Caractérisation des plasmas atmosphériques d'hélium par spectroscopies d'émission et laser; problèmes spécifiques de la haute pression

Nader SADEGHI

LTM & LIPHY, Université Grenoble-Alpes & CNRS Grenoble (France)

GRENOBLE 1 UNIVERSITE JOSEPH FOURIER SCIENCES.TECHNOLOGIE.SANTÉ

LIPhy Laboratoire interdisciplinaire de Physique

cnrs dépasser les frontières

Why measuring the spectral line profile can be important for the plasma diagnostic?

The line shape provides information about gas temperature (Doppler), density of neutral particles (pressure broadening) and of charged particles (Stark broadening).

$\Delta\nu_{Doppler}$ **(FWHM) = 7.16** $10^{-7}\ \nu(T_g/M)^{1/2}$

$\Delta\nu_S$ **(FWHM) å** $a(T_e.n_e).\ n_e$

$\Delta\nu_{VdW}$ **(FWHM) å** $K.\ p\ (T_g)^{-0.7}$

$\Delta\nu_R$ **(FWHM) å** $3.2\ 10^7\ .\ p\ (T_g)^{-1}$

- **At low pressure**, Doppler broadening is dominating and the gas temperature can be deduced from the Doppler width of the line.

Line profile at high pressure

- **At high pressure**, the line profile is a Voigt function with:
  - -its Lorentzian component $\Delta\nu_L = \Delta\nu_{VdW} + \Delta\nu_S$
  - -its Gaussian component $\Delta\nu_G = (\Delta\nu_D^2 + \Delta\nu_A^2)^{1/2}$

  where $\Delta\nu_A$ is the apparatus function

But now, both $\Delta\nu_L$ and $\Delta\nu_G$ depend on gas temperature

$$\Delta\nu_{\mathbf{Doppler}}\ \mathbf{(FWHM) = 7.16\ 10^{-7}}\ \nu\mathbf{(T_g/M)^{1/2}}$$

$$\Delta\nu_{\mathbf{VdW}}\ \mathbf{(FWHM)}\ \text{å}\ K.\ p\ \mathbf{(T_g)}^{-0.7}$$

-If the correspondence between $\Delta\nu_{Doppler}$ and Tg is straight, for $\Delta\nu_{VdW}$ the knowledge of the broadening coefficient *K* is needed.

- Almost 99% of the published *K* coefficients of different spectral lines have been measured in ñThermal plasmasò, in which the Stark broadening also exists and the gas temperature is barely well defined.

- So, to be used for the precise determination of Tg, *K* coefficients need to be revisited in better known experimental conditions.

Laser absorption spectroscopy in rare gases

- He and Ar are the carrier gas in many atmospheric pressure plasmas.

- Their absorption lines in the VUV are hardly reachable with lasers but absorption from atoms in their metastable satates can be used for the determination of T_g.

- For several argon lines ending on metastable states, one can find in the literature *K* coefficient very often measured by emission spectroscopy in thermal plasmas. But sometimes they are different for the same line.

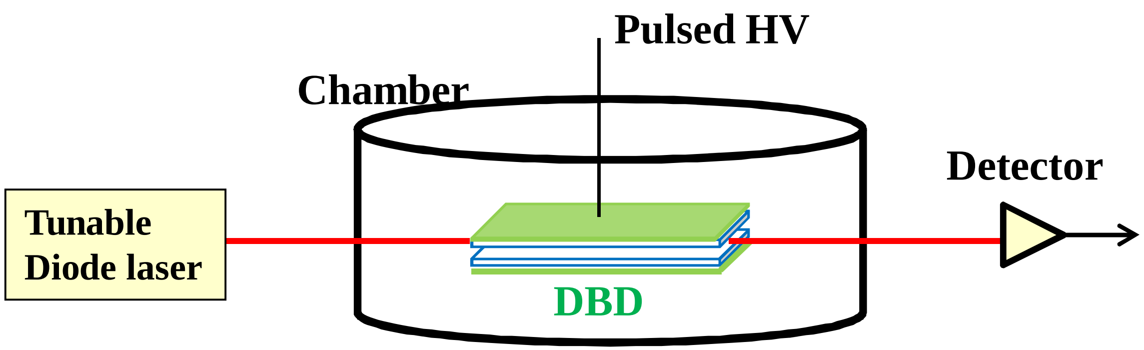
- For helium, 1083 nm line ending on He ($^3S_1$) metastable state, is easily attainable with Diode Lasers, only a few data exist but they poorly agree with each :

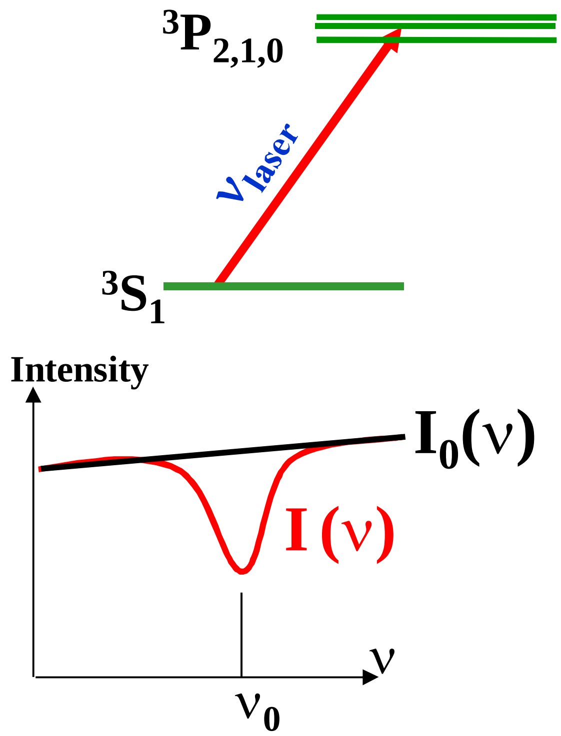
How to choose the right plasma for measuring a *K* coefficients ?

- It must be a high pressure plasma for having **large** $\Delta \nu_{VdW}$
- It must have low electron density for having **negligible** $\Delta \nu_S$
- The gas temperature shouldnα̂t be too high, **not dominant** $\Delta \nu_D$

