Initiation de la décharge : Discussion RPF 2020

Théorie de l'ionisation directe dans le liquide

Formation d'une région de faible densité

Microbulles preexistantes

Théorie de Lewis – formation de cracks 1998

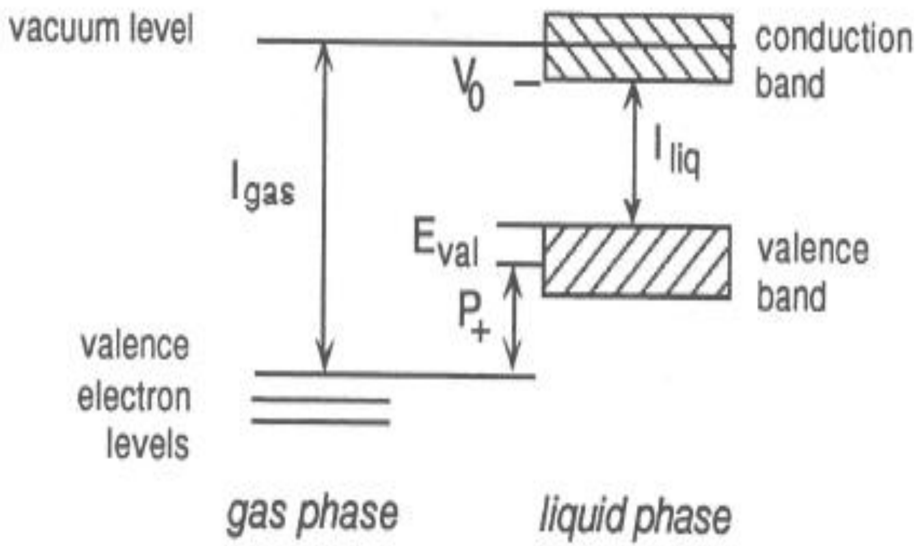
Théorie de l'électrostriction :
formation de nanopores
(cavité vide)

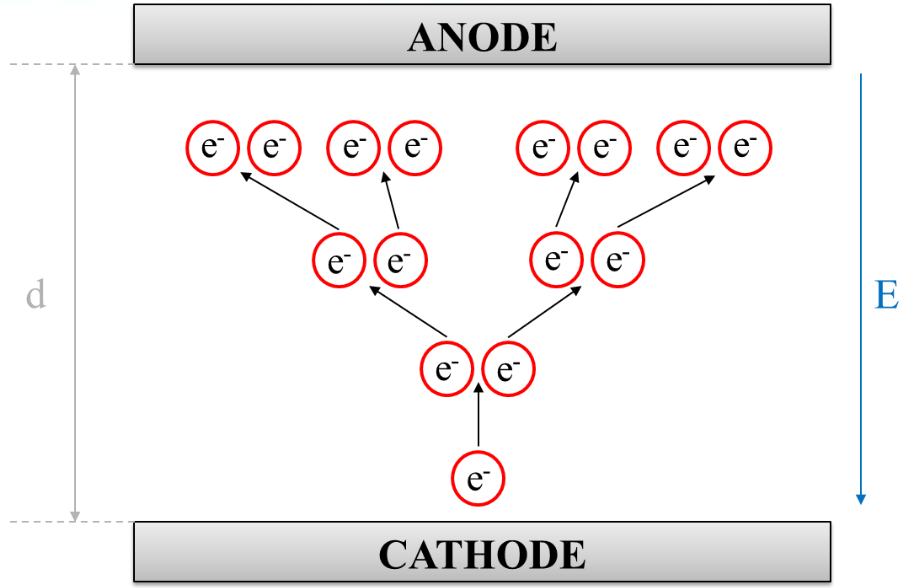
EHD Théorie O. Lesaint

…..

Initiation de la décharge : Discussion RPF 2020

Liquide





Electron mean free path $l = \frac{1}{4\sigma N}$

eEl

"The liquefied noble gases (Ar, Kr and Xe, at least) exhibit a band structure of electronic states, so that the atomic ionization potential should be replaced by the band gap, I_{liq}"

