Utilisation des Diodes Laser pour des mesures d'absorption:

- Détermination de la température de gaz à partir de profil Doppler
- Saturation optique
- Quelques artéfacts

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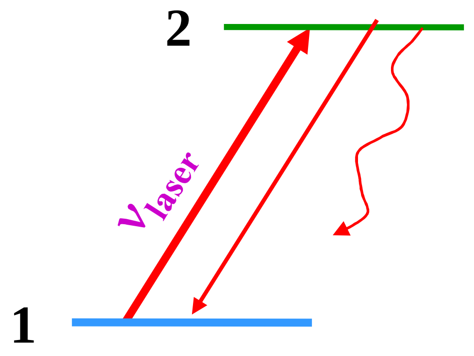
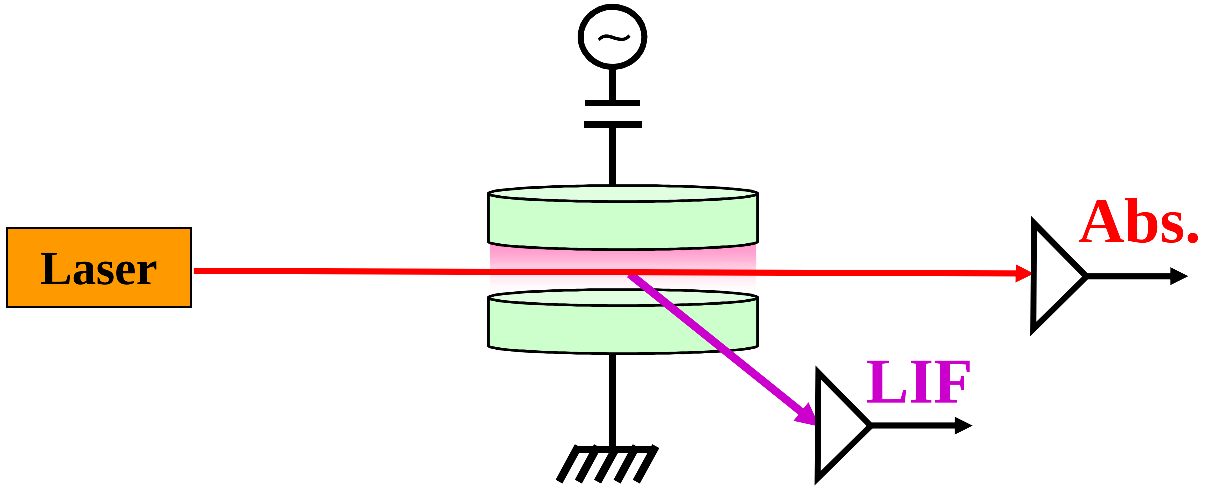
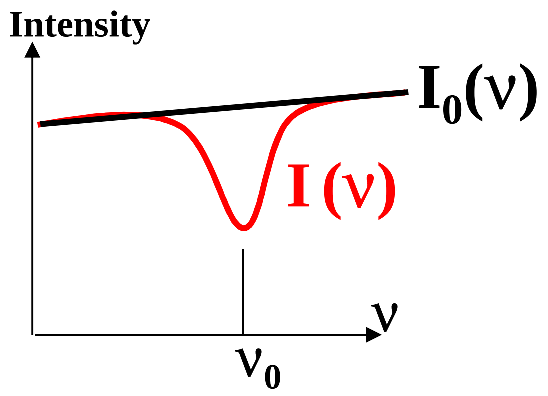
Atelier DL. 17

Spectroscopie d’Absorption Laser

La fréquence du laser est accordée sur une transition spécifique de l’atome



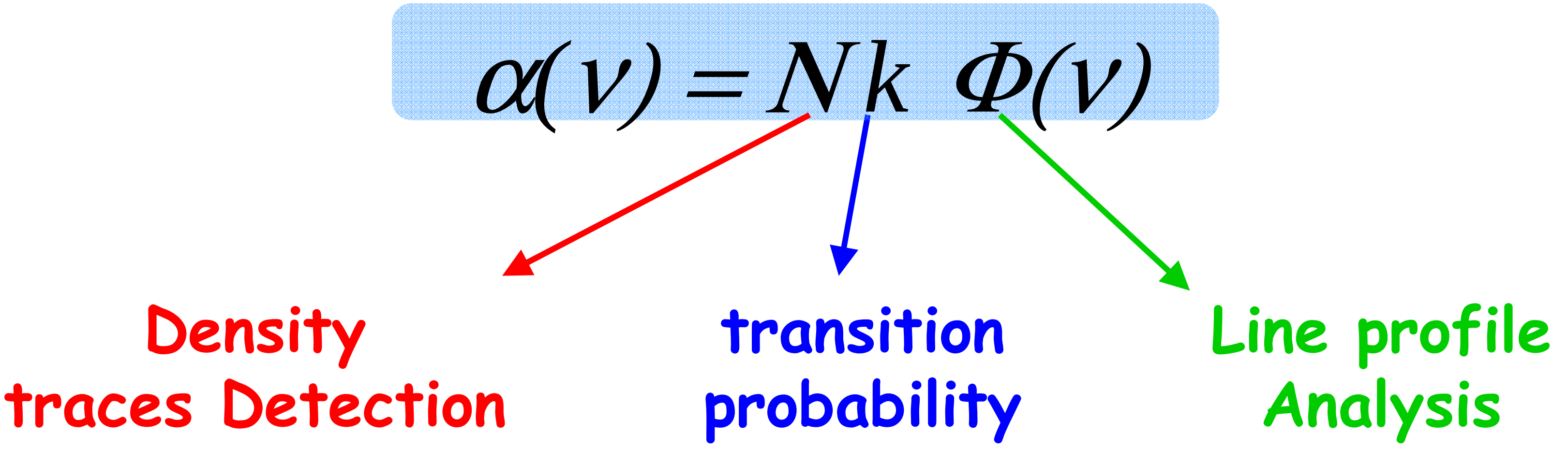




$$Ln(\frac{I_0(\nu)}{I(\nu)}) = l.\alpha(\nu)$$

$$\alpha(\nu) = \frac{4hB_{12}}{\lambda\gamma}\left(n_1(\nu) - \frac{g_1}{g_2}n_2(\nu)\right)$$

What can we learn by measuring α(ν) ?

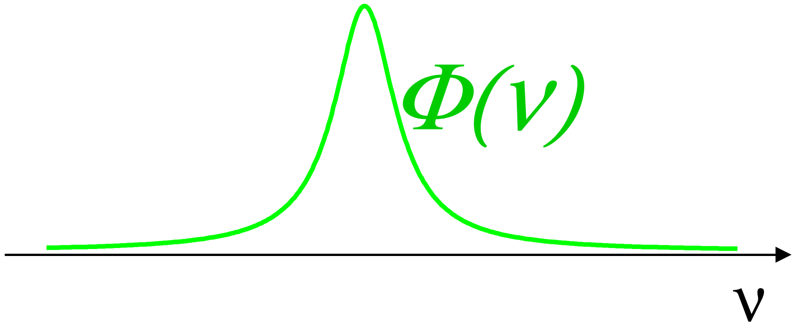


$$\alpha(\nu) = N k \; \Phi(\nu)$$

Density
traces Detection

transition
probability

Line profile
Analysis



Unités utilisées en spectroscopie

$1\ \mathrm{eV} = 1.6 \times 10^{-19}\ \mathrm{J} = 8065\ \mathrm{cm}^{-1}$ **Nombre d ’onde**

$300\ kT = 207\ \mathrm{cm}^{-1}$

$1\ \mathrm{cm}^{-1} = 30\ \mathrm{GHz}$

$$\nu = \frac{c}{\lambda} \qquad \Delta\nu = \frac{c * \Delta\lambda}{\lambda^2}$$

Énergie de photon:

$\lambda = 500\ \mathrm{nm}$ $\quad 1/\lambda = 20000\ \mathrm{cm}^{-1}$

Largeur de raie:

A 563 nm, $\Delta\lambda = 1\ \mathrm{nm} \rightarrow \Delta\nu = 1000\ \mathrm{GHz}$

Profils des raies spectrales

Largeur Homogène: Pour une transition, identique pour tout les atomes:

Sa forme est une Lorentzienne

$$L_L(\nu-\nu_0)=\frac{1}{2\pi}\frac{\delta\nu_L}{(\nu-\nu_0)^2+(\delta\nu_L/2)^2}$$

Largeur naturelle:

$$\delta\nu_n(FWHM)=\frac{1}{2\pi\tau}$$

Largeur Inhomogène: due aux effets collectifs, par exemple l'agitation thermique des atomes (**Elargissement Doppler**):

Sa forme est une Gaussienne

$$L_D(\nu-\nu_0)=\frac{2\sqrt{\ln(2)/\pi}}{\delta\nu_D}\exp-4\ln(2)\frac{(\nu-\nu_0)^2}{(\delta\nu_D)^2}$$

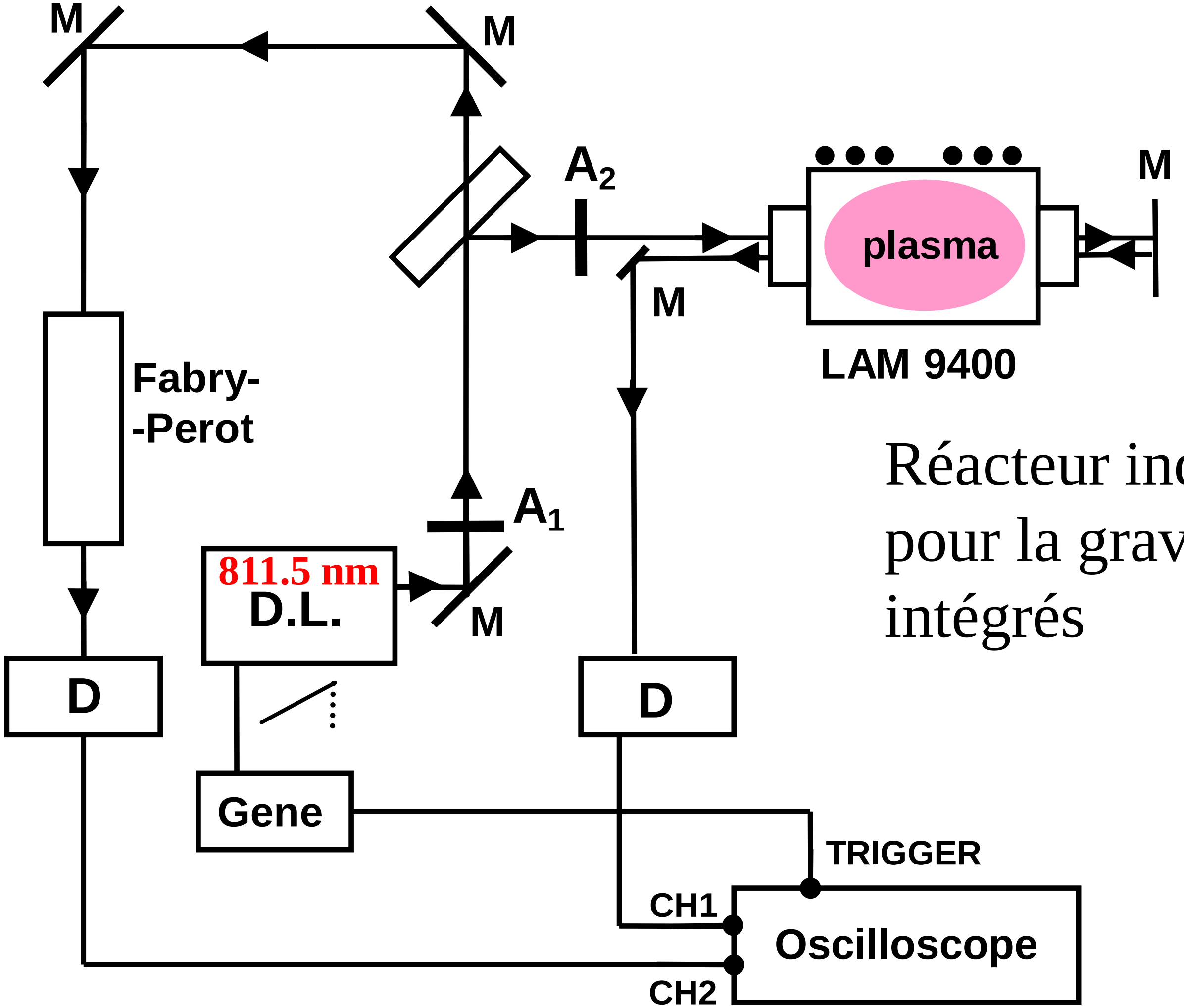
Largeur Doppler :

$$\delta\nu_D(GHz)=(2\nu_0/c)\sqrt{2\ln 2(RT/M)}=7.16\cdot 10^{-16}\nu_0\sqrt{T/M}$$