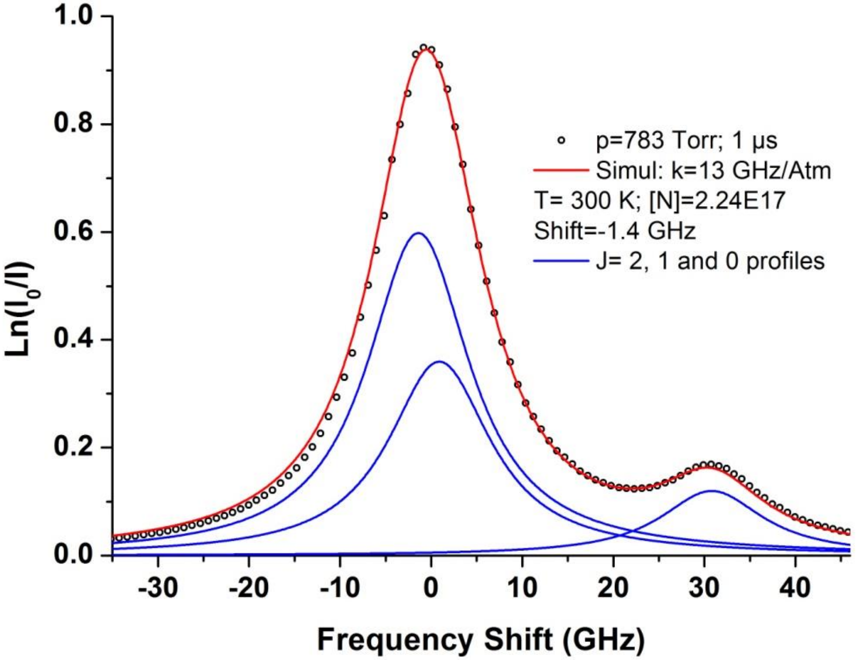
DBD plasma at low power with pulsed HV

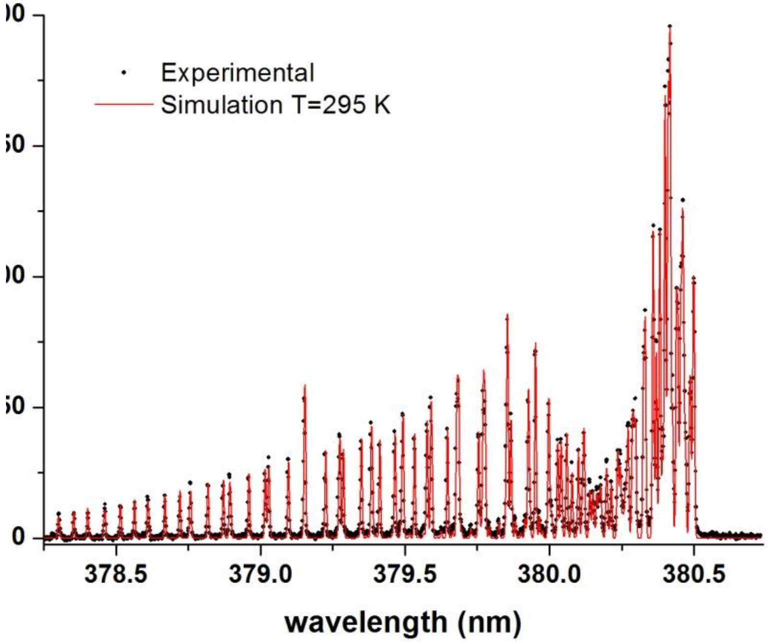
For helium 1083 nm line





Absorption profile of 1083 nm He line





As both $\Delta\nu_{\mathbf{vdW}}$ and $\Delta\nu_{\mathbf{Doppler}}$ depend on gas temperature

$$\Delta\nu_{\mathbf{Doppler}}\ \mathbf{(FWHM) = 7.16\ 10^{-7}}\ \nu\mathbf{(T_g/M)^{1/2}}$$

$$\Delta\nu_{\mathbf{VdW}}\ \mathbf{(FWHM)\ å}\ \boldsymbol{K.\ p}\ \mathbf{(T_g)^{-0.7}}$$

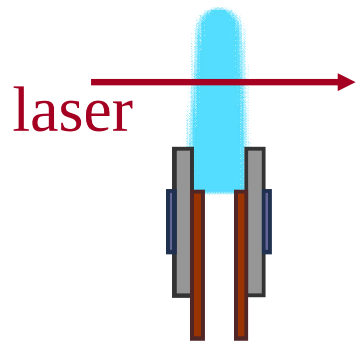
to deduce *K* from simulated profiles, one need to have **independent $\mathbf{T_g}$ measurement**

All known *K* values for the 1083 nm helium line

Ref (Year)	$\Delta\nu_p$ (GHz) @ 1 At & 300 K	Plasma	Pressure	Temperature	
1 (2005)	**14**	Mesh-electrode	1 Atm	300 K Assum but could be 400 K ?	LAS
2 (2004)	**18.5**			310	Theory
3 (2010)	**19.5**	Glass DBD	1 Atm	300 K Assumed	LAS
4 (2010)	**11.2**	RF µ-discharge	1 Atm	300 K Assumed	LAS
5 (2011)	**14.3**	RF µ-discharge	1 Atm	340 K by $N_2(2^+)$	LAS
6 (Present)	**13.5**	**DBD**	**1.1 Atm**	**295 K by $N_2(2^+)$**	**LAS**

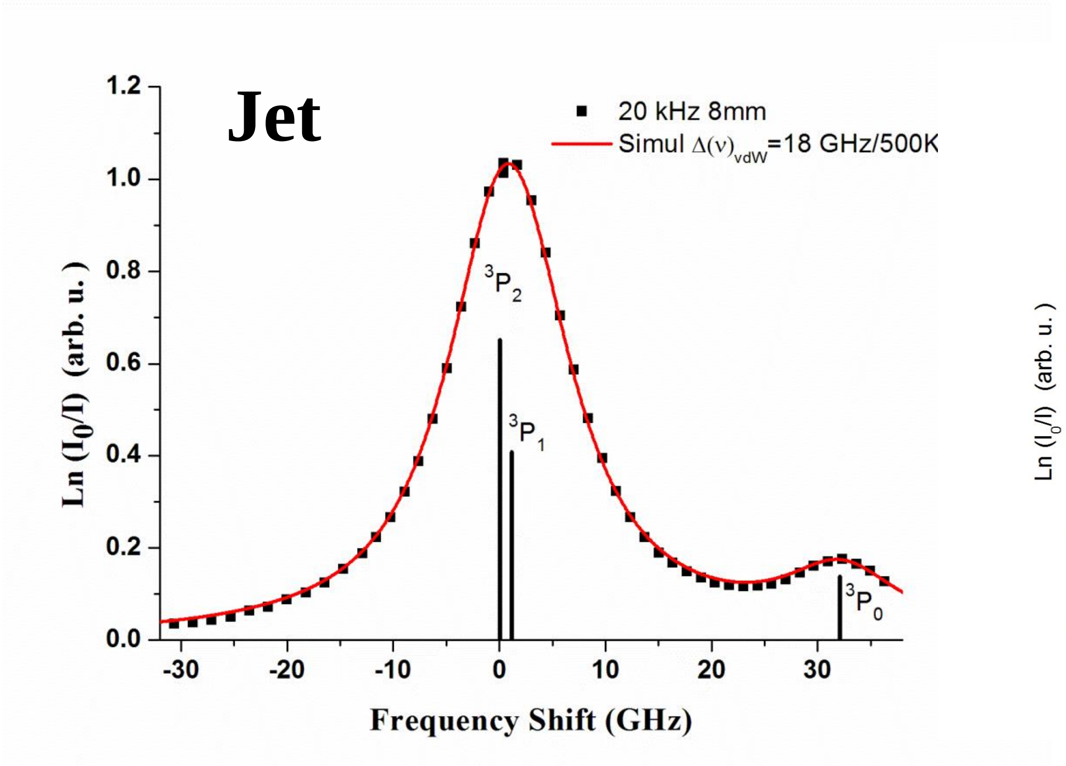
A doubt thinking that probably the real temperature in 1, 4 and 5 was higher than the assumed values !!!! $\Delta \nu_{VdW}$ **(FWHM) å** $K.\,p\,(T_g)^{-0.7}$

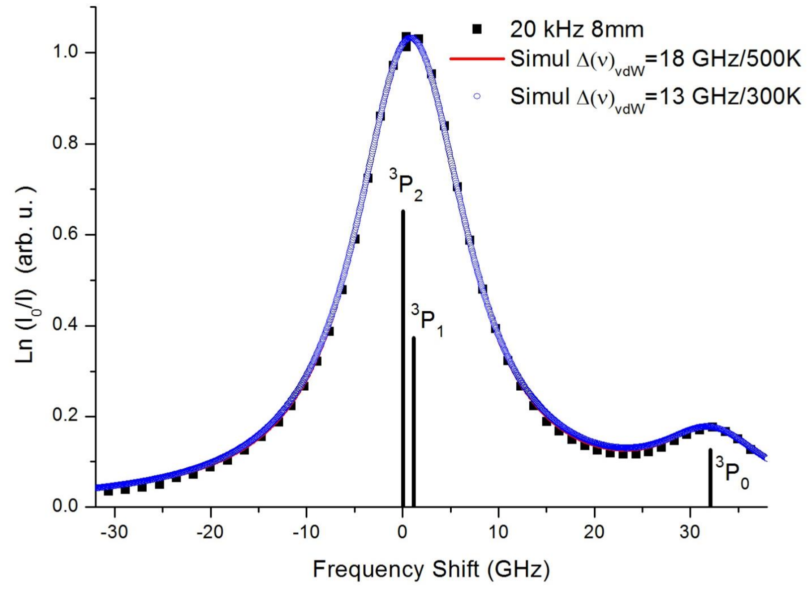
Also because the good agreement of 3 with theory



Then comes the line profile recorded in the plasma jet of Orsay with $\Delta \nu_{VdW}$ =13 GHz which confirmed the lower values

Comparison of 1083 nm He line profile fitted with different couple of parameters





The experimental data from plasma jet can be fitted by assuming
K=18 GHz (@ 1 Atm & 300 K) and Tg=500 ï 600 K **Too hot**
Or with **K=13 GHz** (@ 1 Atm & 300 K) and Tg=300 K

