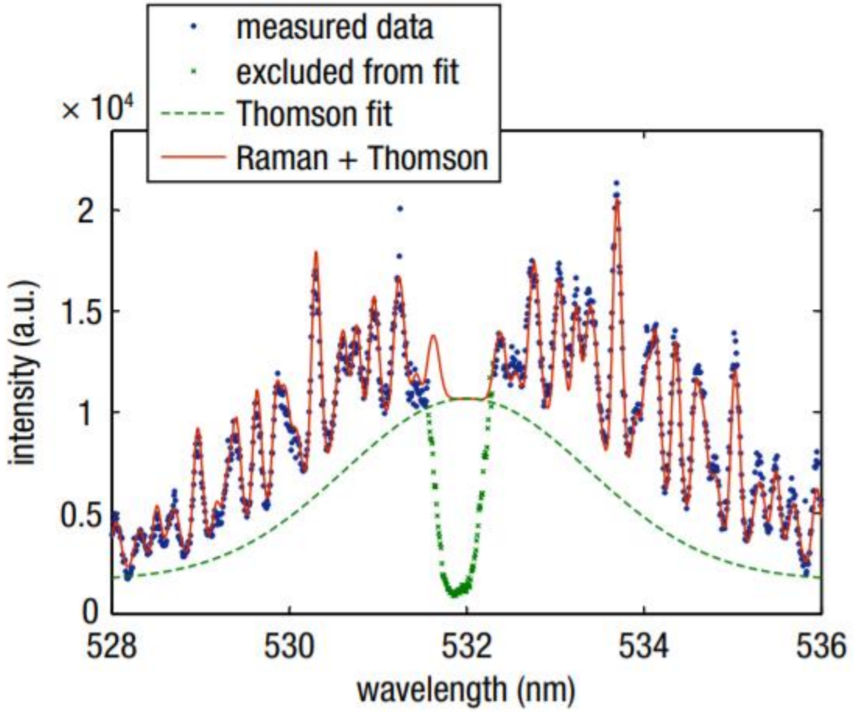




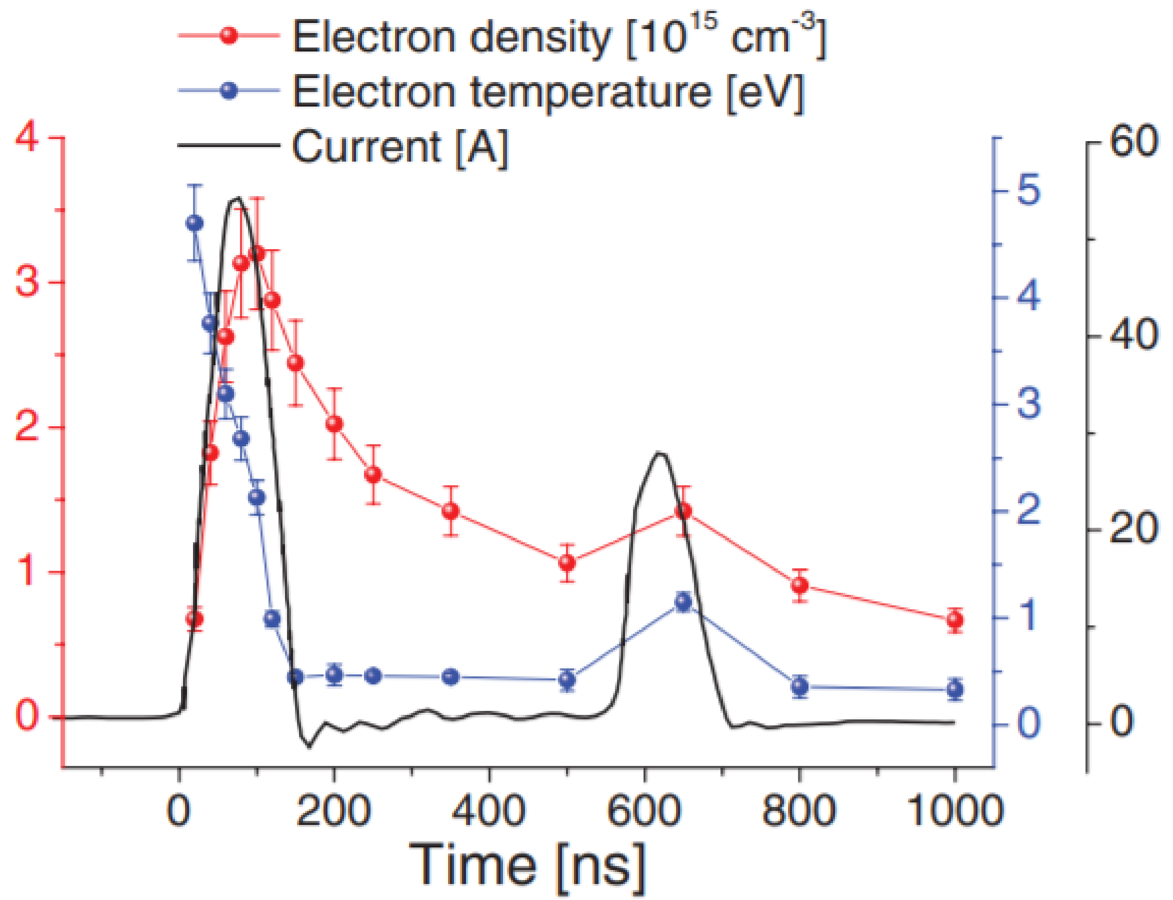


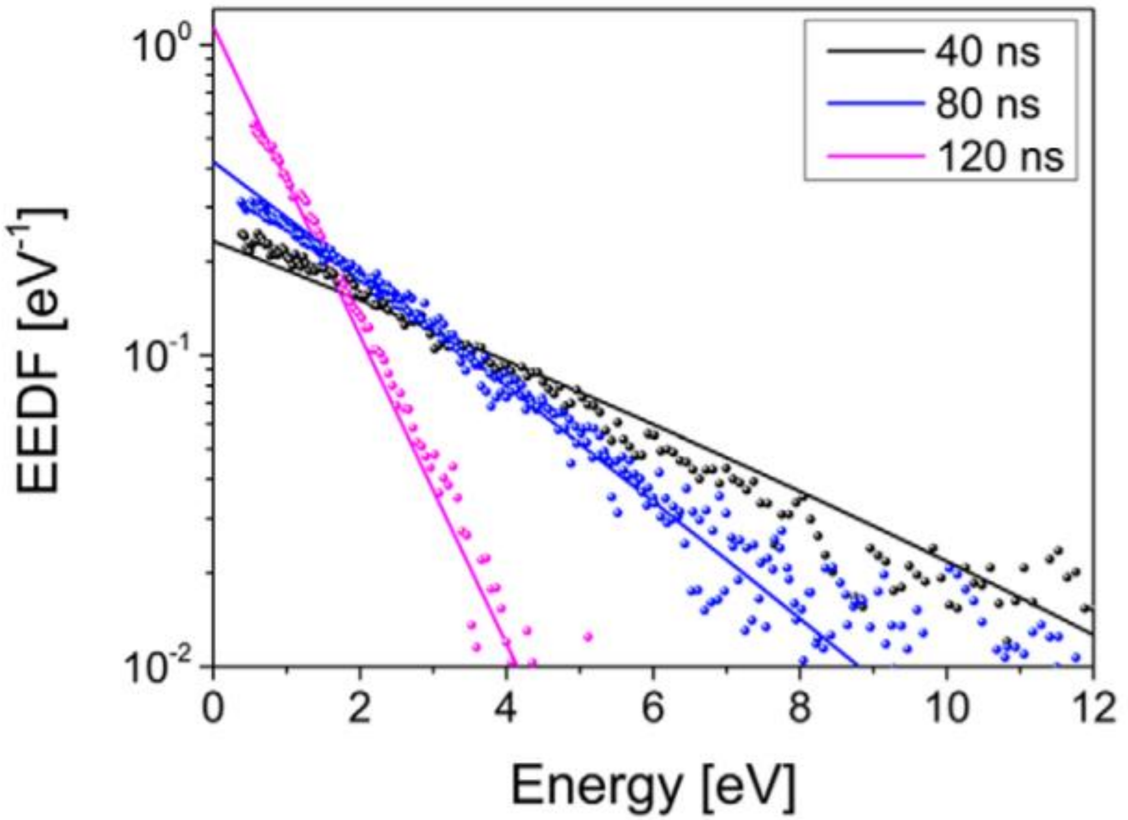