Pour la raie 589.1 nm de sodium (τ=16 ns) à 500 K $\delta\nu_n$=0.01 GHz

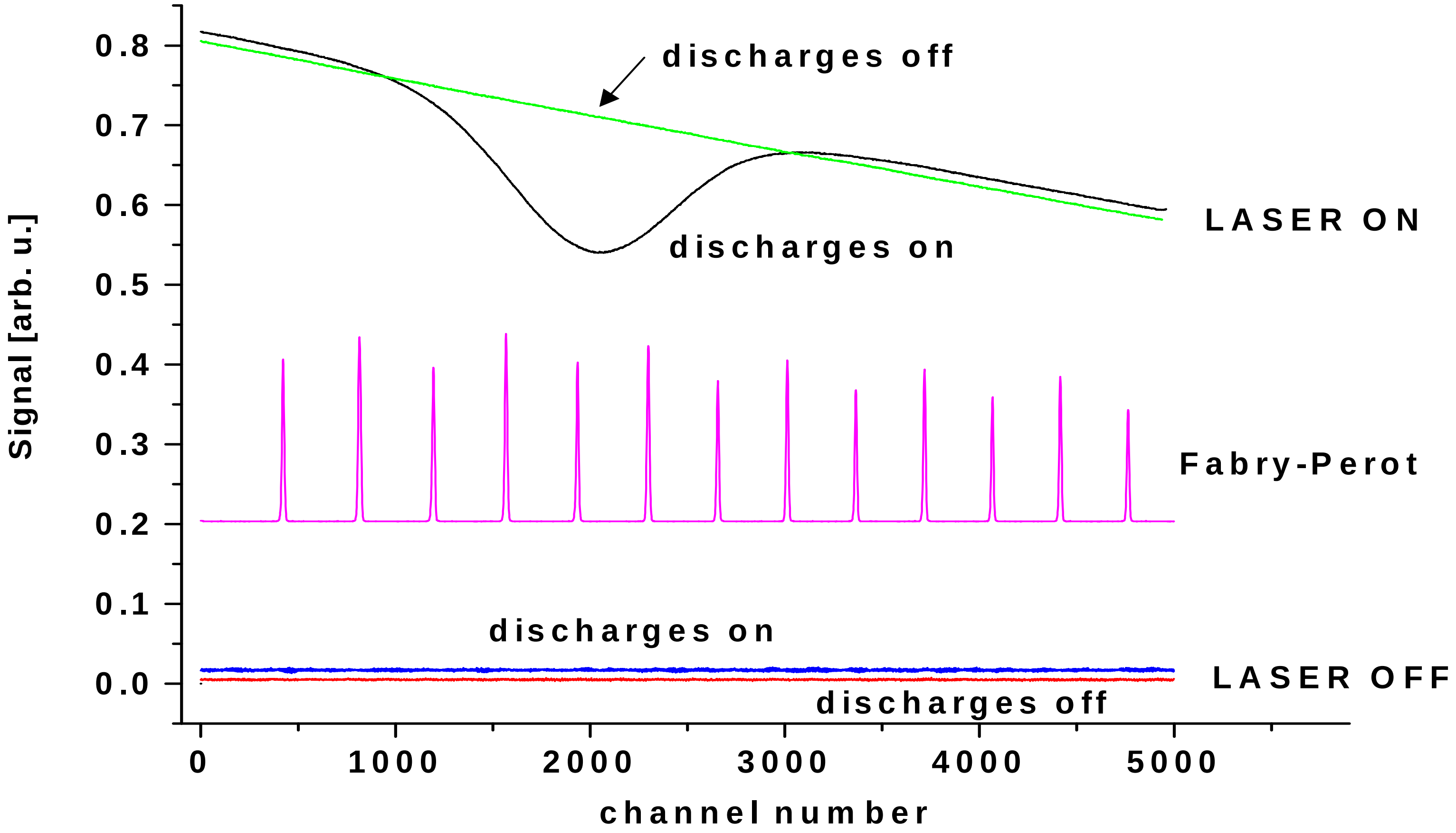
$\delta\nu_D$=1.7 GHz

Montage expérimental



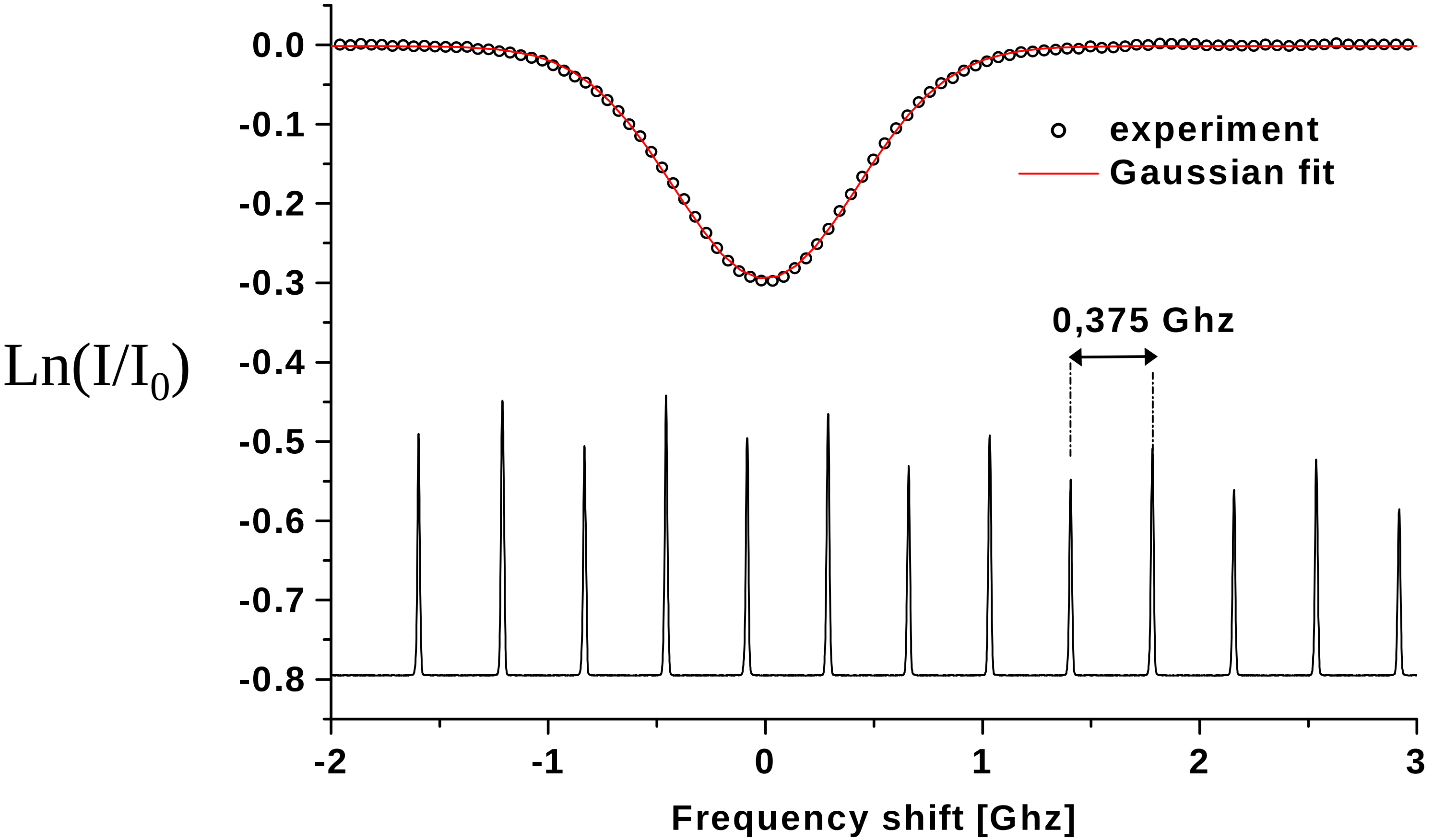
Réacteur industriel utilisé pour la gravure de circuits intégrés

Signaux enregistrés



Density≈Ln(I_0/I) I_0=Laser$_{\text{on-plasma off}}$-BG I=Laser$_{\text{on-plasma on}}$-Plasma

Détermination de la largeur Doppler



Détermination de la densité et la température des métastables Ar*($^3P_2$)

S, la surface de la raie d'absorption est donnée par l'équation :

$$S = \int_0^\infty \ln\left(\frac{I(0,\nu)}{I(l,\nu)}\right) d\nu = h\nu_0 B_{ik} l \langle N_i \rangle$$

D'où on peut déduire la densité moyenne des espèces absorbantes :

$$\langle N_i \rangle = \frac{1}{h\nu_0 B_{ik} l} S = \frac{4\varepsilon_0 m_e}{e^2 f_{ik} l} S = \frac{1}{l f_{ik}} 3{,}8 \times 10^{14} S$$

***S*, la surface en GHz, <Ni> en m^{-3} et f_{ik} la force oscillateur de la raie:**

Pour la raie 811.5 nm absorbée par les atomes Ar*($^3P_2$), f_{ik} = 0,46

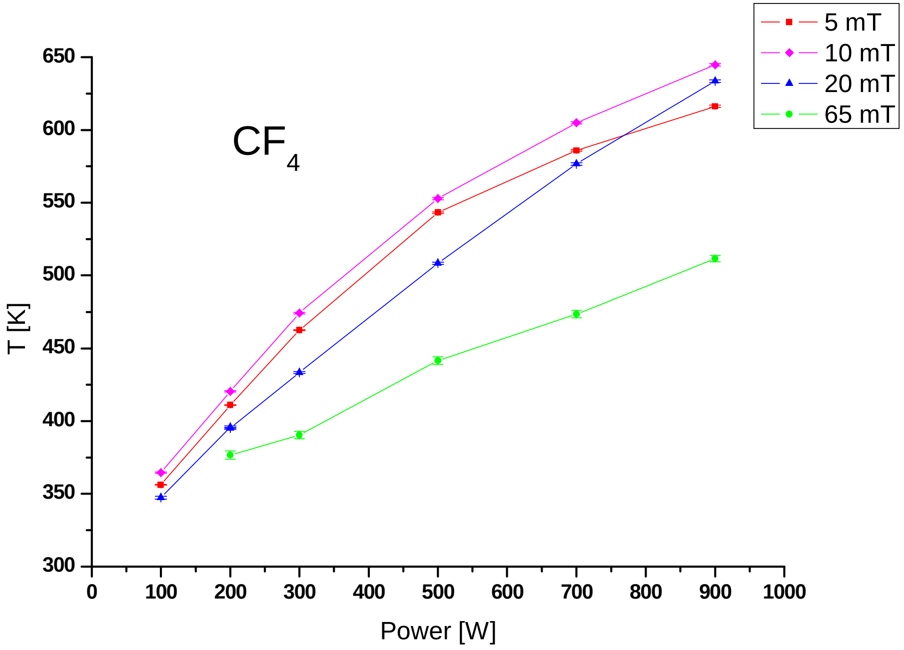
Donc **<Ni> = 8.08 x 10^{14} . S / *l***