So an independent temperature measurement is absolutely needed

Conclusion on1083 nm helium line broadening

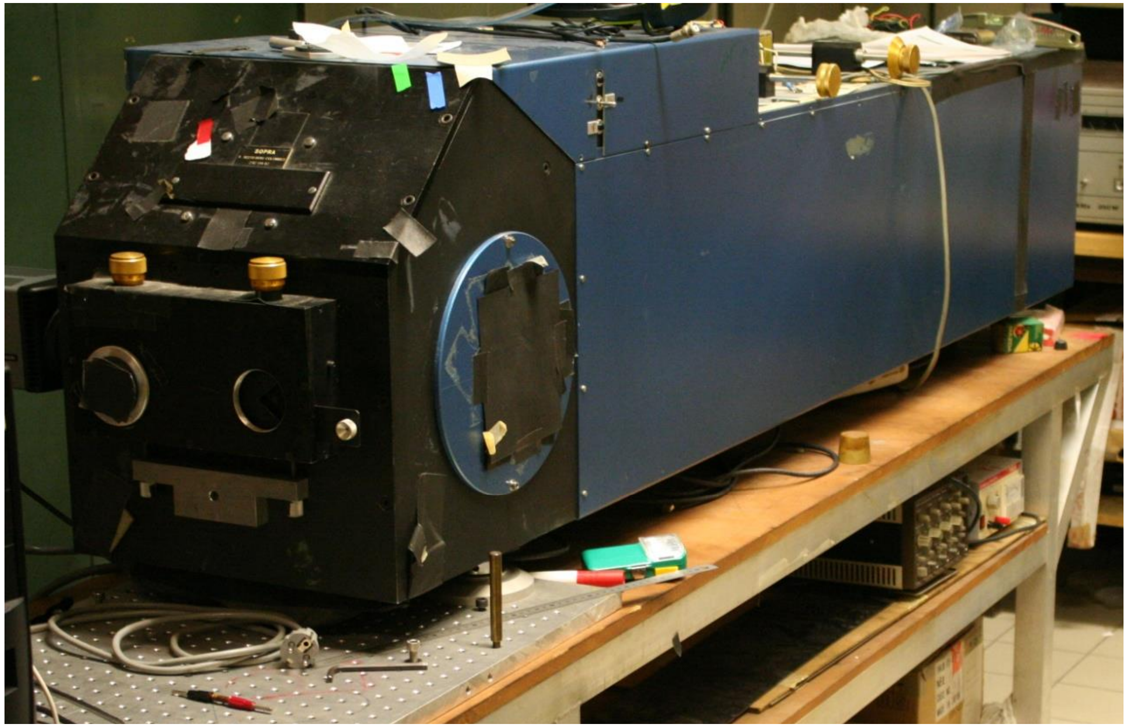
Ref (Year)	**$\Delta\nu_p$ (GHz) @ 1 At & 300 K**	**Plasma**	**Pressure**	**Temperature**	
1 (2005)	**14**	Mesh-electrode	1 Atm	300 K Assum but could be 400 K ?	LAS
2 (2004)	**18.5**			310	Theory
3 (2010)	**19.5**	Glass DBD	1 Atm	300 K Assumed	LAS
4 (2010)	**11.2**	RF µ-discharge	1 Atm	300 K Assumed	LAS
5 (2011)	**14.3**	RF µ-discharge	1 Atm	340 K by $N_2(2^+)$	LAS
6 (Present)	**13.5**	**DBD**	**1.1 Atm**	**295 K by $N_2(2^+)$**	**LAS**

I finally trust more the low value *K* about 14 GHz

En artifact can still exist: the static Stark effect due to E field created by charges on the dielectric surface ?

More investigation is needed

Broadened line width deduced from emission spectroscopy with a high resolution spectrometer



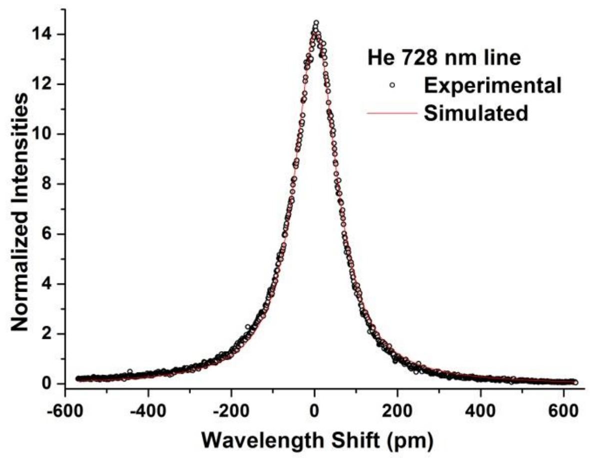
.

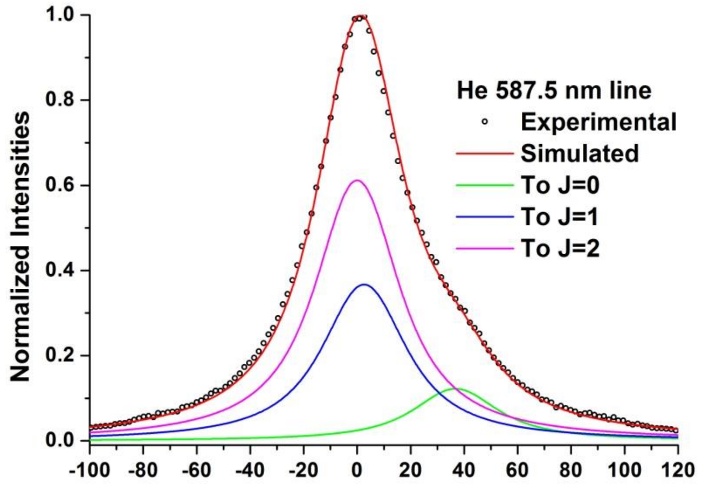
2 m focal spectrometer equipped with a 1200 groves/mm grating and working at 2nd to 5th diffraction order which was backed with a 13 µm pixels CCD camera. Spectral resolution can be down to 2 pm

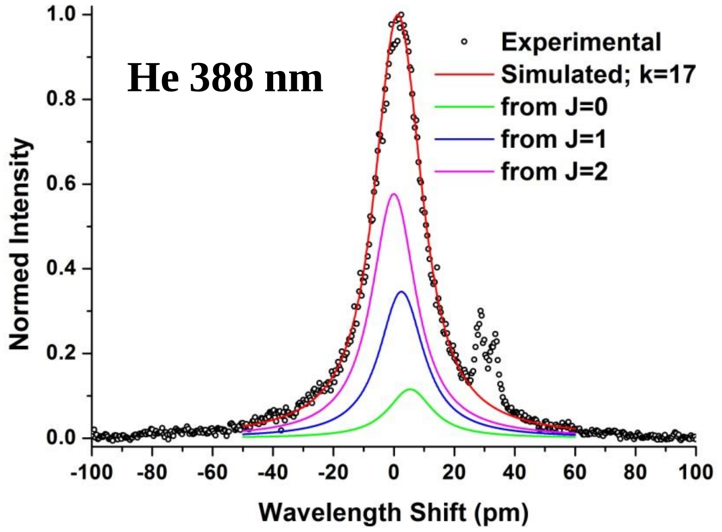
Now located at Paris 11 (Villetaneuse) & available to RPF members

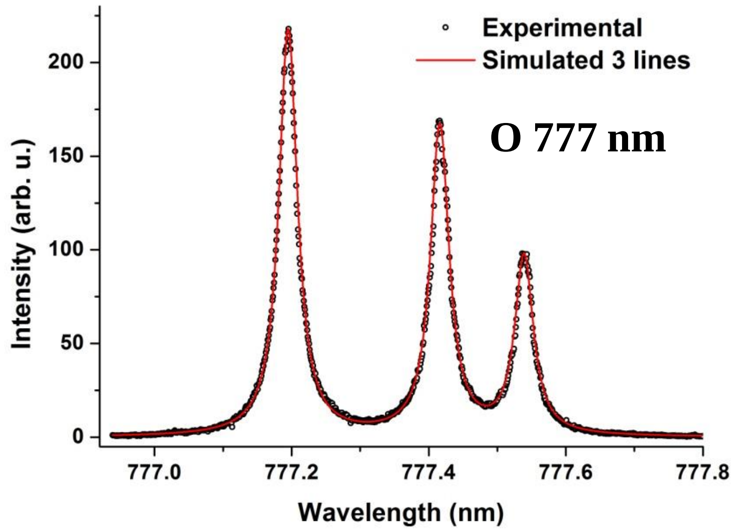
Emission line profiles recorded with spectrometer