Rare Gas Liquid Detectors

Gas		liquid
$2\ 10^{19}\ cm^{-3}$	→	$2\ 10^{22}\ cm^{-3}$

Initiation de la décharge : Discussion RPF 2020

Mobilité électronique – Liquides purifiés

G2E Lab
Grenoble Génie Electrique
Grenoble Electrical Engineering

Liquid	T(K)	μ_{el} cm^{2}V^{-1}s^{-1}	I liq - Eg (eV)	free electron lifetimes	
Ar	85	475-625	**14,3**	**>4 msec 0,1ppb of O2**	**Quasi-free**
Kr	117	1800	**11,7**		
Xe	165	2950-2000	**9,22+-0,01**		
Methane	111	400			
Tetramethylsilane	295	99		100-200µs CERN TMP	
Neopentane	295	65			
Ethane	296	47			
Isooctane	296	7			
He	4.2	2 10^{-2}	**25,5**		**Electron bubble 17 Å**
Cyclohexane	296	0.4			**Localized**
N pentane	296	0.16			
Water	293	18 10^{-4}			**Localized (solvated)**

W F Schmidt
Liquid State Electronics of Insulating Liquids 1997

Electronic Excitations in Liquified Rare Gases 2005

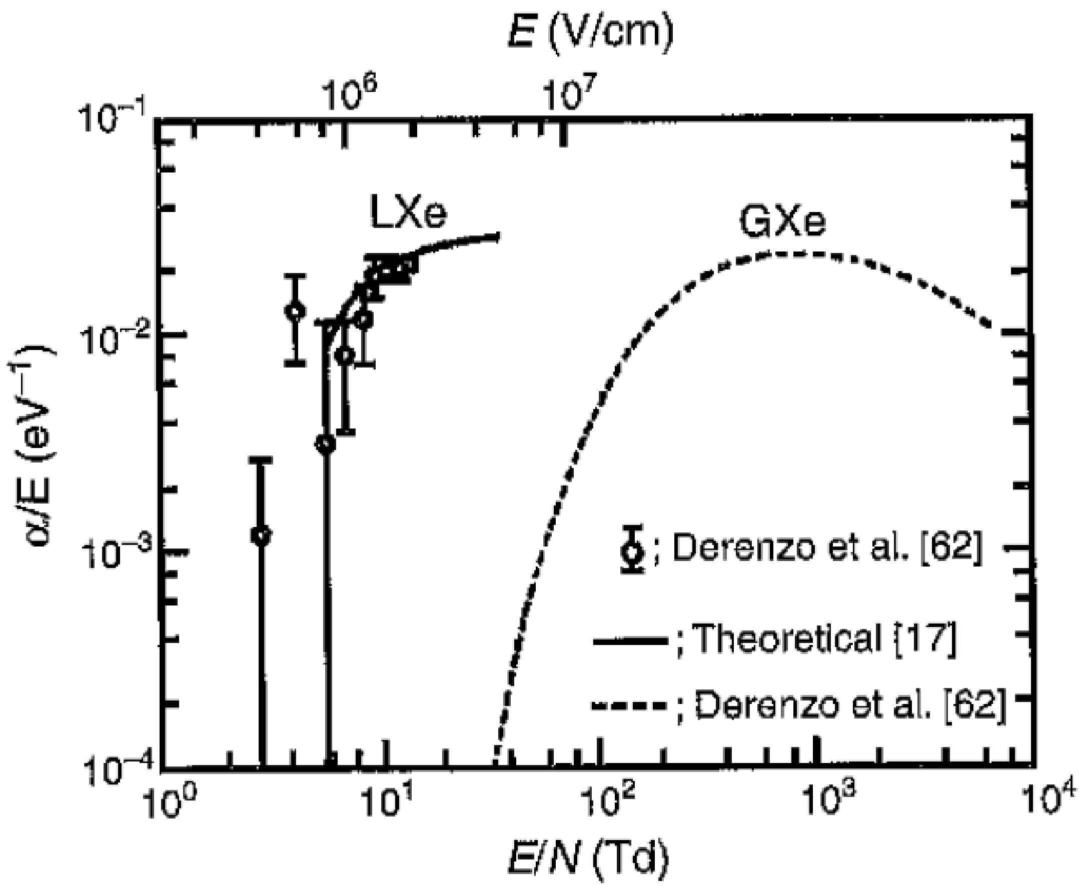
Avalanche électronique en phase liquide

Derenzo et al Phys. Rev. A 9, 2582 1974

First Townsend coefficient α

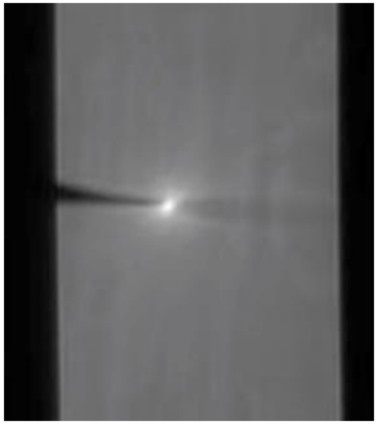
Xe « pur »