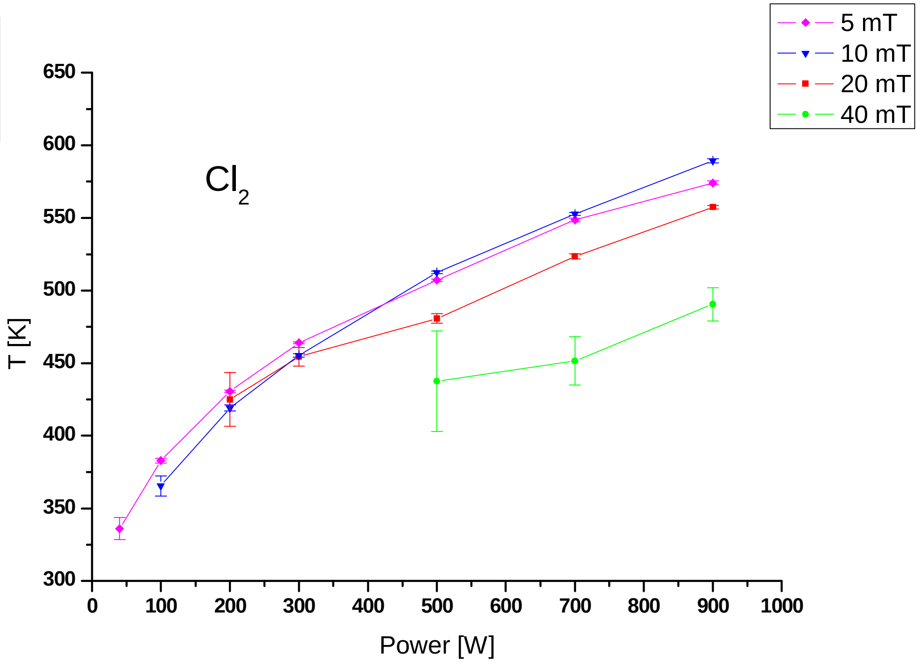
La largeur Doppler est: $\delta\nu_D(GHz) = 7.16x10^{-16}\nu_0\sqrt{T/M}$

Pour la raie 811.5 nm de l'argon , **T=572.$(\delta\nu_D)^2$**

Température du gaz en fonction de la puissance RF

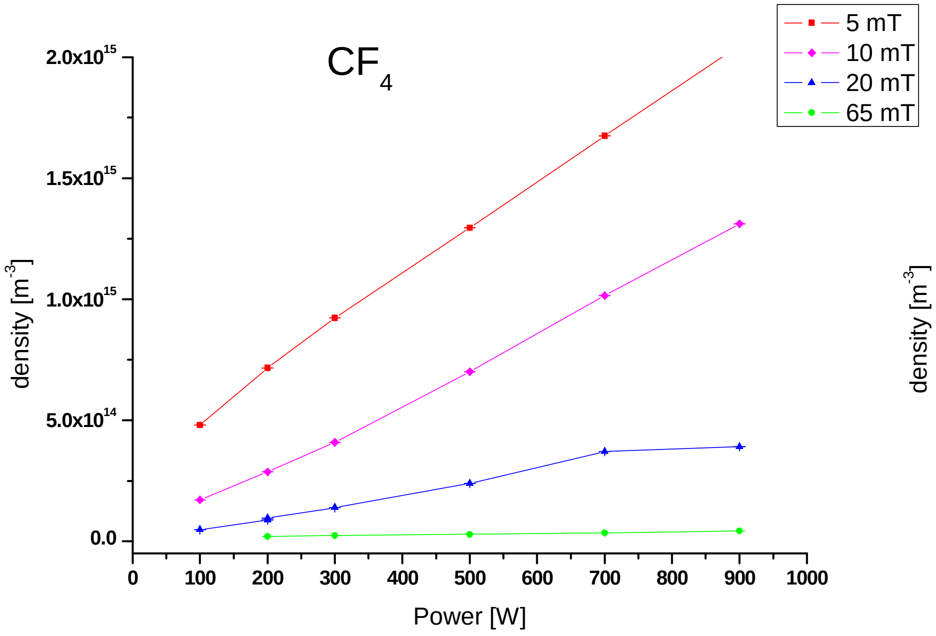
5% d’argon est ajouté au gaz pour obtenir T à partir de $\delta\nu_D$

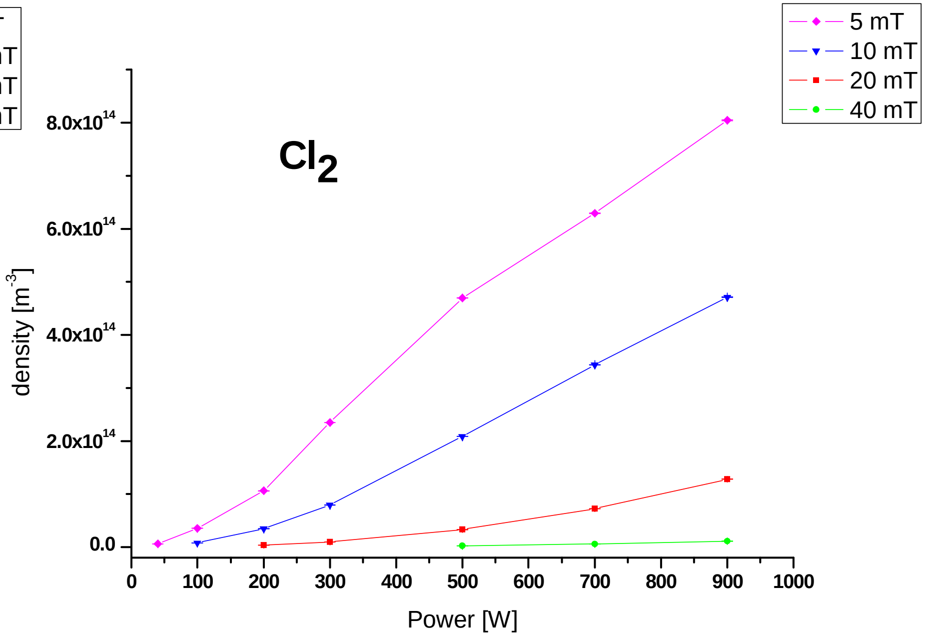




T augmente avec P_{RF}, mais dépend peu de la nature du gaz

Densité de Ar*($^3P_2$) en fonction de P_{RF}



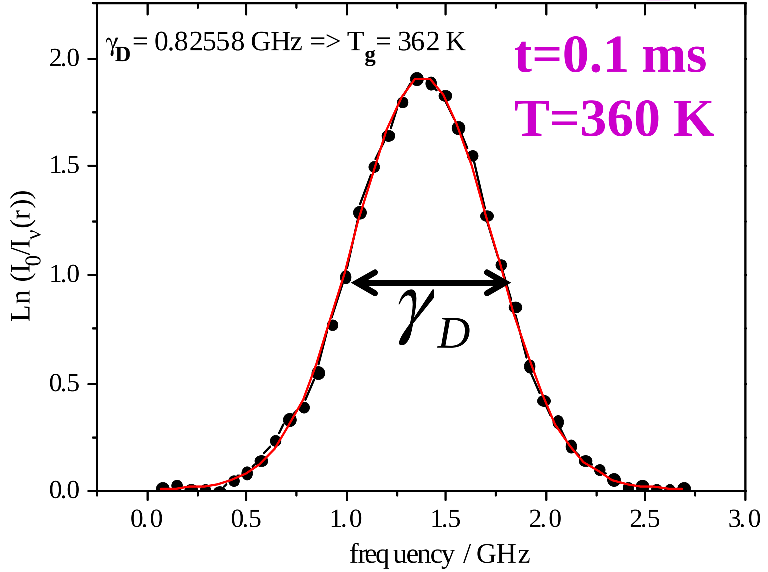


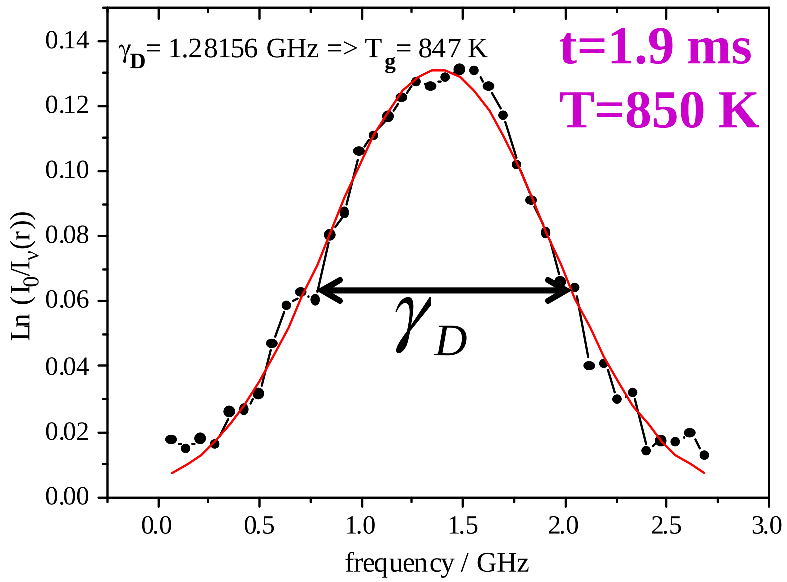
A 100 W, la densité de Ar*($^3P_2$) est l5 fois plus faible dans Cl_2 que dans CF_4 car $k_q(Cl_2)$= 71 x 10^{-17} $m^3.s^{-1}$ et $k_q(CF_4)$= 4 x 10^{-17} $m^3.s^{-1}$

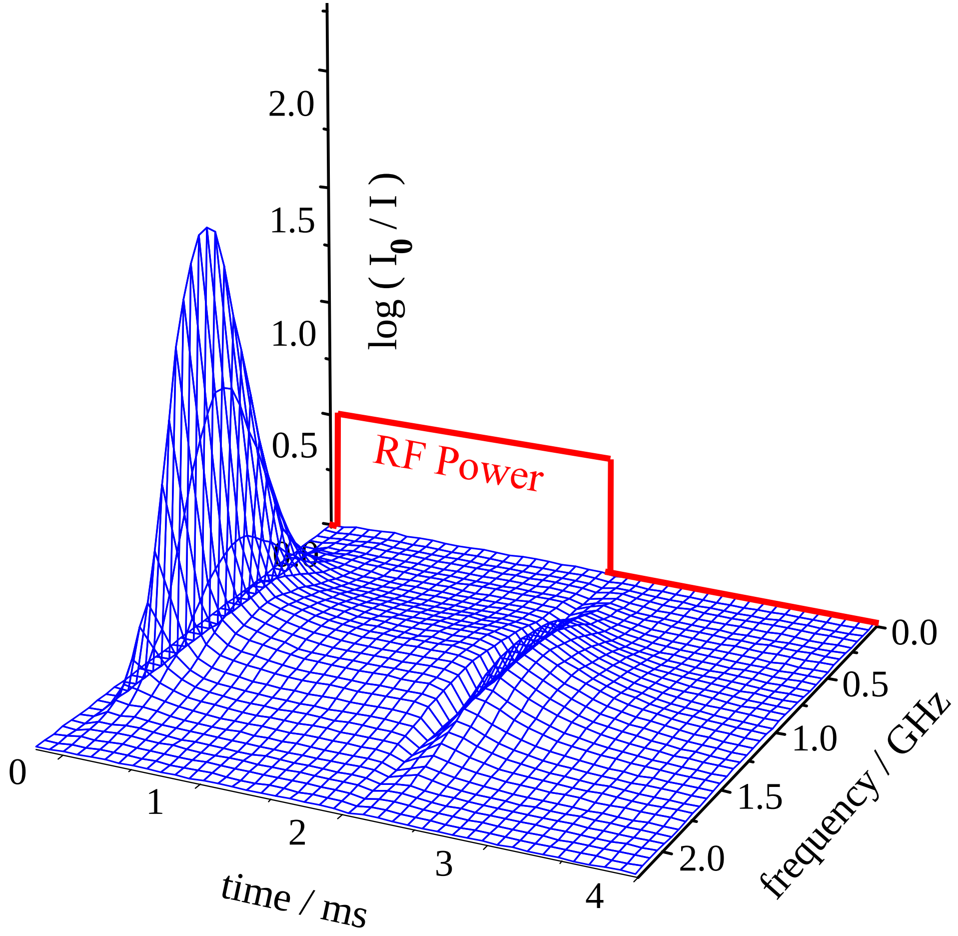
Voir J.E. Velazco *et al*, J. Chem. Phys. **68** (1978) 4357