Emission from the same DBD plasma than for the LAS: T_g=300 K









Pressure broadened linewidths (FWHM) measured by emission spectroscopy with 2 m SOPRA spectrometer

Line (nm)	Transition	Mono order	pm/pixel	width (pm)
He 501.5	$3\ ^1P_1$ - $2\ ^1S_0$	3rd	0.677	33.6 ± 0.5
He 504.7	$4\ ^1S_0$ - $2\ ^1P_1$	3rd	0.654	145 ± 25 VN
He 667.8	$3\ ^1D_2$ - $2\ ^1P_1$	2nd	1.482	105.0 ± 0.5
He 728.1	$3\ ^1S_0$ - $2\ ^1P_1$	2nd	1.171	123.9 ± 1.2
He 388.8	$3\ ^3P_J$ - $2\ ^3S_1$	4th	0.41	18.5 (17.0) ± 0.6
He 471.3	$4\ ^3S_1$ - $2\ ^3P_J$	3rd	0.86	88.6 ± 4.8 VN
He 587.5	$3\ ^3D_J$ - $2\ ^3P_{J'}$	2nd	1.793	44.7 (35.0) ± 0.5
He 706.5	$3\ ^3S_1$ - $2\ ^3P_J$	2nd	1.293	78.8 (65) ± 0.6
O 777		2nd	0.822	(30.7) ± 0.6
H 486.1		3rd	0.776	60.1 ± 0.5
H 656.3		2nd	1.532	63.8 ± 0.4

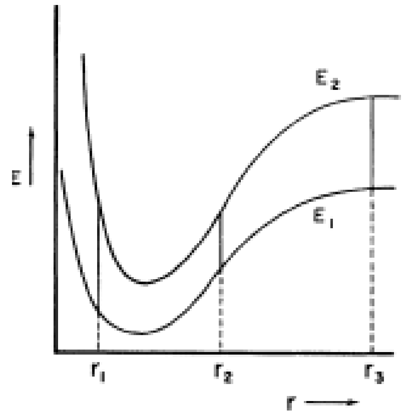
Theory of line broadening by neutral particle collision

See N. Allard and J. Kielkopf, Rev. Mod. Phys. 54, (1982) 1103

Different approaches have been proposed during years:

- Wave train and phase shift approaches
- The quasi-static approach and statistics of emission assuming the Franck-Condon principle

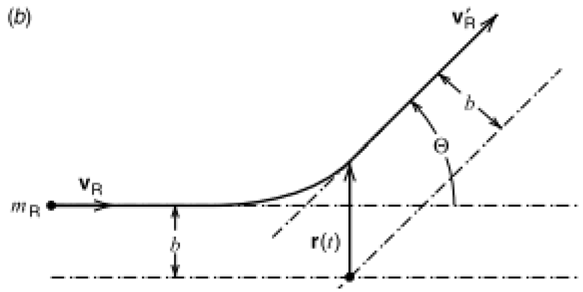
$$\Delta\nu = \frac{\Delta V}{h} \qquad V_i = \frac{1}{4\pi\epsilon_0}\frac{C_n}{R^n}$$



Impact theory: time variation of the relative velocity and of the phase of the oscillation, φ between states

When the collider is a foreign gas, the interaction is of dipole-induced dipole interaction and n=6.

The complete calculation is given in Allard *et al* but the practical formula reported in NIST website (with an error) are:



Practical formula are given in "A Physicist's Desk Reference, AIP 1989, ISBN 0-88318-629-2, page 101ñ and in the NIST website (but with the sign ñ-ò missing on the exponents of 10^n)

$$\frac{\Delta\lambda}{N} = 3.0x10^{-15}\lambda^2 (C_6)^{2/5} (T_g / \mu)^{3/10}$$

where λ, and $\Delta\lambda$ (FVHM) are in nm, μ is the reduced mass, N, the density, in cm^{-3} and T_g is the gas temperature.

$C_6 = C_{6u} - C_{6l}$, where each of Wan der Waals coefficients $C_{6i} = 9.8x10^{-10}\alpha_p R_i^2$ of the upper (u) and lower (l) states of the observed transition of perturbed atom is related to the polarizibility α_p (in cm^{-3}) of the perturber and to a parameter R_i^2 (in unit of Bohr radius a_0) defined as :

$$R_i^2 = 2.5[\frac{I_H}{I - E_i}]^2.[1 + \frac{I - E_i}{5.I_H}.(1 - 3.l_i(l_i + 1))]$$

where I_H is the ionization potential of hydrogen atom, I and E_i are the ionization potential and the energy of the considered state of the perturbed atom to which the observed transition belongs and l_i is the orbital angular momentum of the optical electron.

α_p = 0.201 10^{-24} cm^3 for helium and 1.62 10^{-24} cm^3 for argon

Pressure broadened linewidths (FWHM) measured by emission spectroscopy with 2 m SOPRA spectrometer

Line (nm)	Transition	Exp width (pm)	Theory vdW (pm)	Theory Resonance (pm)
He 501.5	$3\,^1P_1 - 2\,^1S_0$	33.6 ± 0.5	23.2 (27.7)	12.0 (14.4 GHz)
He 504.7	$4\,^1S_0 - 2\,^1P_1$	145 ± 25 VN	38.8 (45.6)	48.3 (56.9 GHz)
He 667.8	$3\,^1D_2 - 2\,^1P_1$	105.0 ± 0.5	34.1 (22.9)	87.4 (58.8)
He 728.1	$3\,^1S_0 - 2\,^1P_1$	123.9 ± 1.2	47.3 (26.8)	104.0 (58.8 GHz)
He 388.8	$3\,^3P_J - 2\,^3S_1$	18.5 (17.0) ± 0.6	13.6 (26.9 GHz)	
He 471.3	$4\,^3S_1 - 2\,^3P_J$	88.6 ± 4.8 VN	31.6 (42.7 GHz)	
He 587.5	$3\,^3D_J - 2\,^3P_{J'}$	44.7 (35.0) ± 0.5	26.9 (23.4 GHz)	
He 706.5	$3\,^3S_1 - 2\,^3P_J$	78.8 (65) ± 0.6	40.5 (24.3 GHz)	
O 777		(30.7) ± 0.6	21.2 (10.5 GHz)	
H 486.1		60.1 ± 0.5	45.9 (58.3 GHz)	
H 656.3		63.8 ± 0.4	45.4 (31.6 GHz)	