20 cm



Initiation de la décharge : Discussion RPF 2020

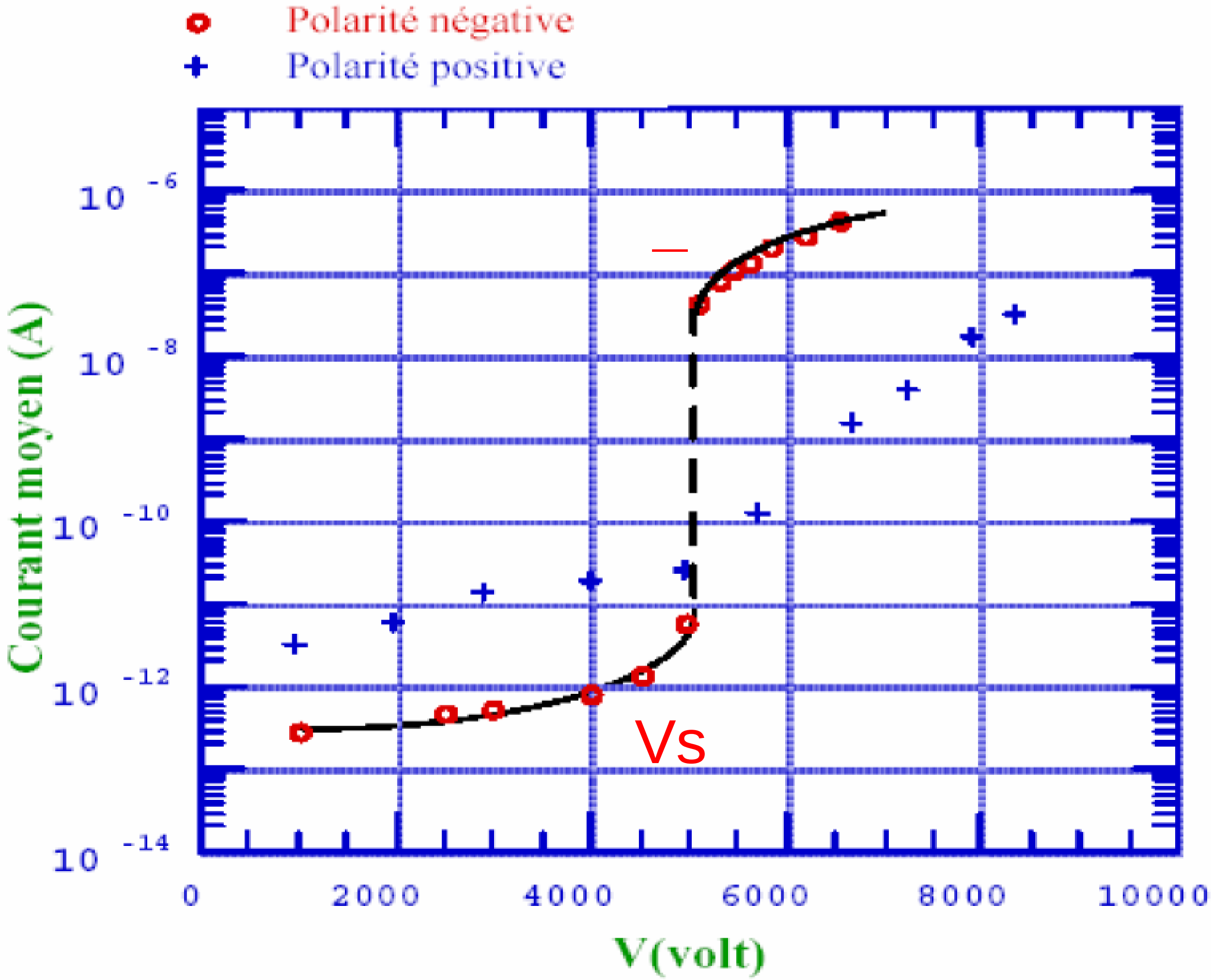
Experiences G2E.lab Cyclohexane « purifié »