A forte P_{RF}, Cl_2 est dissocié et $k_q(Cl)$< $k_q(Cl_2)$ donc [Ar*] augmente

Densité et Température des atomes Ar* dans un plasma pulsé Helicon







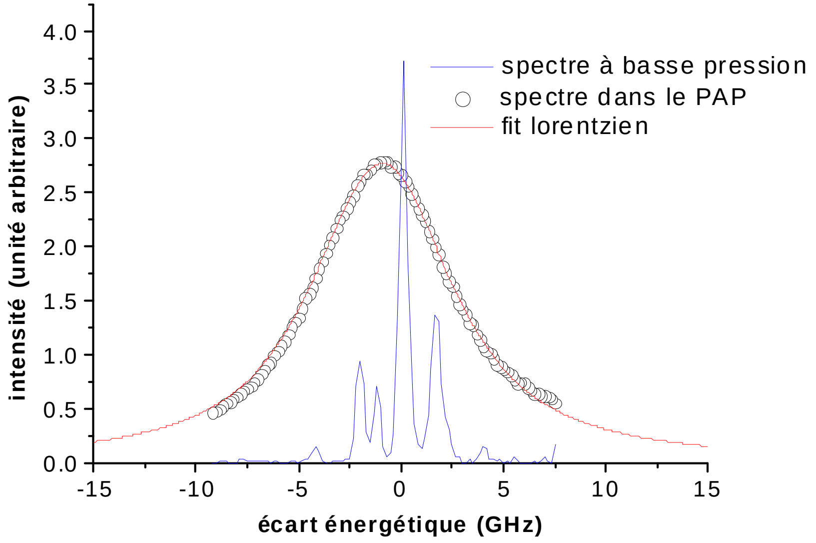
$$\gamma_D(t) = \frac{2\sqrt{Ln2}}{\lambda_0}\sqrt{\frac{RT(t)}{M}}$$

Artifacts

Xenon Line Profiles Broadened by pressure (Ne 800 mBar)

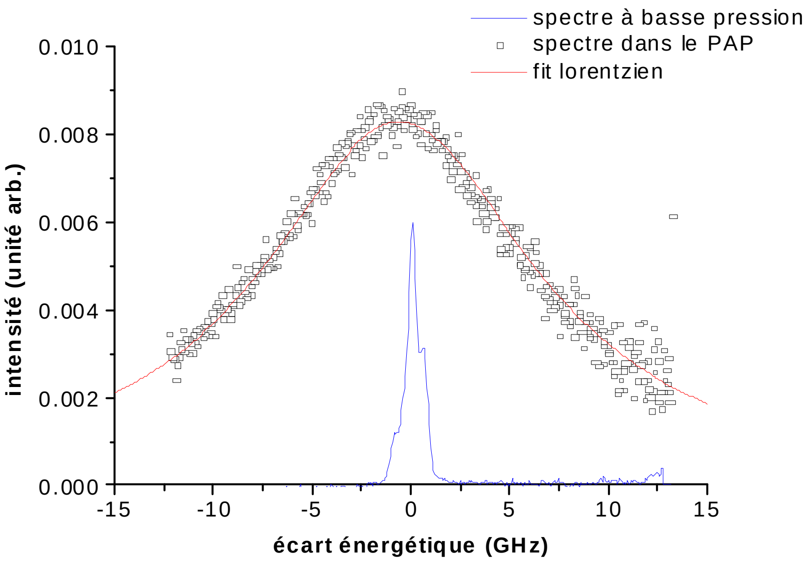
A 823nm :

⇨Lorentzian profile with Δν=7,2 GHz, shifted by –1,1 GHz



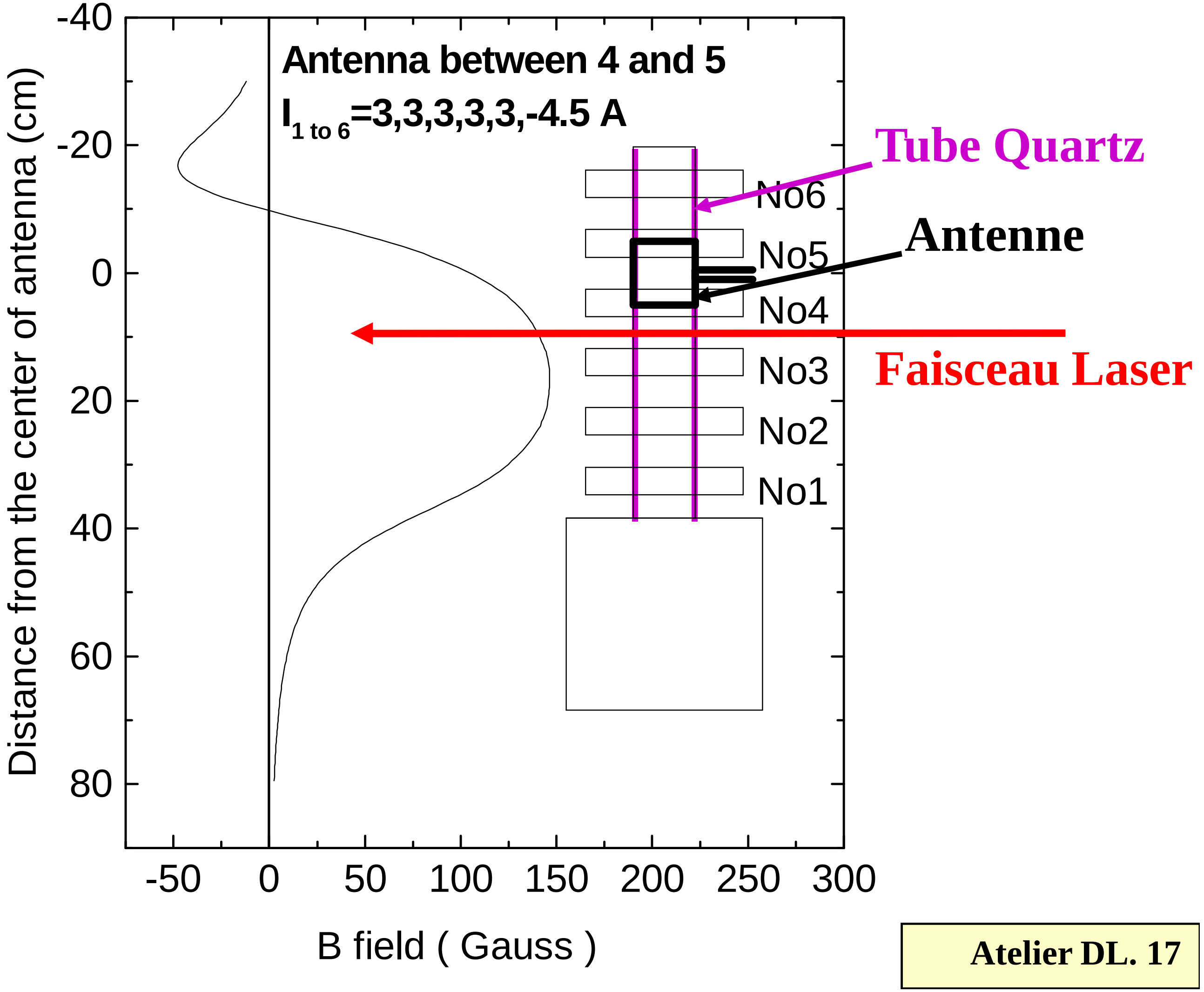
A 828 nm :

⇨Lorentzian profile with Δν=16,8 GHz, shifted by –0,72 GHz



Profil de raie en présence de champ magnétique

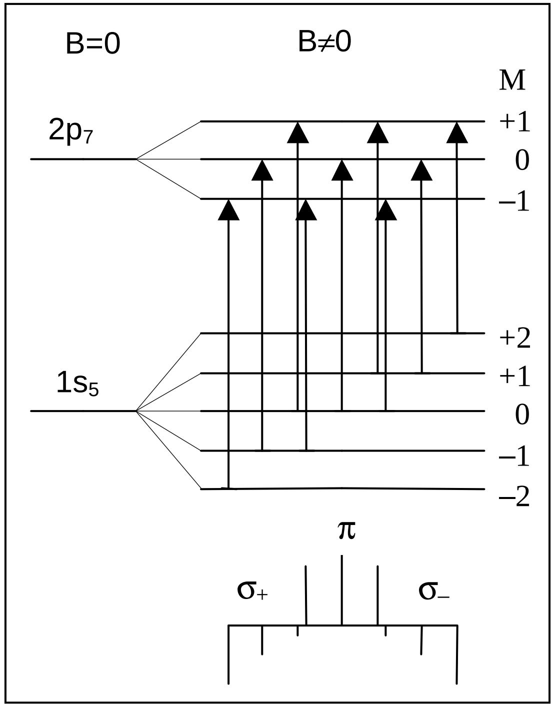
Plasma d'argon basse pression; p= 0.9 à 10 µbar, réacteur Helicon



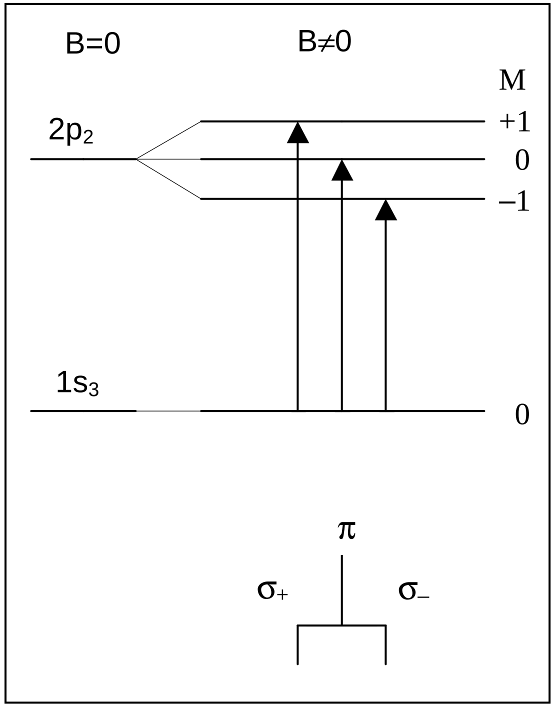
Profil de raie en présence de champ magnétique