Time-resolved n_e, T_e and EEDF





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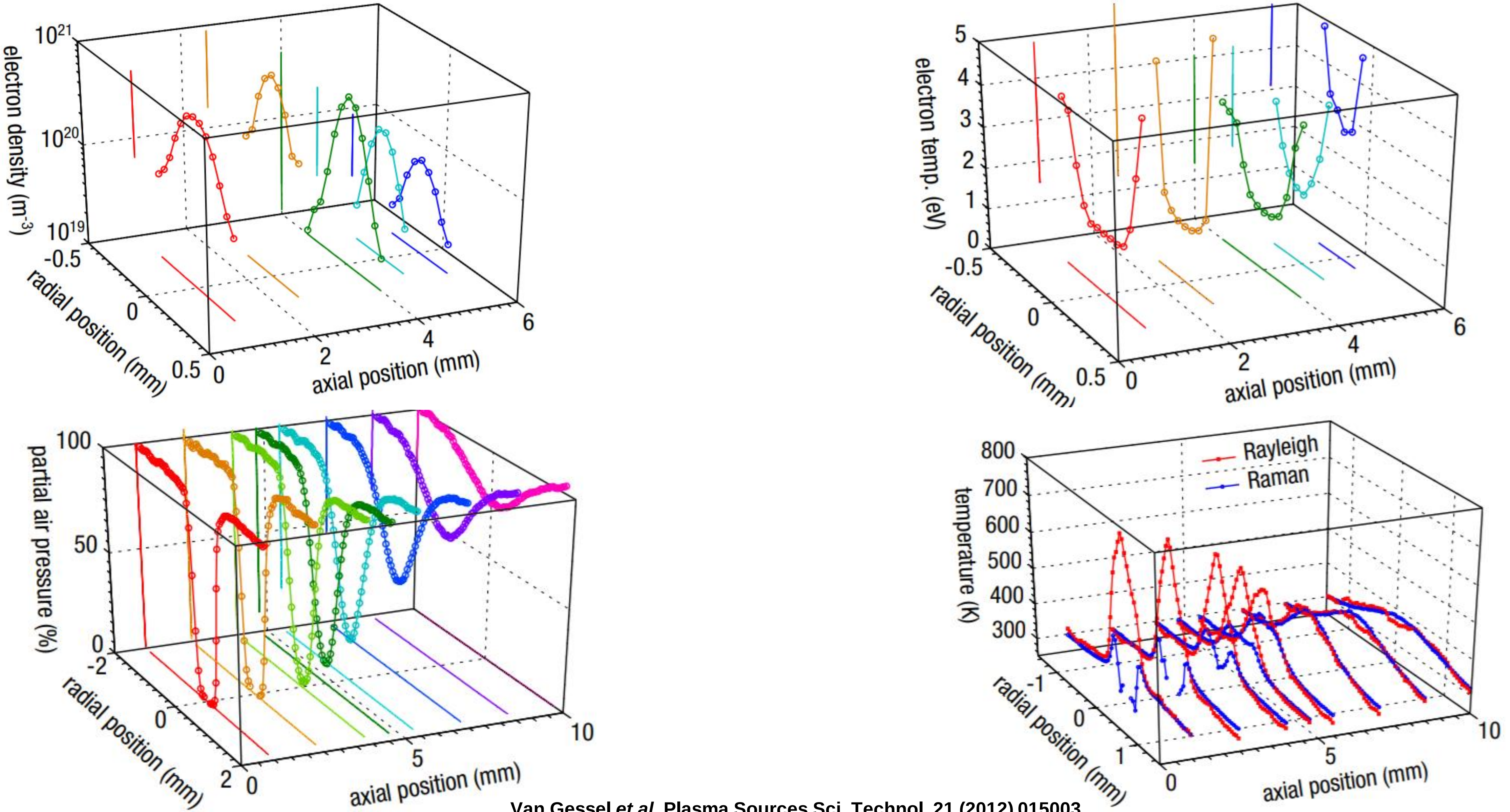
Spatially-resolved Measurements: Microwave Plasma Jet



Van Gessel *et al*, Plasma Sources Sci. Technol. 21 (2012) 015003

Thank you for your attention!!