DC -/+

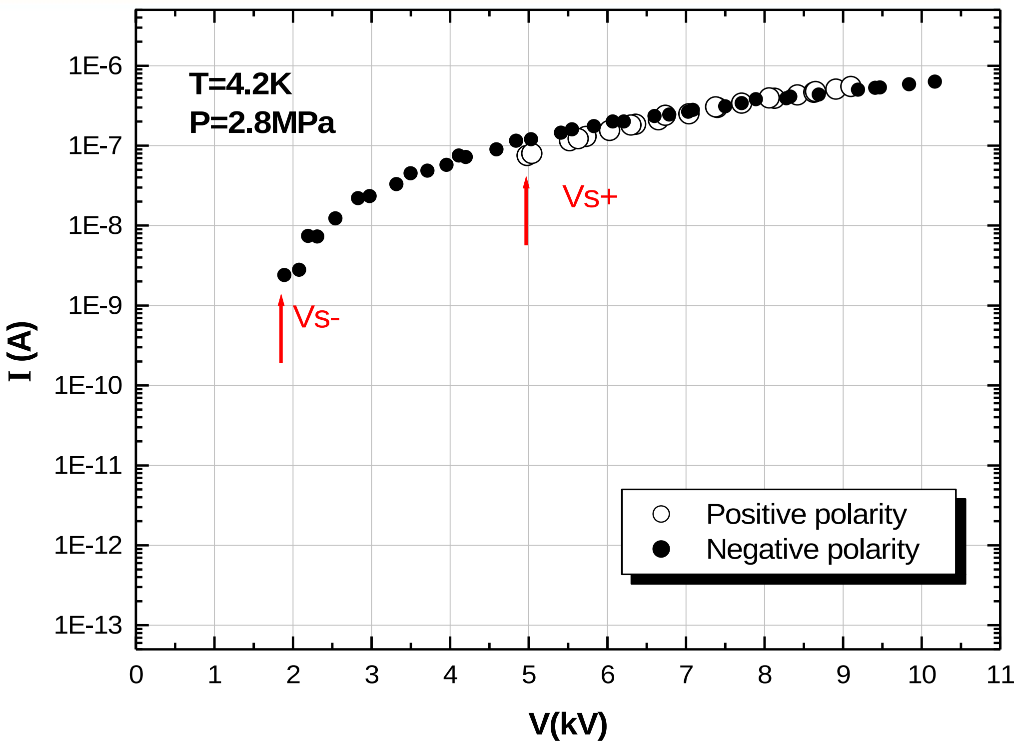
Pointe 0,1-2µm

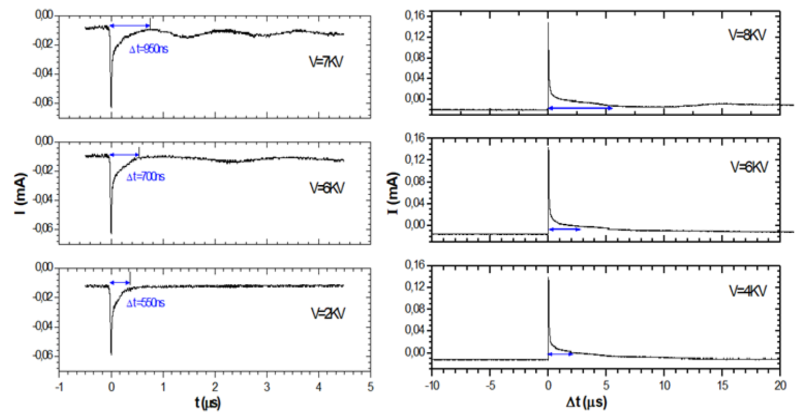
courant résiduel



Initiation de la décharge :
Discussion RPF 2020

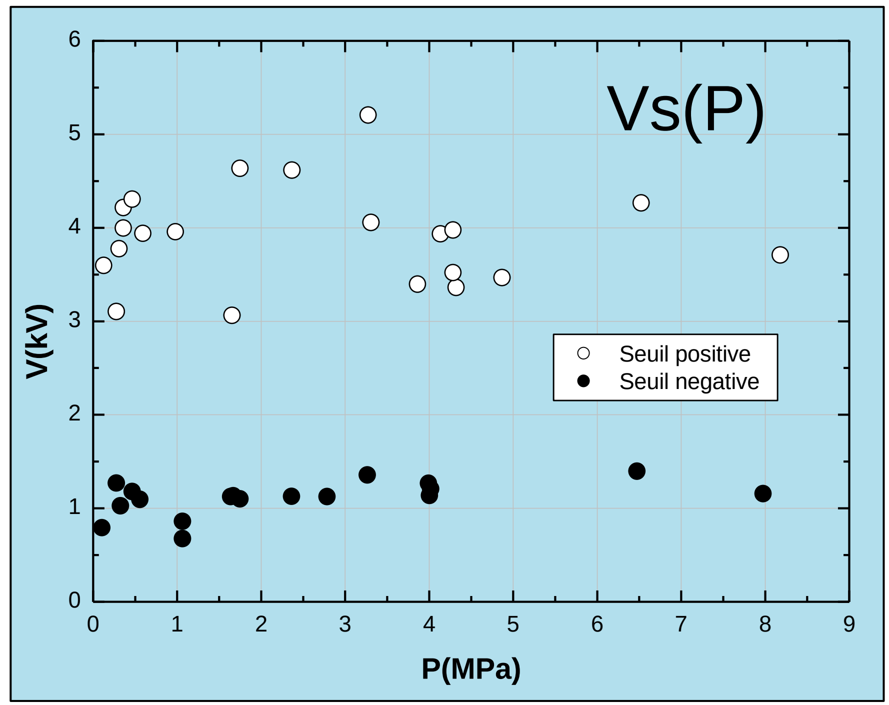
Helium - Argon liquide





~~Courant residuel~~

Vs is independent of external pressure



Initiation de la décharge : Discussion RPF 2020

Théorie de l'ionisation directe dans le liquide

Formation d'une région de faible densité

Application de la spectroscopie à l'étude des décharges électriques dans les milieux denses.

<u>N Bonifaci</u>

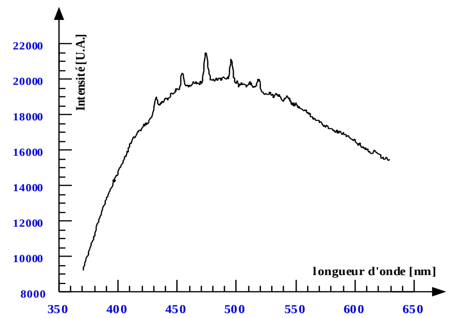
CNRS, G2Elab, F-38000Grenoble, France

Nelly.Bonifaci@g2elab.grenoble-inp.fr

Joel Rosato, Sylvain Iséni, Jussi Eloranta, Olivier Lesaint, Zhiling Li , Vladimir Atrazhev, Yann Cressault, Nader Sadeghi.

OES $(T_e, T_k, T_{rot}, T_{vib}, T_{ex})$

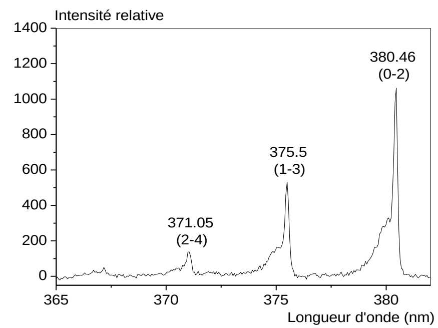
- Continuum