composantes Zeeman des raies d'absorption de l'Argon

Raie 772.38 nm; $2p_7 \leftarrow {}^3P_2$



Raie 772.42 nm; $2p_2 \leftarrow {}^3P_0$

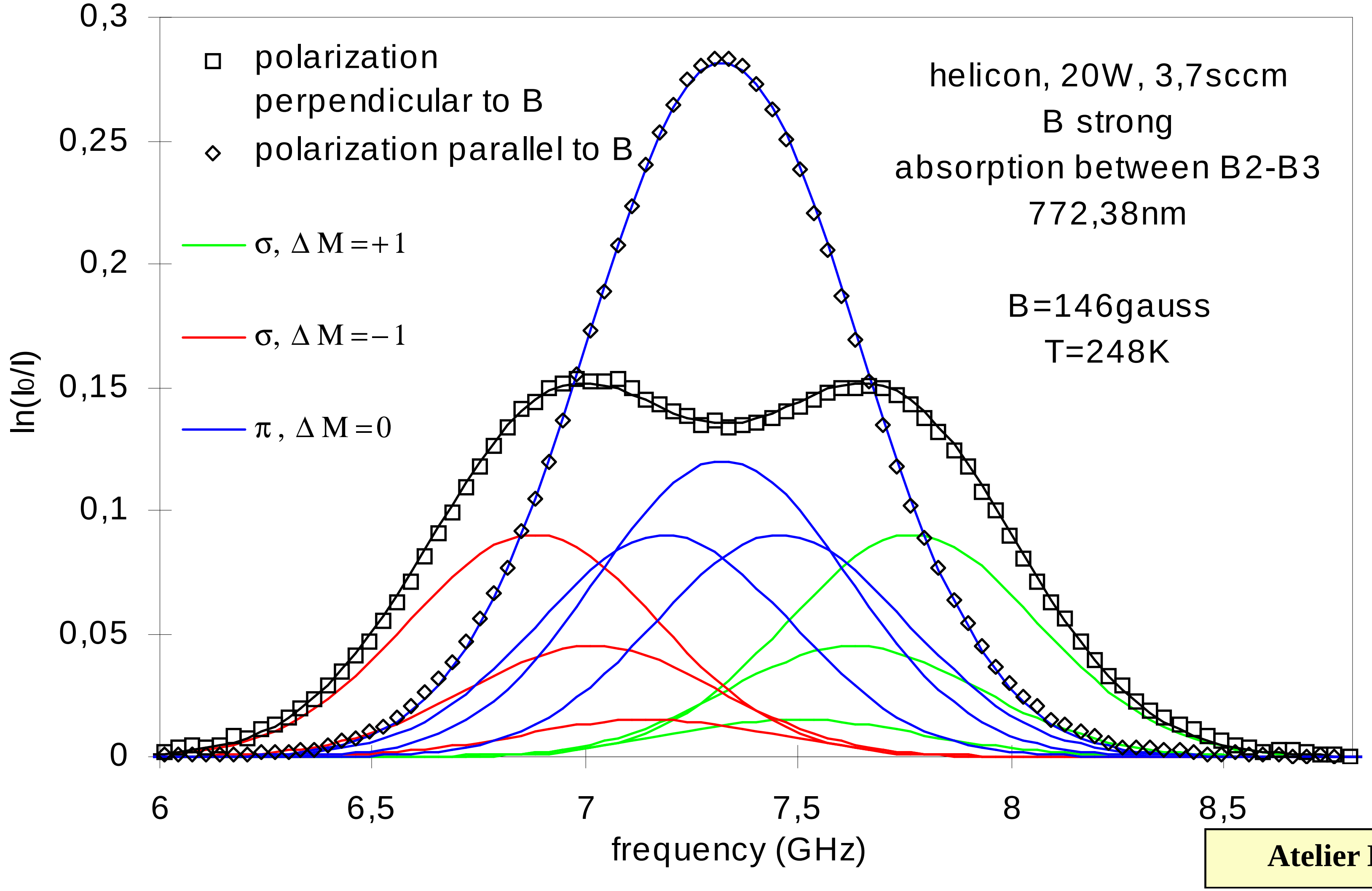


$\vec{k} \perp \vec{B}$ si $\vec{E} \perp \vec{B}$ seulement les raies σ^+ et σ^- existent

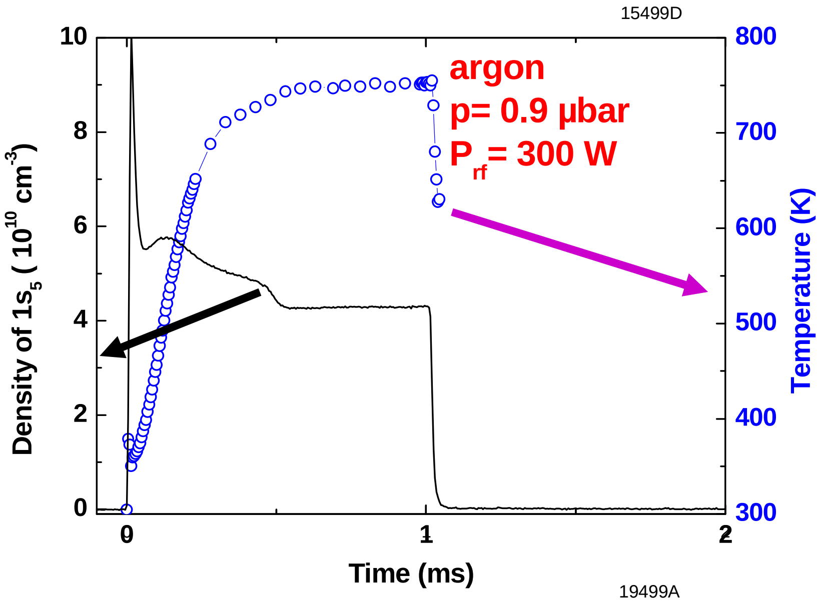
$\vec{k} \perp \vec{B}$ si $\vec{E} \,//\, \vec{B}$ seulement les raies π existent

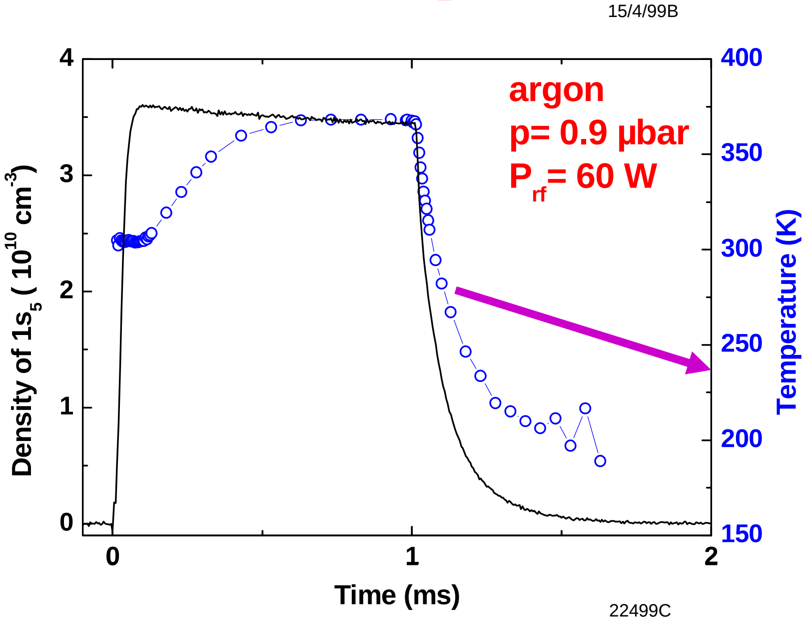
$\vec{k} \,//\, \vec{B}$ Alors seulement les raies σ^+ and σ^- existent

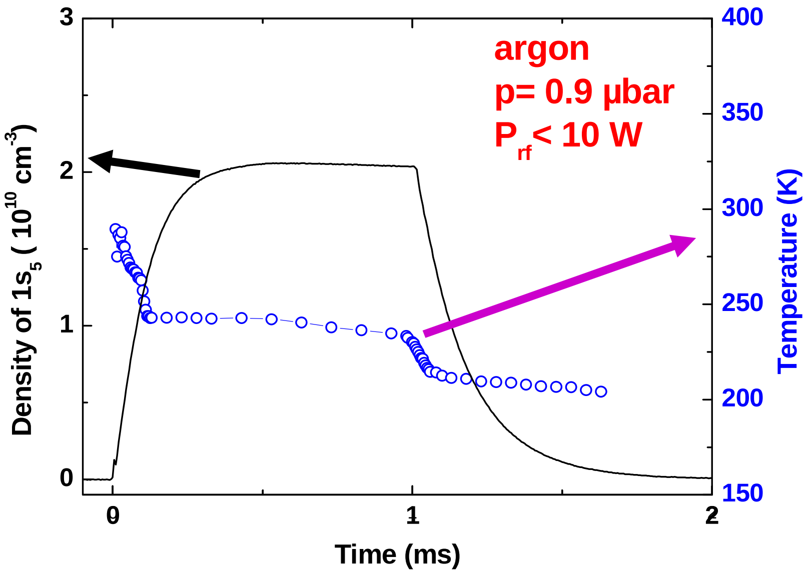
Profils expérimentaux de la raie 772.38 nm avec deux polarisations différentes: somme de Gaussians

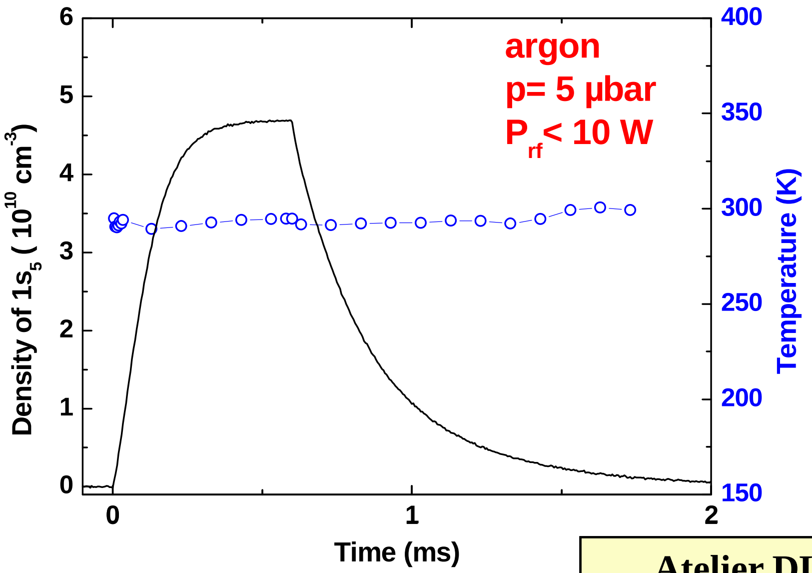


Dans une décharge pulsée et à très faible pression d'argon, on mesure $T < T_{parois}$!!!









What is wrong?

Metastable atoms are created by electron impact excitation of argon atoms

$$\mathbf{Ar + e \rightarrow Ar^* + e}$$

At p< 100 μbar, they are destroyed by:

$$\mathbf{Ar^* + e \rightarrow Ar + e \quad or \quad Ar^+ + 2e} \qquad \mathbf{(e)}$$

$$\mathbf{Ar + wall \rightarrow Ar} \qquad \mathbf{(w)}$$

The mean free path (*mfp*) of Ar* in Ar is ≅ 5 (cm)/p(μbar)

The plasma tube radius (ρ) is 4.5 cm

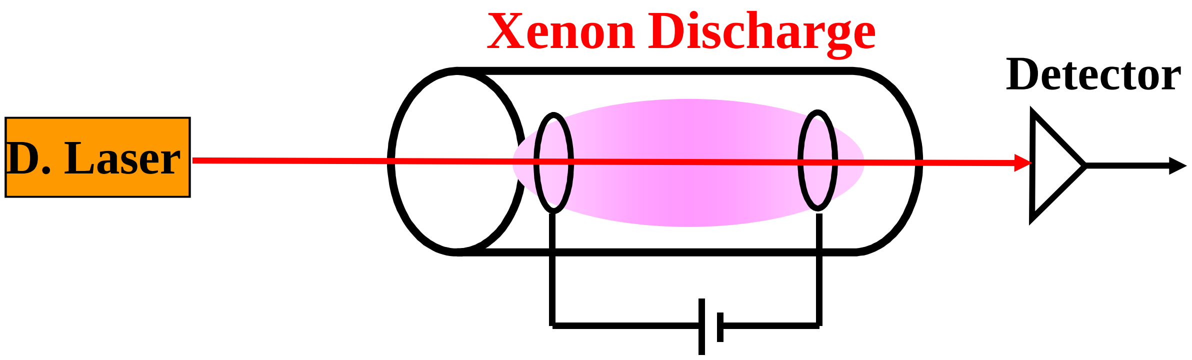
At high electron density, $n_e \geq 10^{17}$ m^{-3}, (e) is the dominant mechanism: Ar* are destroyed before one *mfp*. The velocity distribution function (*vdf*) of Ar* is the same than the *vdf* of Ar atoms. We measure the gas temperature.