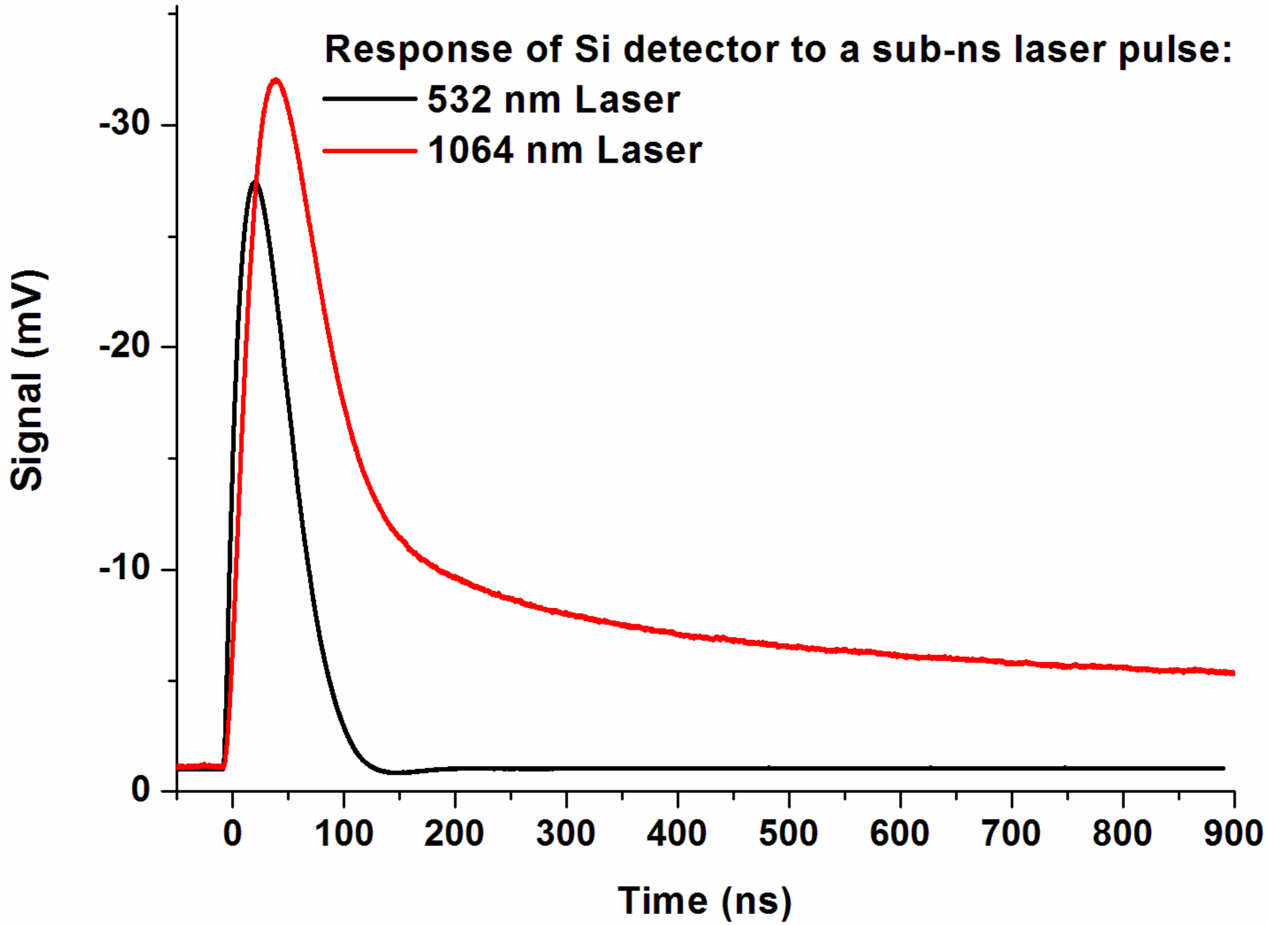
Artifacts occurring in LAS experiments of high pressure plasmas

Å Wavelength sensitive response time of the detector

Å Lensing effect due to the high density of absorbing species

Å Spatial non homogeneity of the absorbing atoms density within the laser

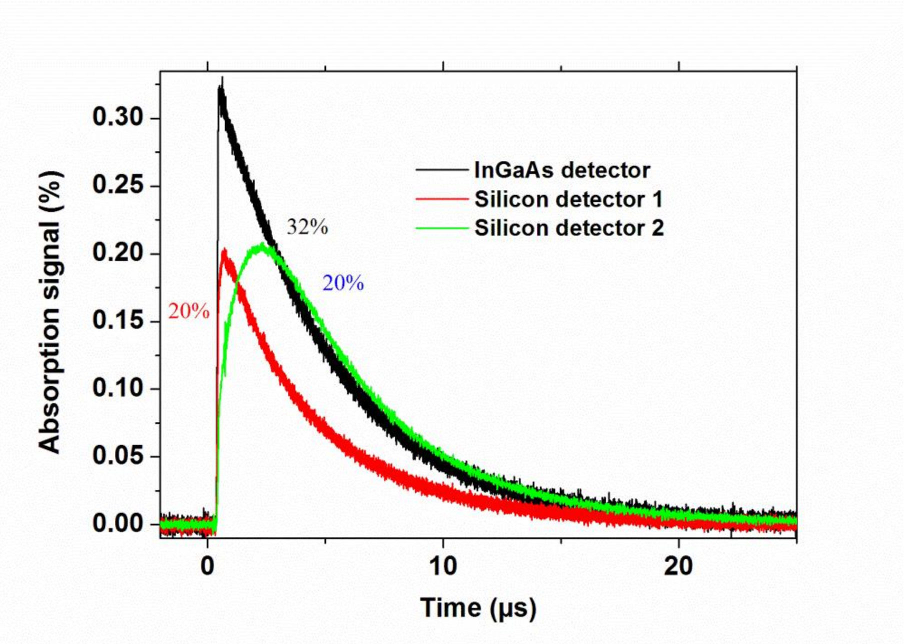
Response of Si detector to sub-ns laser pulses
Big influence of the laser wavelength



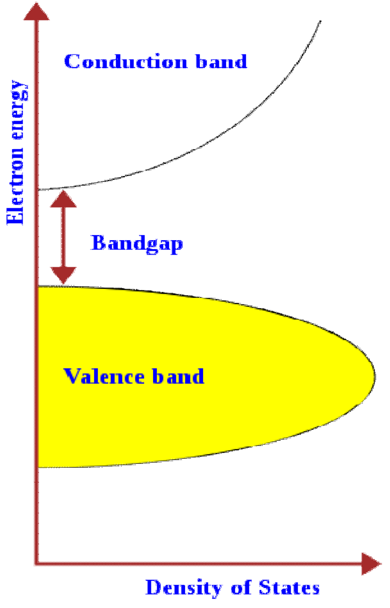
Detectors response time at 1083 nm

We have realized that the shape of the absorption signal depends on silicon detector used to detect the signal.

It comes out that these detectors, which had a good response time at 532 nm, present a long tail at 1083 nm.



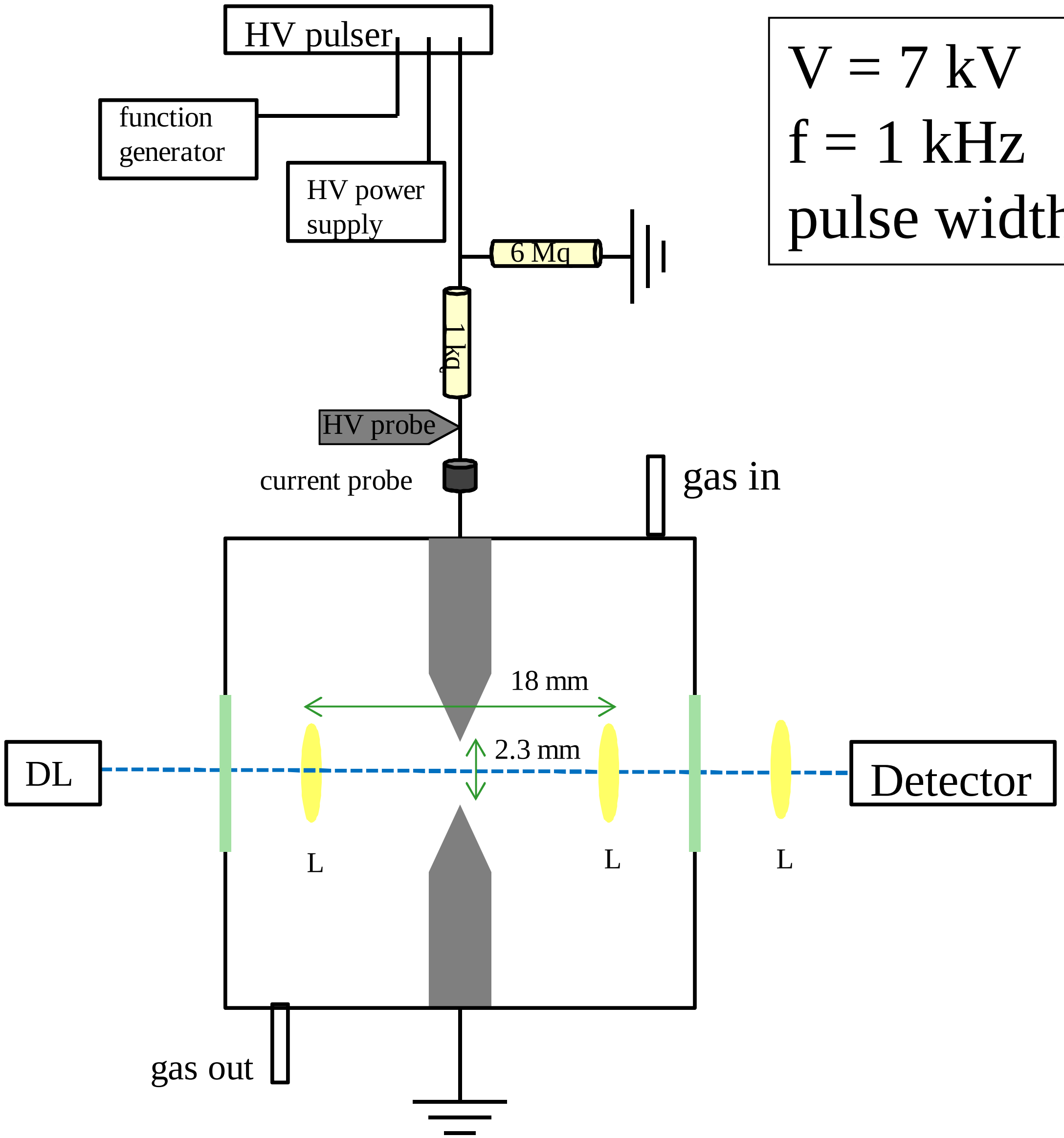
This comes from the 1.11 eV band gap of silicon which is very close to the 1.13 eW energy of 1083 nm photons.