Theoretical background of optical emission spectroscopy for analysis of atmospheric pressure plasmas
T. Belmonte, C. Noël, T. Gries, J. Martin and G. Henrion, Plasma Sources Sci. Technol. 24, 064003 (2015).

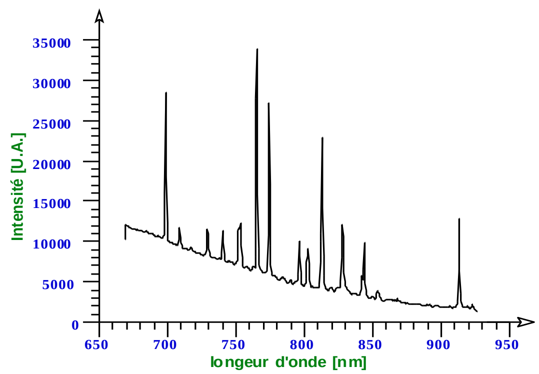
Présentation RPF 2020 Yann Cressault
Laboratoire LAPLACE, Toulouse

- Molecular spectra



Présentation RPF 2020 Yann Cressault
Laboratoire LAPLACE, Toulouse

- Atomic spectra



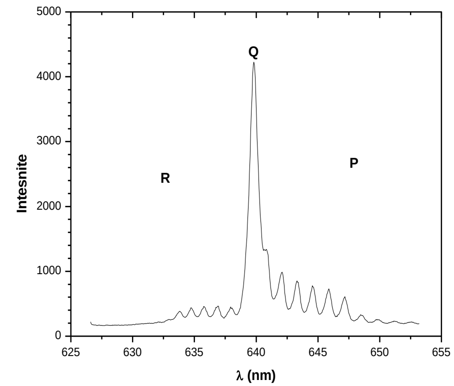
Molecular spectra

T_e: electronic term, G(v): vibrational term, $F_v(J)$: terme rotationnel

$$G(\nu) = \omega_e\left(\mathrm{v}+\frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2 + \omega_e y_e\left(\mathrm{v}+\frac{1}{2}\right)^3 + \cdots$$

$$F_V(J) = B_V J(J+1) - D_V J^2 (J+1)^2 + \ldots$$

J rotational quantum number



If the rotational states are in equilibrium they are distributed according to a Boltzmann law:

$$N_u = \frac{N_0\, g_u}{Q(T_r)} e^{-E_u/kT_r}$$

T_r, T_v.....