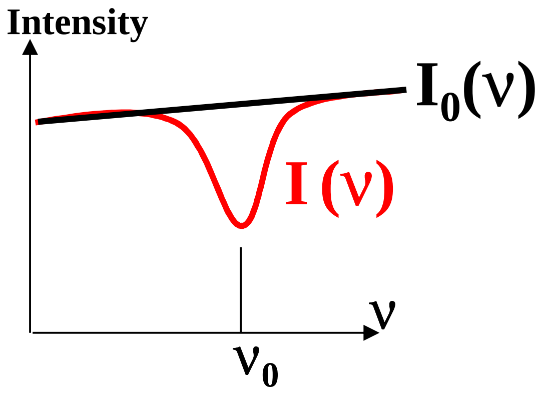
At low n_e, and p=0.9 μbar, (w) is dominant and the *mfp* of Ar* is comparable to ρ, therefore, Ar* with large radial velocity are destroyed more more efficiently. Their *vdf* is no more a Gaussian (non equilibrium). The deduced T from a Gaussian profile is not the gas temperature.

At p=5 μbar, Ar* and Ar are in collisional equilibrium. T is gas temperature.

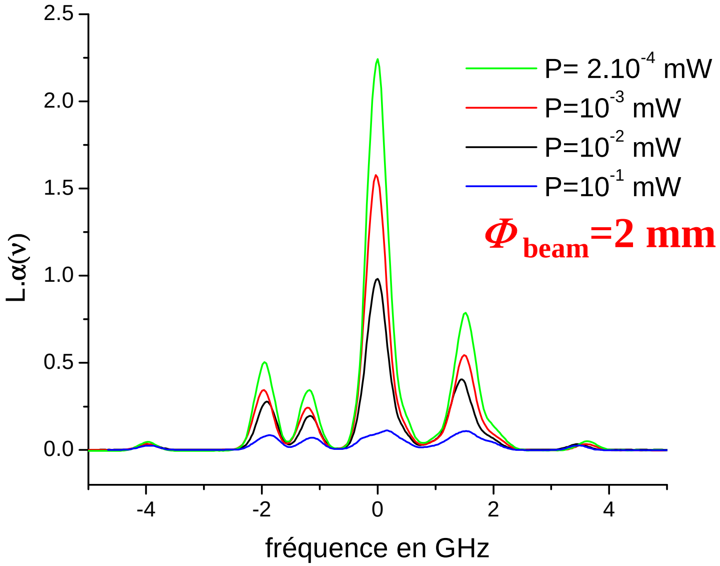
Optical Saturation

Influence of laser power on line profile and on measured absorption rate

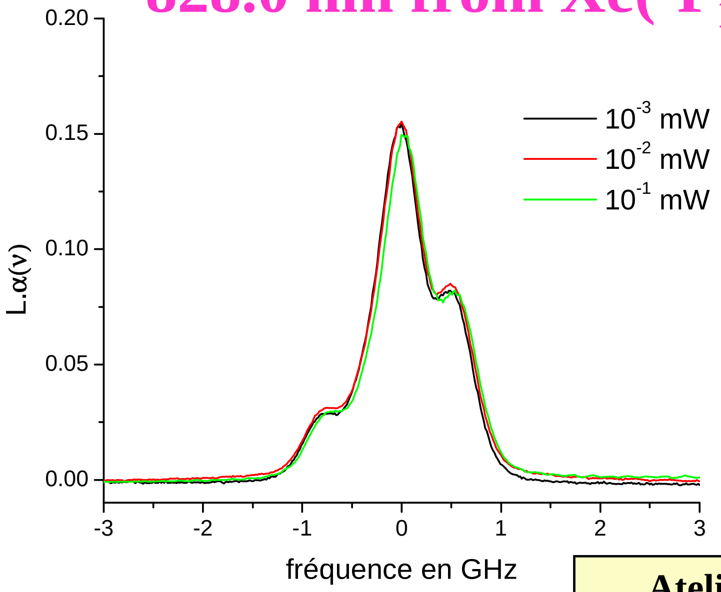




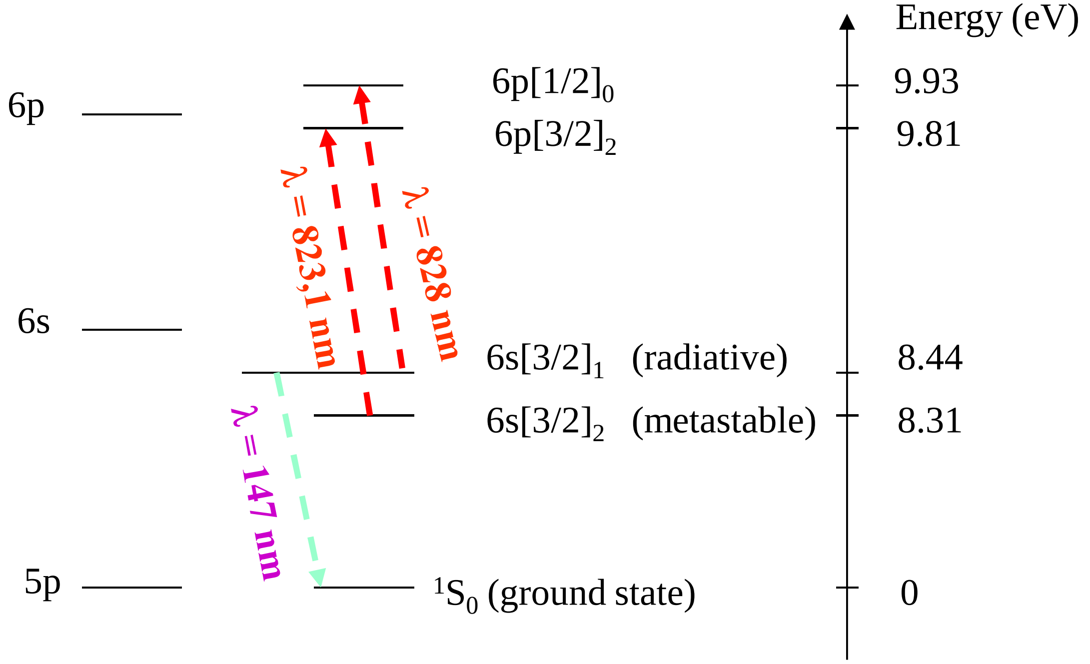
823.1 nm from Xe($^3P_2$)



828.0 nm from Xe($^3P_1$)



Xenon Excited states of interest



7 most important stable isotopes :

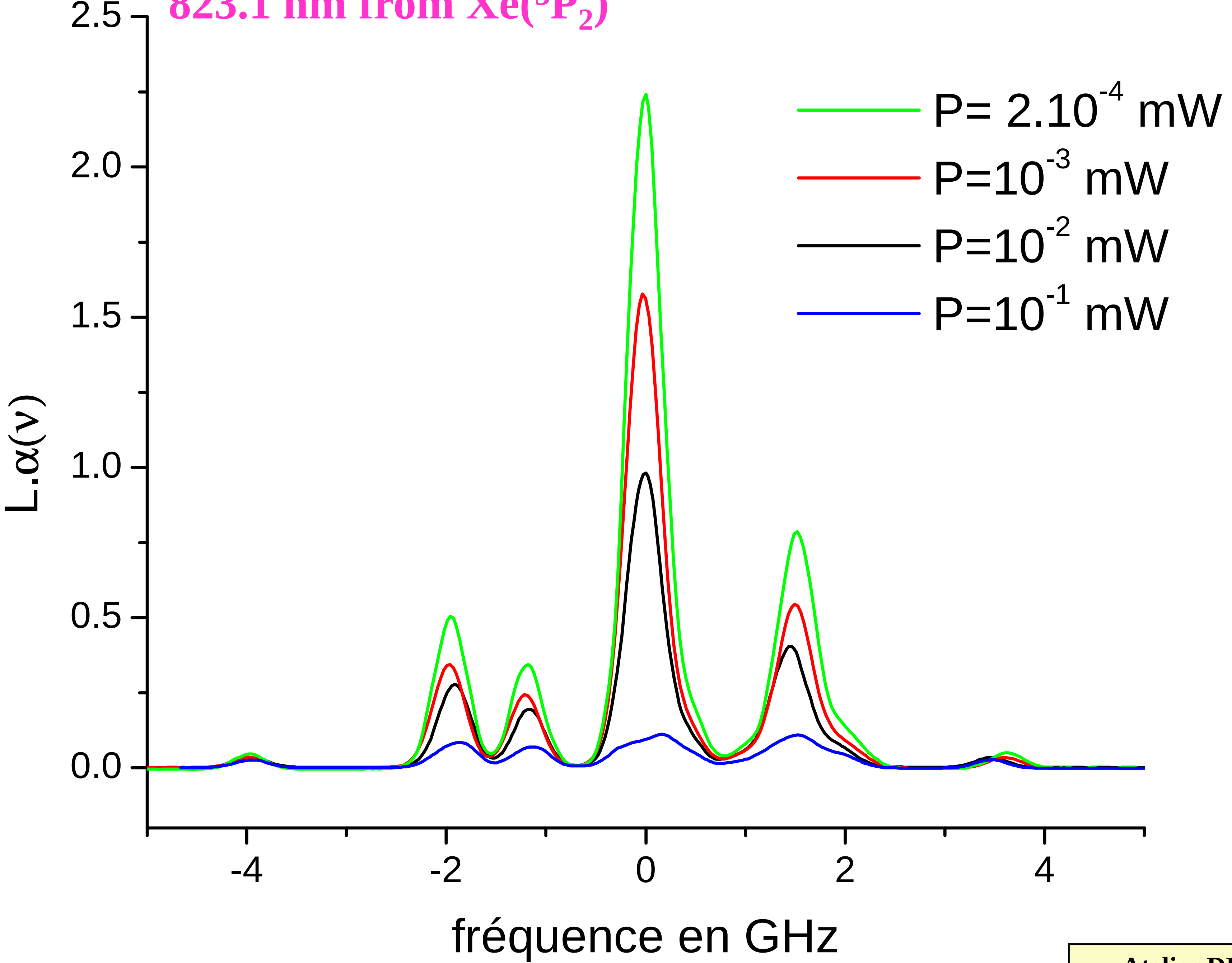
Z = 128	1.9 %
Z = 129	26.4 %
Z = 130	4.1 %
Z = 131	21.2 %
Z = 132	26.9 %
Z = 134	10.4 %
Z = 136	8.9 %

*** Complex line structures result from Isotope Shifts and Hyperfine Structure.**

*** Power saturation on 823.1 nm line because $Xe^*(^3P_2)$ depletion.**

*** No saturation on 828 nm line because $Xe^*(^3P_1)$ lifetime ≃ 10 ns**

823.1 nm from Xe($^3P_2$)



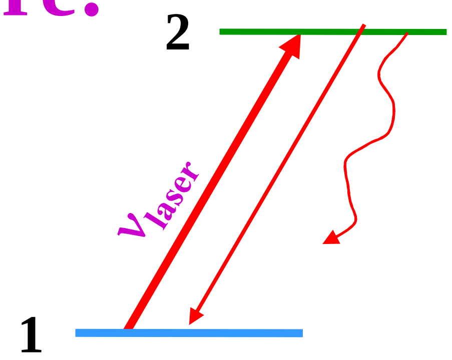
Origin of optical saturation

$$\alpha(\nu) = \frac{4hB_{12}}{\lambda\gamma}\left(n_1(\nu) - \frac{g_1}{g_2} n_2(\nu) \right)$$