Artifacts occurring in LAS experiments of high pressure plasmas

Å Lensing effect due to the high density of absorbing species

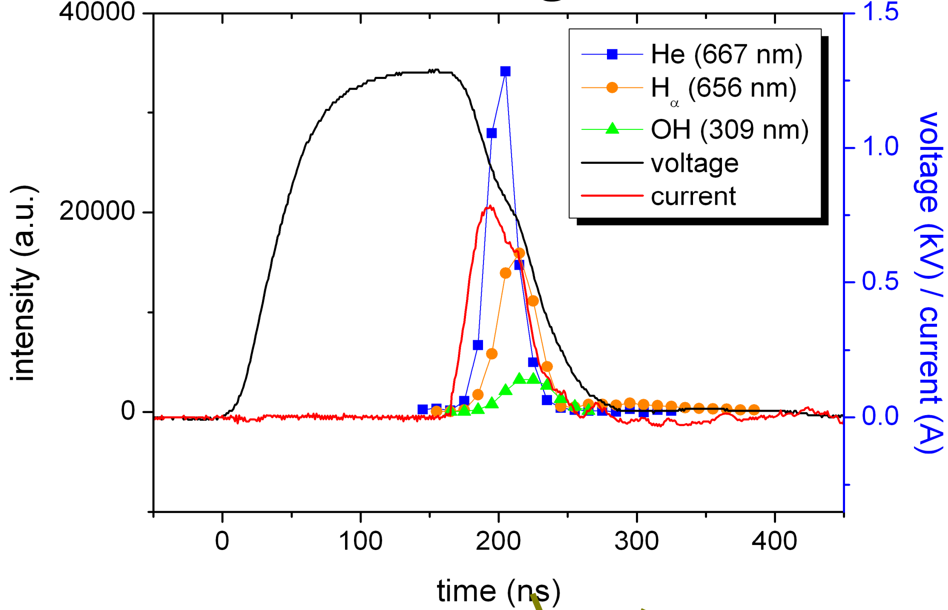
Experimental set-up for measuring He*($^3S_1$) density an atmospheric pulsed plasma (Eindhoven)



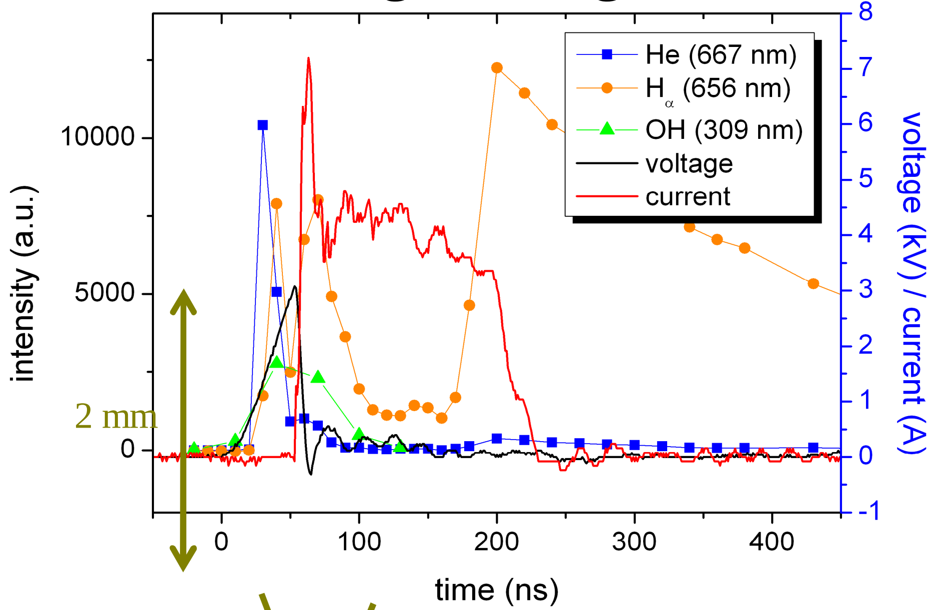
V = 7 kV
f = 1 kHz
pulse width = 170 ns

There are two plasma regimes:

Low Voltage

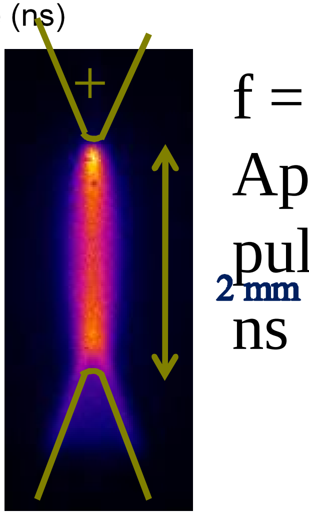


High Voltage



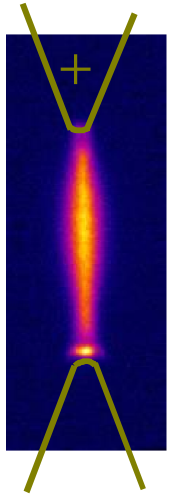
$n_{e,max}$ = 2.5 10^{21} m^{-3}

W = 0.03 mJ



f = 1 kHz

Applied voltage pulse width = 170 ns



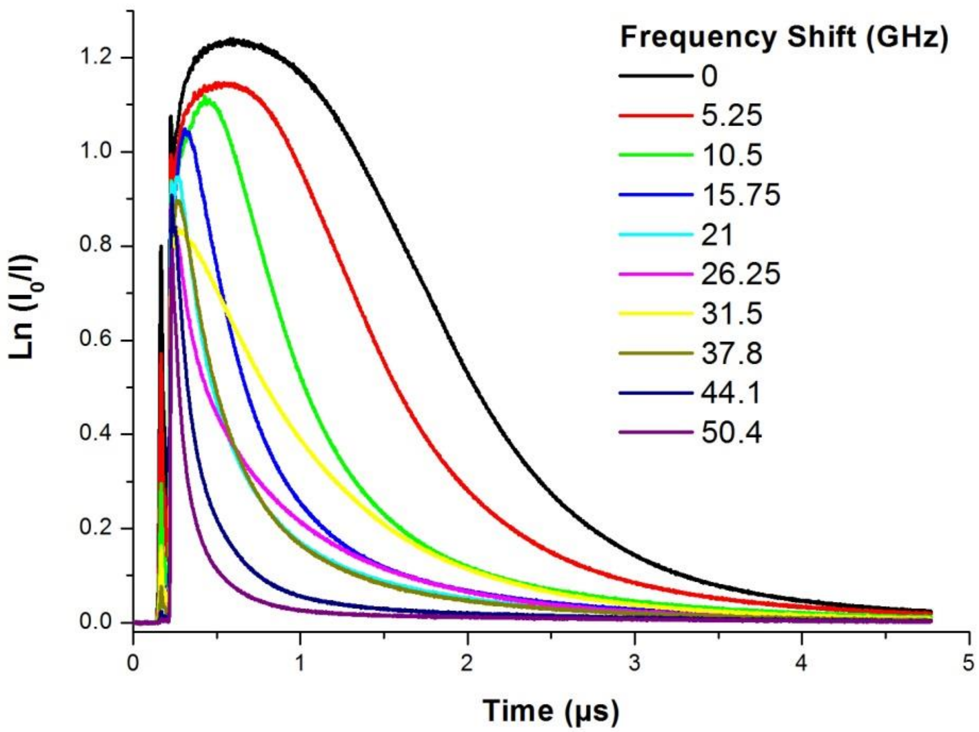
$n_{e,max}$ = 3 10^{22} m^{-3}

W > 0.2 mJ

T. Verreycken, R. Joosten, E. Van Veldhuizen, P. Bruggeman (submitted)

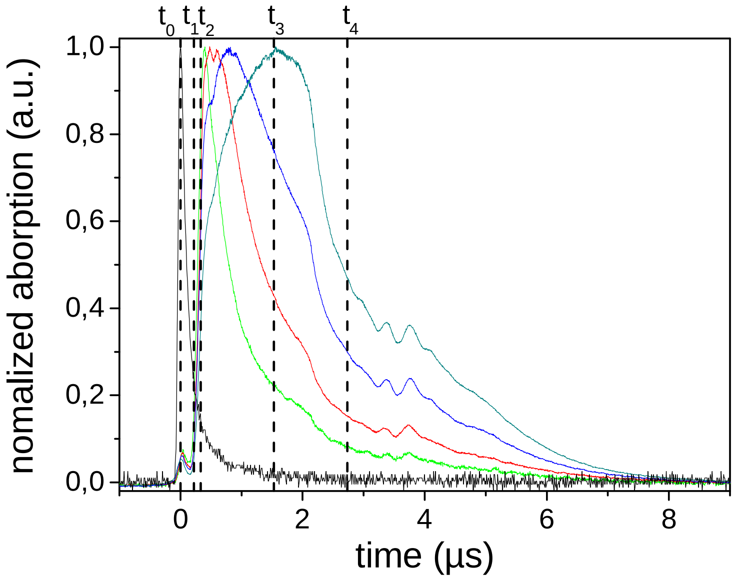
Measurement procedure with time varying absorbance curves recorded at different laser frequencies

Time varying absorbance curves recorded with different shift on laser frequency



Method of Analysis

t	ν1	ν2	ν3	ν4
t1	0.45	0.7	0.9	1
t2	0.5	0.75	0.95	1.05
t3	0.55	0.8	1	1.1
t4	0.6	0.85	1.05	1.15



The matrix is transposed

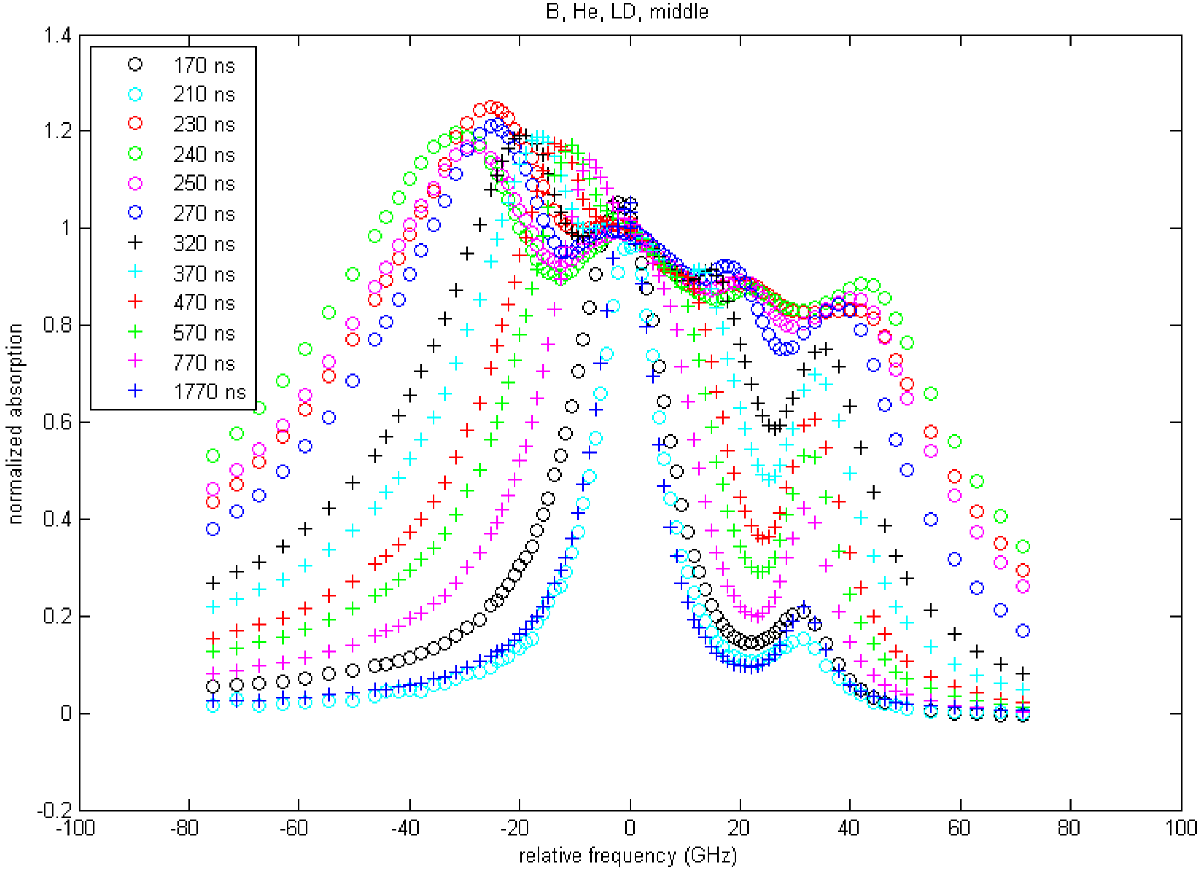
Each column gives the spectra corresponding to one time step

t	t1	t2	t3	t4
ν1	0.45	0.5	0.55	0.6
ν2	0.7	0.75	0.95	1.05
ν3	0.9	0.8	1	1.1
ν4	1	0.85	1.05	1.15

Profiles obtained at different times when the peack He($^3S_1$) density was high

Line profiles at different times obtained after transposing the matrix of data

The broad and strange line profiles at short times cannot be due to the Stark or Zeeman effects



Lorentzian absorption Profile is always associated with the dispersion profile of the index of refraction

Absorbance:

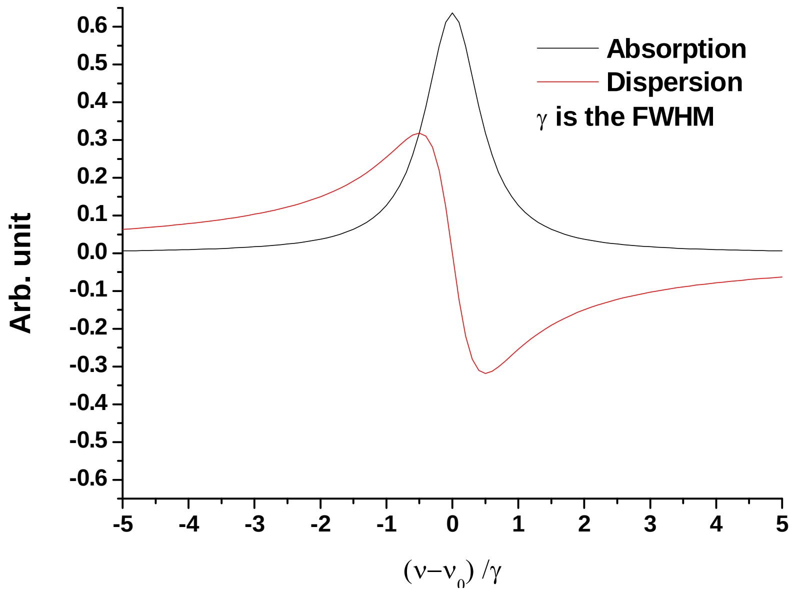
with N the density of atoms and f the oscillator strength of the resonance line.

$$Ln\frac{I_0(\nu)}{I(\nu)} = \frac{e^2}{4\pi\varepsilon_0 mc}.N.f\,\frac{2.\gamma}{4.(\nu-\nu_0)^2+\gamma^2}$$

In a gas, the index of refraction at frequency ν resulting from the presence of a resonance line at frequency ν_0 writes:

$$n-1 = \frac{e^2}{8\pi^2\varepsilon_0 m}.N.f\,\frac{\nu_0^2-\nu^2}{(\nu_0^2-\nu^2)^2+\nu^2.\gamma^2}$$

with N the density of atoms and f the oscillator strength of the resonance line.