B. Pearse and A. G. Gaydon
The identification of Molecular Spectra Chapman and Hall 1976

G. Herzberg, Molecular Spectra and Molecular Structure:
I. Spectra of Diatomic Molecules, 2nd edn.
(Van Nostrand, Princeton, NJ, 1950)

I. Kovacs, Rotational structure in the spectra of diatomic molecules (Adam Higer Ltd., London, 1969)

Home made code

5. Conclusion : **et les logiciels?**

- **Multitude de logiciels**
- **Systèmes moléculaires disponibles ?**
- **Quels paramètres/constantes spectro ?**
- **Quel couplage ?**
- **Quelle fonction d'appareil ?**
- **Quelles hypothèses ???**

LIFBASE

TABLEAU 1.1 Molécules et systèmes traités dans le logiciel LIFBASE

Molécule	Transition	Système	v_{max}
OH	A–X	Violet	8
OD	A–X		3
NO	A–X	γ	5
	B–X	β	7
	C–X	δ	1
	D–X	ϵ	5
CH	A–X		3
	B–X		1
	C–X		2
CN	B–X	Violet	8
CF	A–X		3
	B–X		5
SiH	A–X		2
N_2^+	B–X	Premier Négatif	6

Ar-N_2, 1atm (A-M Kassir, PhD Thesis, 2020)

SPECAIR

TABLEAU 1.2 Molécules et systèmes traités dans le logiciel SPECAIR

Molécule	Système	Version *demo*
OH	Violet	✓
	Meinel	×
C_2	Swan	×
CN	Violet	✓
	Rouge	×
CO	Infrarouge, Quatrième Positif	✓
N_2	Premier Positif, Second Positif	×
N_2^+	Meinel	×
	Premier Négatif	✓
NH	A–X	×
NO	Infrarouge, γ, β	✓
	δ, ϵ, β', γ'	×
O_2	Schumann-Runge	×
Raies atomiques	C, N, O	✓

SPARTRAN

TABLEAU 1.3 Molécules et systèmes traités dans le logiciel SPARTAN

Molécule	Système
CO_2	Infrarouge
H_2	Lyman, Werner
C_2	Swan, Philips, Mulliken, Deslandres-D'Azambuja, Fox-Herzberg, Ballik-Ramsay
CN	Violet, Rouge
CO	Infrarouge, Quatrième Positif, Angstrom, Troisième Positif, Triplet, Asundi
CO^+	B–A, B–X, Comet Tail
N_2	Premier Positif, Second Positif
N_2^+	Premier Négatif
NO	γ, β, δ, ϵ, β', γ'
O_2	Schumann-Runge, Schumann-Runge Continuum
Raies atomiques	H, C, C^+, N, N^+, O, O^+, Ar, Ar^+, Hg, Xe, Xe^+
Photo-ionisation	H, C, C^+, N, N^+, O, O^+, Ar, Ar^+ CO_2, C_2, N_2, O_2, CO, CN, NO
Photo-détachement	C^-, N^-, O^-
Bremsstrahlung	N, O, N_2, O_2