α becomes no more proportional to n_1

- **1- Laser beam transfers a significant number of atoms from the lower to the upper state and n_2 becomes no more negligible compared to n_1. (short pulse lasers)**
- **2- Atoms in the upper state are lost by radiation, or collisional transfers, to a 3rd state and atoms in the lower state are not renewed fast enough: the lower state becomes depleted. (cw lasers)**

Rate equations governing the population densities N_1 and N_2 of states $|1\rangle$ and $|2\rangle$ are:



$$dN_1/dt=(B_{21}\rho+A_{21})N_2-(B_{12}\rho+1/\tau_1+\sum_q k_{1,q}M_q)N_1+C_1$$

$$dN_2/dt=B_{12}\rho N_1-\left(B_{21}\rho+A_{21}+A_{23}+\sum_q k_{2,q}M_q\right)N_2+C_2$$

$B_{21}=\frac{g_1}{g_2}B_{12}=\frac{\lambda_0^3}{8h\pi}A_{21}$ is the Einstein coefficient for stimulated emission

we assume $g_1 = g_2$, ρ is the energy density of the beam,

C_i accounts for the repopulation of state $|i\rangle$ from different paths, including diffusion transport into the laser volume and radiative cascades

$\Re_1=1/\tau_1+\sum_q k_{1,q}N_q$ and $\Re_2=\sum_{i=lower}A_{2i}+\sum_q k_{2,q}N_q$

are the total relaxation rates of the states in steady state, ($dN_i/dt=0$) the density difference of states $|1\rangle$ and $|2\rangle$ is:

$$\Delta N = N_1 - gN_2 = \Delta N^0 \Big/ \left(1 + S\frac{\Re_2 - A_{21} + g\Re_1}{\Re_1 + \Re_2}\right)$$

Where $\Delta N^0 = N_1^0 - gN_2^0 = \frac{C_1}{\Re_1} - \frac{C_2}{\Re_2}(g - A_{21}/\Re_1)$ is in the absence of laser beam (ρ=0),

and $S = B_{12}\rho/\Re^*$ is **The saturation parameter**

related to the **mean relaxation rate** $\Re^* = \Re_1\Re_2/(\Re_1 + \Re_2)$

:

The resulting population density in the lower state is:

$$N_1 = \frac{C_1(gS + R_2/\Re^*) + C_2(gS + A_{21}/\Re^*)}{S[R_2 - A_{21} + gR_1] + (R_1 + R_2)}$$

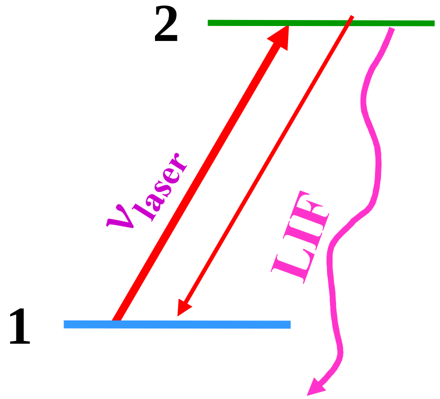
When $C_2 \searrow 0$

$$N_1 = \frac{C_1(gS + R_2/\Re^*)}{S[R_2 - A_{21} + gR_1] + (R_1 + R_2)}$$

Larger S is, lower the measured population will be

When $\rho \to 0$, $N_1 = \frac{C_1}{\Re_1}$ For $\rho \to \infty$ $N_1 = \frac{g(C_1 + C_2)}{\Re_2 - A_{21} + g\Re_2}$

Intensity of Laser Induced Fluorescence signal



LIF signal is proportional to N_2 density given by:

$$I_{23} \propto N_2 A_{23} \propto N_1(El,V,R) A_{23} \frac{B_{12}\rho}{B_{21}\rho + \Re_2}$$

When LIF is used to determine the relative population of two different especies, m and n:

At low laser power limit, the LIF signal ratio is:

$$\frac{I_{23}(m \to 3)}{I_{23}(n \to 3)} = \frac{N_1(i)}{N_1(j)} \frac{B_{im}}{B_{jn}} \frac{A_{m3}}{A_{n3}} \frac{\tau_m}{\tau_n}$$

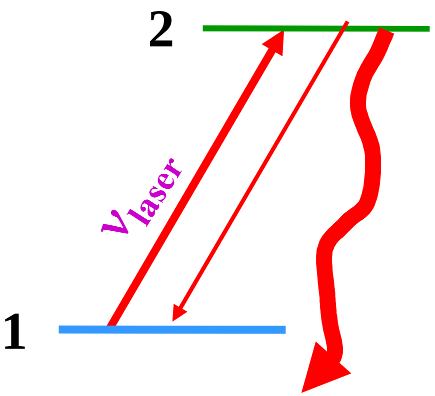
τ could be p and T dependent

At high laser power limit, the LIF signal ratio is:

$$\frac{I_{23}(m \to 3)}{I_{23}(n \to 3)} = \frac{N_1(i)}{N_1(j)} \left(\frac{g_i}{g_m}\right)\left(\frac{g_n}{g_j}\right) \frac{A_{m3}}{A_{n3}}$$

Estimation of saturation parameter S

For a cw laser:



λ= 590 nm ;

τ_2=16 ns ; hence $R_2=1/\tau_2=6.25\ 10^7\ s^{-1}$

But $A_{21}=6\ 10^6\ s^{-1}$;

R_1=(1/transit time inside a beam of ϕ=2 mm)=(0.5 km.s^{-1})/(2 mm)=**$2.5\ 10^5\ s^{-1}$**

Laser power: P=1 mW; $\Delta\nu_L$= 1 MHz <<$1/(2\pi\tau_2)$;

Laser beam diameter =2 mm

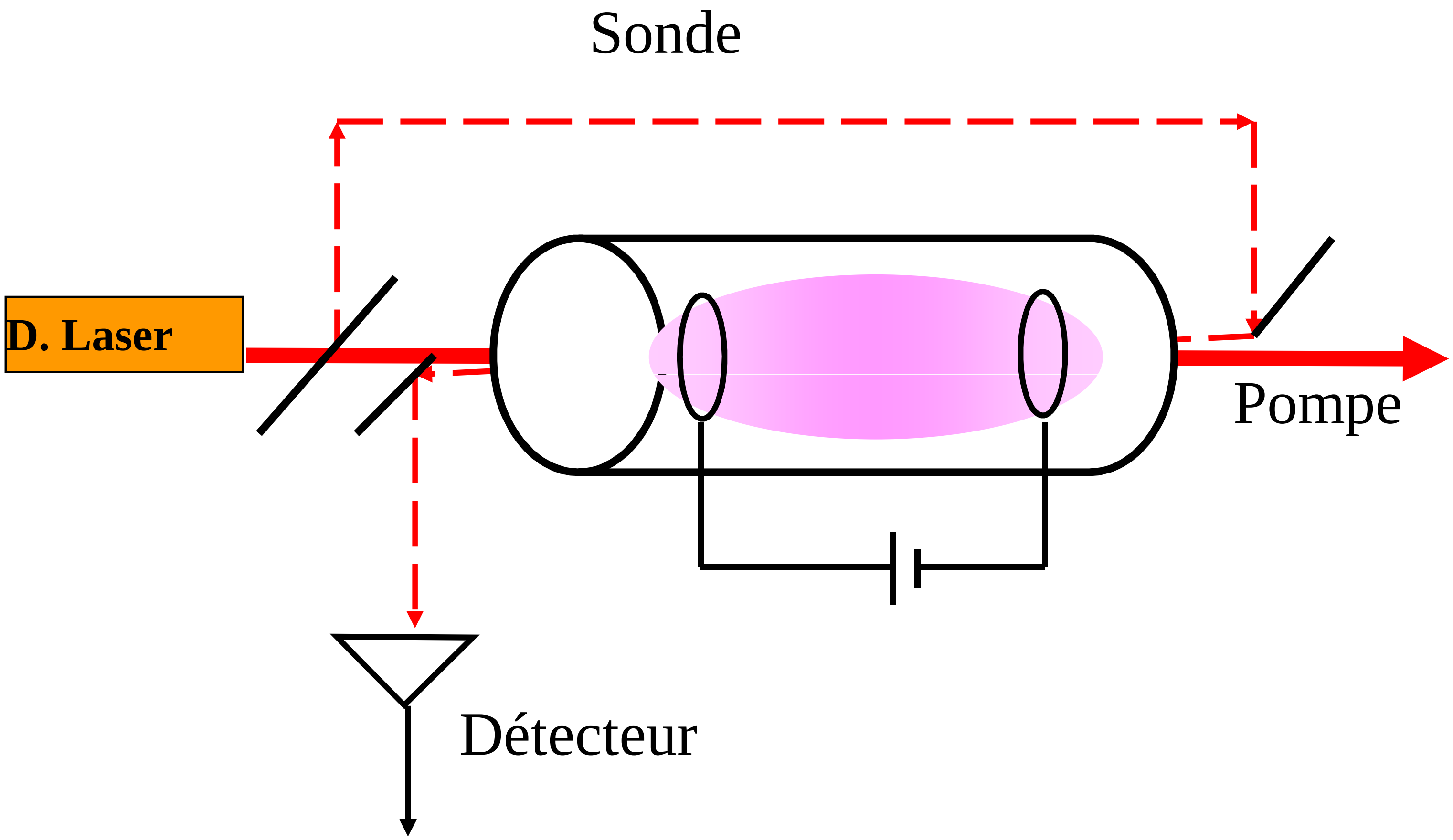
We can calculate

$$\boxed{S=\frac{B_{12}*\rho}{R_1}=20}$$

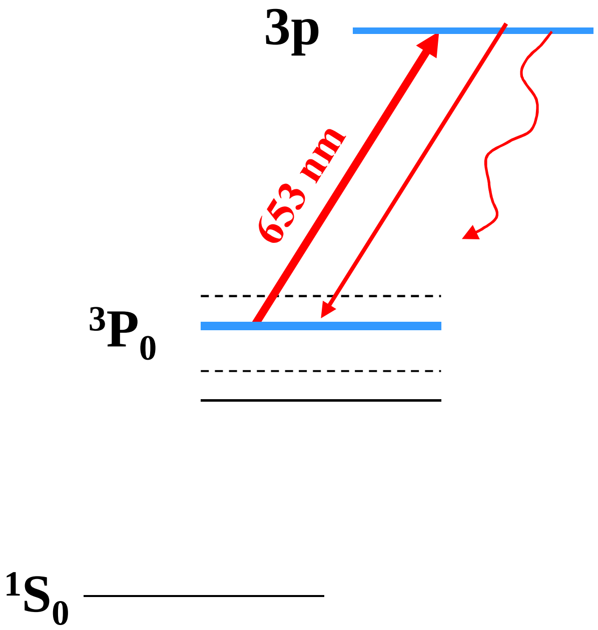
Hence the density measured by absorption will not be correct with so large S value because $N_1=N_1^0/(1+S)$ However,

as $\delta\nu_S=\delta\nu*\sqrt{1+S}=4.5*\delta\nu=45$ **MHz is much smaller than the Doppler width (1.7 GHz), the line profile can still provide the gas temperature**