Numerical application for ground state He atoms (He gas) when the laser is scanned over the ^3p_J-$^3S_1$ line

The monitoring wavelength λ=1083 nm (ν~9230 cm^{-1}) is very fare from the resonance line of He @ λ=58 nm (ν_0~172000 cm^{-1}), which means $\nu_0 >> \nu$.

Then the equation
$$n-1=\frac{e^2}{8\pi^2\varepsilon_0 m}.N.f\,\frac{\nu_0^2-\nu^2}{(\nu_0^2-\nu^2)^2+\nu^2.\gamma^2}$$

Is reduces to:
$$n-1=\frac{e^2}{8\pi^2\varepsilon_0 m}.N.f\,\frac{1}{\nu_0^2}=1.4x10^{-29}.f.N$$

At atmospheric pressure of He and 300 K, N=2.5 x 10^{25} m^{-3} and with f~0.5 one can deduce n-1~2 x 10^{-4}

When a temperature gradient exists, the lensing effect can occur

Numerical application when He metastable atoms $^3S_1$ are responsible for the diffraction phenomenon

The monitoring wavelength λ=1083 nm (ν~9230 cm^{-1}) is now very close to the ^3p_J-$^3S_1$ line resonance which means $\nu_0 \sim \nu$.

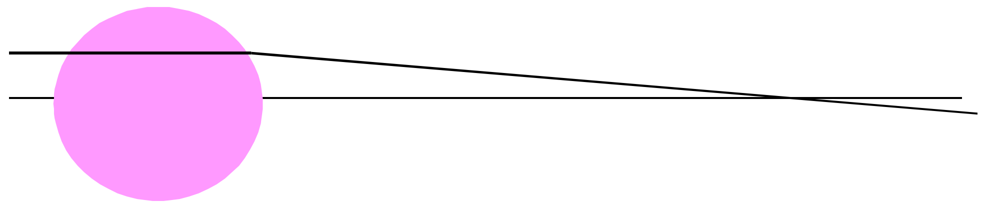
Then, for $\nu - \nu_0 = \gamma/2$ the equation $n-1=\frac{e^2}{8\pi^2\varepsilon_0 m}.N.f\frac{\nu_0^2-\nu^2}{(\nu_0^2-\nu^2)^2+\nu^2.\gamma^2}$

Is reduces to: $n-1=\frac{e^2}{8\pi^2\epsilon_0 m}.N.f\frac{2.\nu_0.\gamma/2}{2.\nu_0{}^2.\gamma^2}=\frac{e^2}{8\pi^2\epsilon_0 m}.N.f\frac{1}{2.\nu_0.\gamma}$

With N the density of [$^3S_1$] atoms =3 x 10^{19} m^{-3} and with f~0.3 for the $^3p_2$-$^3S_1$ line, one deduce n-1~5 x 10^{-4}

The diffraction by 3 x 10^{19} m^{-3} metastable atoms is comparable to the diffraction by 1 atmosphere of helium!!!

Numerical application for lensing effect with $n-1 \sim 5 \times 10^{-4}$



With radius d and index n, the focal of the spherical lens is:

$$f = \frac{d.{}^{n}/_{n_0}}{2.({}^{n}/_{n_0} - 1)} \sim \frac{d}{2.(n - n_0)}$$

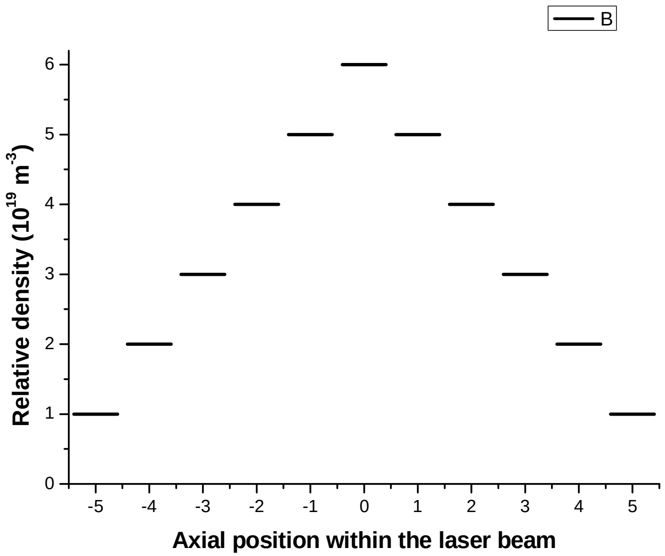
The deviation angle with this lens is: $\theta = \dfrac{d}{\left(\dfrac{d}{2.(n-n_0)}\right)} = 2.(n - n_0)$

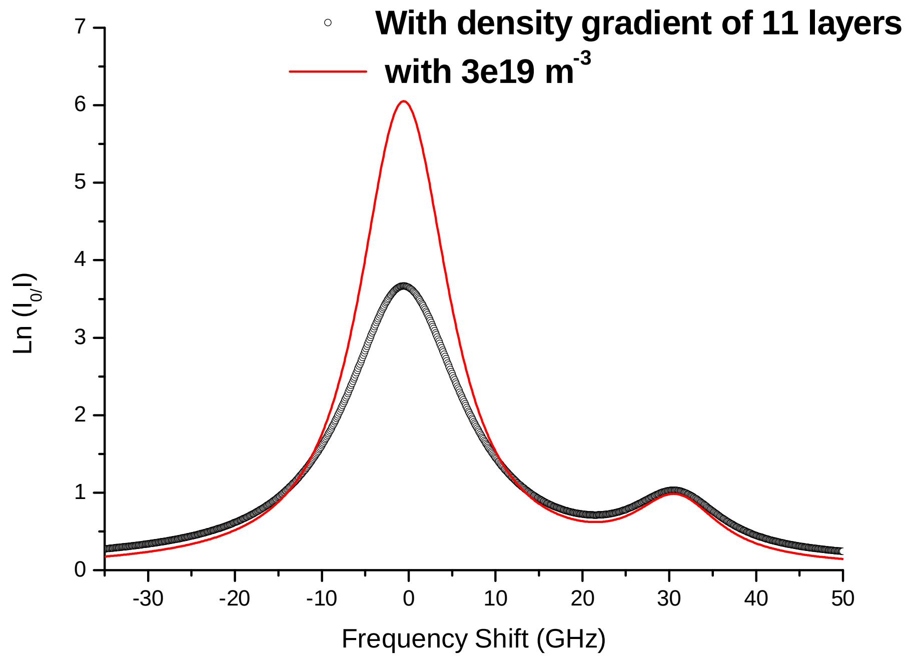
With $n\text{-}n_0$=5 10^{-4}, The deviation at a distance of 40 cm can reach 0.2 mm, which was not negligible compared to the 0.6 mm diameter of the detector

Artifacts occurring in LAS experiments of high pressure plasmas

Å Spatial non homogeneity of the absorbing atoms density within the laser

Radial non homogeneity of the absorbing atoms density within the laser spot





The discrepancy comes from the non linearity of the Log function:

$\sum Ln({}^{I_0}/_{I_i}) \neq Ln(\frac{\sum I_0}{\sum I_i})$ excepted when $I=(1-\varepsilon_i)I_0$ with $Ln(I_0/I)=\varepsilon$

The absorbance being 8 times weaker at the small line (f=0.06) than on the central line (f=0.48), the disturbance is almost negligible

See poster (anti-poster) from Laurent Invernizzi