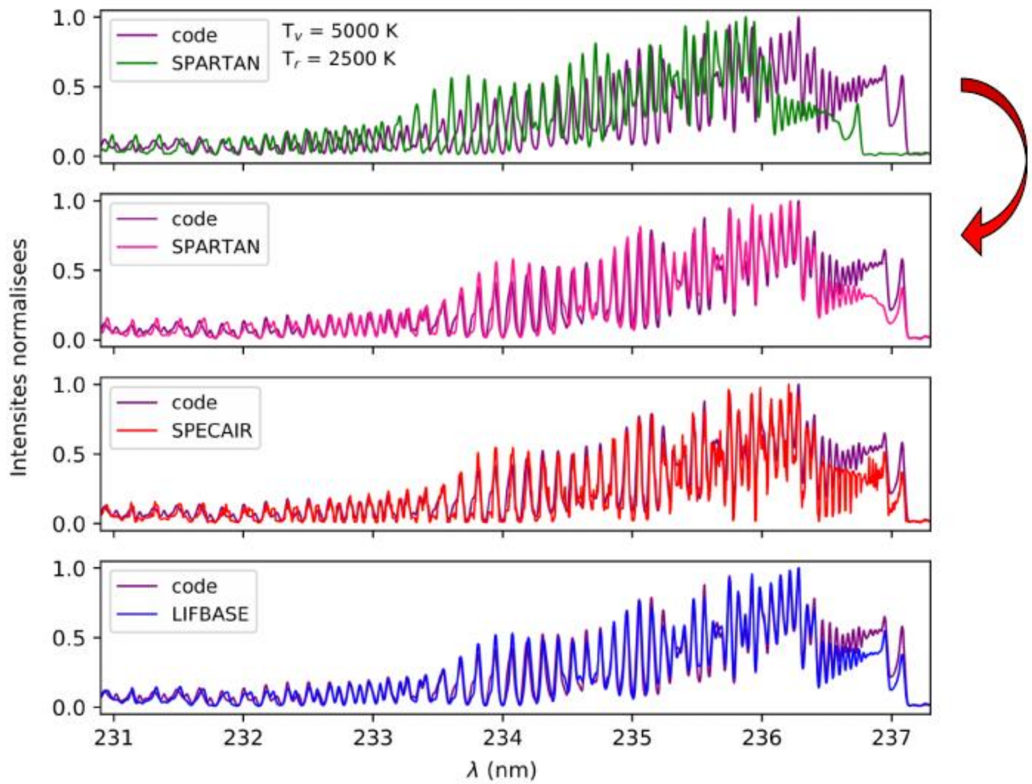
MASSIVE OES

TABLEAU 1.4 Systèmes traités dans le logiciel *massiveOES*

Molécule	Transition	Système	Base de données	Réfs.
N_2^+	B–X	Premier Négatif	LIFBASE	[LC99a]
OH	A–X	Violet	LIFBASE	[LC99a]
N_2	C–B	Second Positif	→	[LK92], [FS98], [Nas+04]
NH	A–X		PGOPHER	[Len73], [SPS94], [RB10], [Wes17]
NO	B–X	β	LIFBASE	[LC99a]

Simulation de spectres radiatifs : une aide précieuse pour le diagnostic des plasmas

5. Conclusion : **et les logiciels?**



Ar-N$_2$, 1atm (A-M Kassir, PhD Thesis, 2020)

Système γ du radical NO
Cas d'un plasma thermique

Quand ca marche pas !!!

- Décalage en longueur d'onde de 0.235 nm ;
- Pas de dédoublement Λ dans l'état $^2\Pi$.
- Cas de couplage de Hund considéré pour le niveau fondamental ;
- Facteurs de Hönl-London différents.

	LIFBASE	SPECAIR	SPARTAN	Concordance
NO γ (A—X)	included	included	Included	
NO β (B—X)	included	included	Included	
NO δ (C—X)	included	included	Included	
NO ε (D—X)	included	included	Included	
NO β' (B'—X)	-	included	Included	
NO γ' (E—X)	-	included	Included	
NO 11000 Å (D—A)	-	included	-	-
NO Infrarouge (X—X)	-	included	-	-
N_2^+ Meinel (A—X)	-	included	-	-
N_2^+ Premier Négatif (B—X)	included	included	Included	
N_2 Premier Positif (B—A)	-	included	Included	
N_2 Second Positif (C—B)	-	included	Included	
O_2 Schumann-Runge (B—X)	-	included	Included	

Ar-N_2, 1atm (A-M Kassir, PhD Thesis, 2020)

Laplace
Etude des molécules diatomiques
C-H-O-N

- Comparaisons des logiciels
- Etudes expérimentales

Molecular spectra

The rotational temperature of a molecule is often use as a probe of the gas temperature ?

Second positive band system N_2 (C-B)
Ultraviolet band system OH (A-X)
First negative band system N_2^+ (B-X)

$$Tr_{N2} \neq Tr_{OH}$$

Collisional time
Radiative life time
Quenching

"…. *observing a rotational Boltzmann distribution is a necessary but not sufficient condition for assuming that the rotational distributions are in equilibrium with the gas kinetic temperature. ….. ….an overpopulation of high rotational states occurs, which in the absence of thermalization of the rotational states would typically lead to a larger rotational temperature parameter in comparison with the gas temperature*."