Une expérience d’absorption saturée

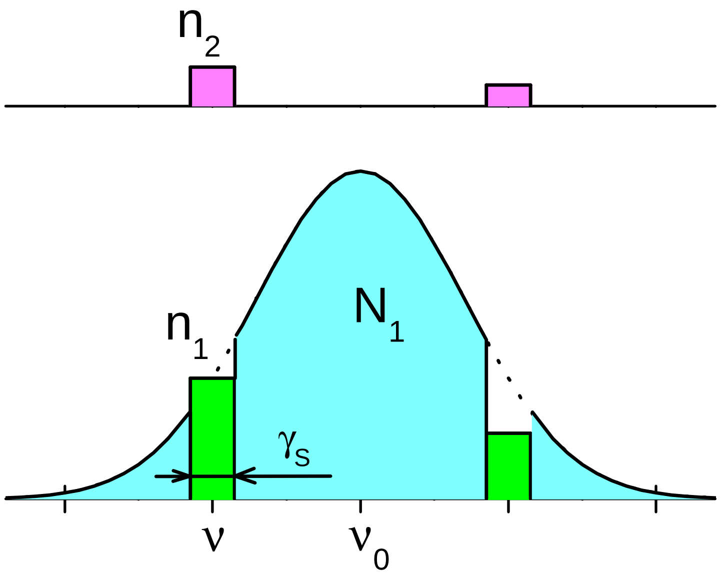


Comment agissent les deux faisceaux qui se propagent en sens opposés



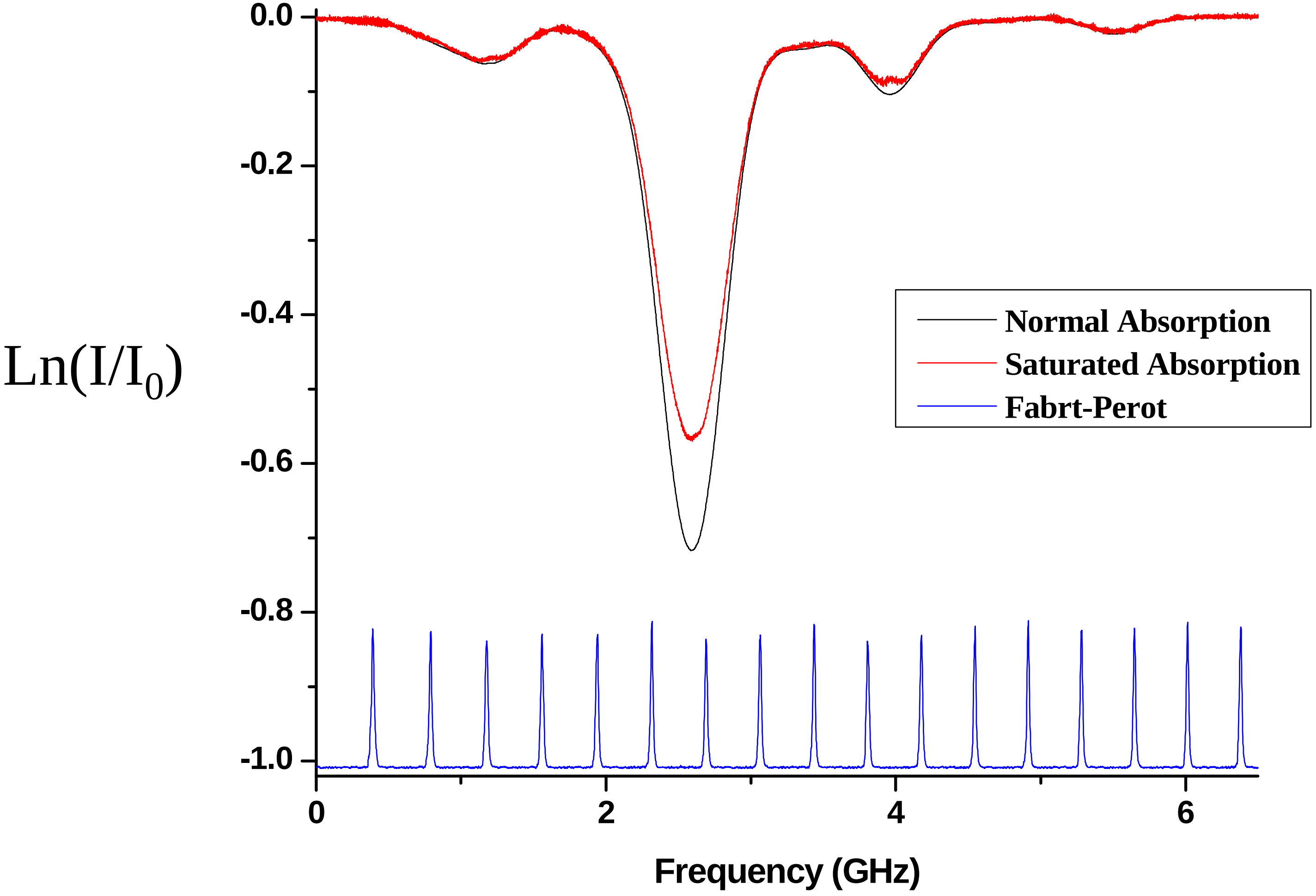
Neon energy levels

Laser frequency is $\nu=\nu_0$-v/c

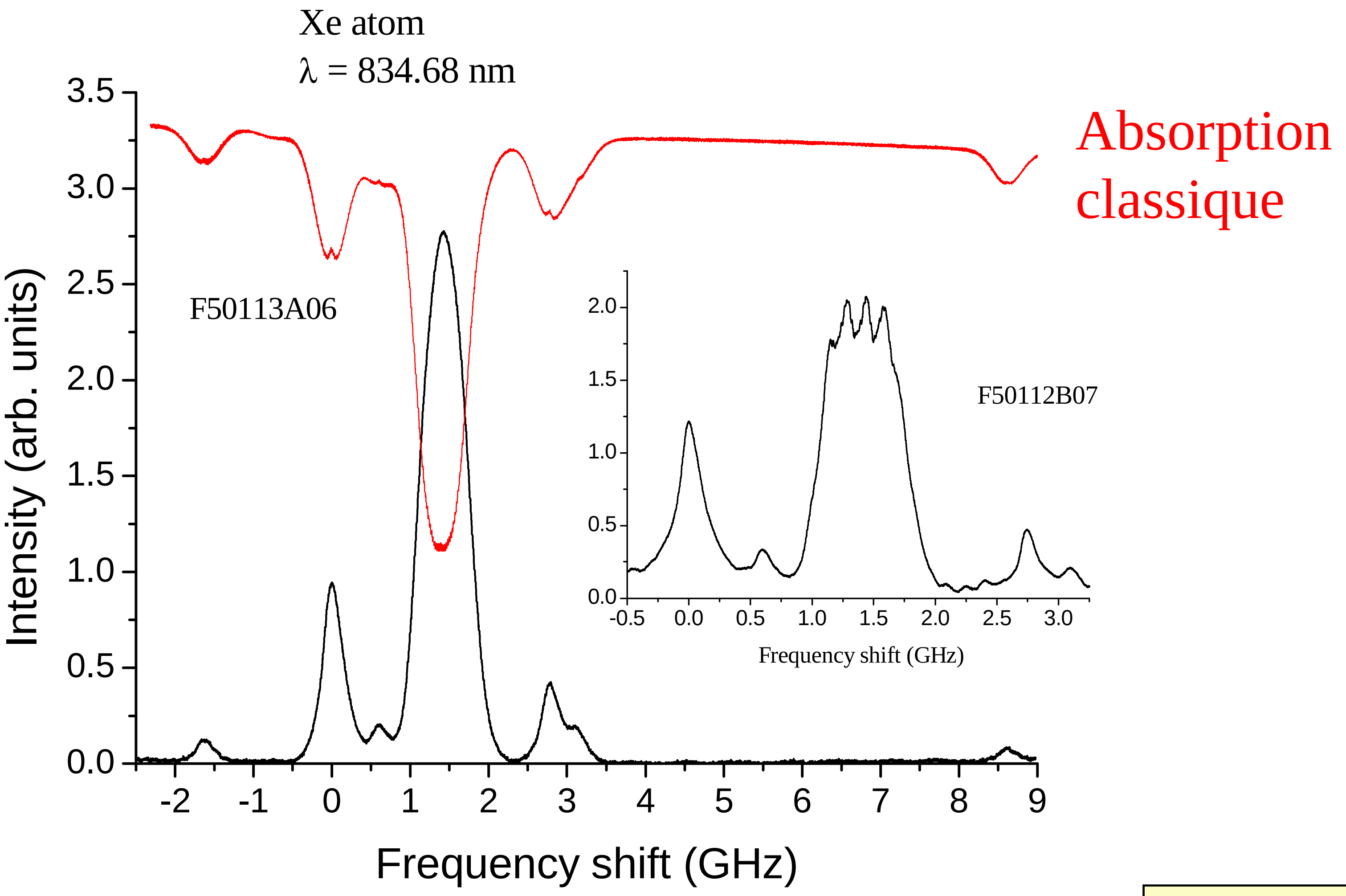


Groups of atoms in $^3P_0$ and 3p states

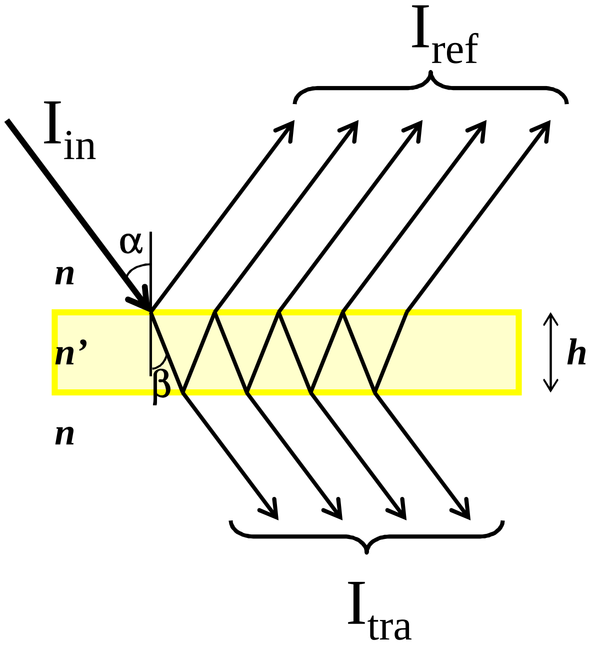
L’influence du faisceau pompe sur le profil d’absorption de la raie Xe (834.68 nm)



Signal d’absorption saturée avec une détection synchrone à la fréquence de modulation du faisceau pompe



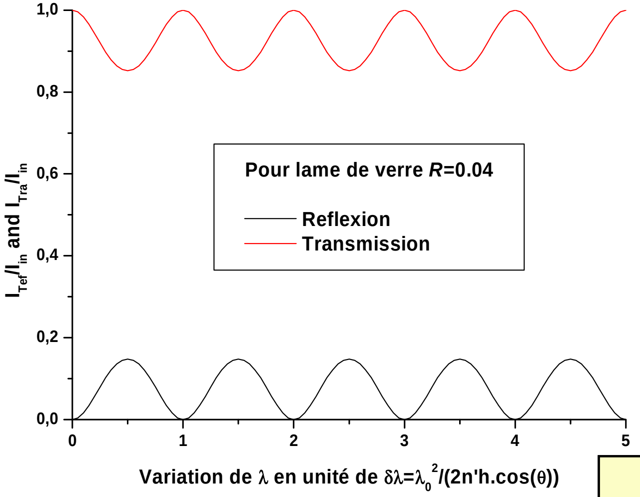
L’effet d’interférence dans la traversée d’une lame



Différence de phase entre deux faisceaux successifs est: $\delta=\frac{4\pi}{\lambda}n'h.\cos\beta$

$$I_{ref}=\frac{4R\sin^2(\delta/2)}{(1-R)^2+4R\sin^2(\delta/2)}I_{in}$$

$$I_{Tra}=\frac{(1-R)^2}{(1-R)^2+4R\sin^2(\delta/2)}I_{in}$$



Pour α et h fixes, à chaque fois que $\delta/2=k.\pi$, I_{ref} passera par zero et I_{tra} par un maximum = à I_{in}

Entre deux minima, λ change de

$\delta\lambda=\lambda_0^2/(2n'h.\cos(\beta))$ et ν de $\delta\nu=1/(2n'h.\cos(\beta))$