P J Bruggeman Nader Sadeghi et al Plasma Sources Sci Technol 23 (2014) 023001

Two « Temperatures » Model – 3 T
Boltzmann Plot

Spectral Line Profile $P_e(\lambda)$

$$\varepsilon_\lambda = \frac{hc}{4\pi\lambda_{ul}} A_{ul} P_e(\lambda) N_u$$

$$h\nu_{ul} = \frac{h\omega_{ul}}{2\pi} = \frac{hc}{\lambda_{ul}} = E_u - E_l$$

A_{ul} : Einstein transition probability of spontaneous emission [s^{-1}],
h : Planck constant,
λ the wavelength of the emitted photon [m^{-1}].
N_u : number density of emitting species [m^{-3}] in the u state.

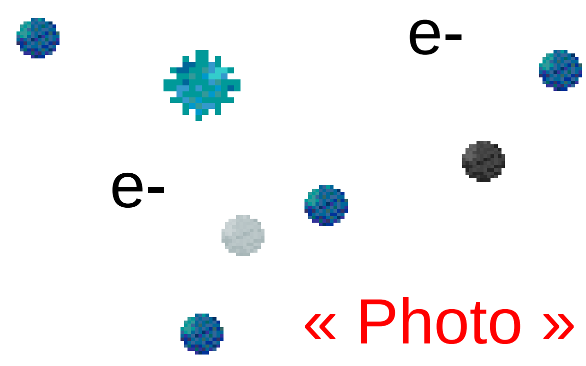
R. Stringanow and N. S. Sventitskii, Tables of Spectral Lines of Neutral and Ionized Atoms Plenum New York 1968.

NIST ASD Output: Lines http://physics.nist.gov/cgi-bin/ASD/lines1.pl

Atomic Spectral Line Database http://cfa-www.havard.edu/ ~~(OI 777nm)~~ (Cu I)

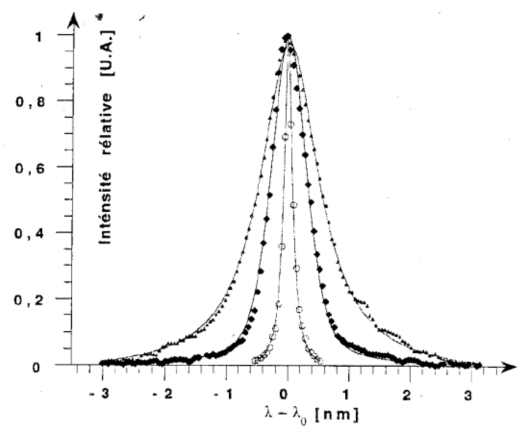
Spectral Line Profile $P_e(\lambda)$

Microscopic probe

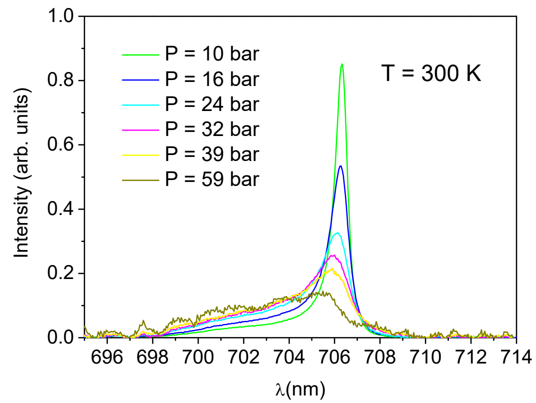


Line width $\Delta\lambda_{FWHM}$
Line shift $d=\lambda_{max}-\lambda_{vacuum}$

FWHM : Full Width at Half Maximum



Asymmetry
Satellite band
Forbidden line
Self-absorption



Broadening mechanisms

Natural Broadening ~~Δλnatural~10⁻⁴ Å~~

Doppler Broadening

$$\Delta\lambda_D = 2\lambda\sqrt{\frac{2kTLn2}{Mc^2}} = 7.157\times10^{-7}\,\lambda\sqrt{\frac{T}{M}}$$

Gaussian Profile

Particle Temperature

	T	**$\Delta\lambda_D$**
He	10000	0,02 nm
Ar	10000	0,0057 nm
H_β	5000	0,025 nm

Instrumental Broadening → Gaussian profile

Pressure Broadening → Lorentzian profile (Complex line)

Pressure Broadening

The radiation emitted from an atom is changed by the force field of a neighboring atom. Frequency and amplitude are therefore no longer constant in time.... The change is so great, however, that the phase of the vibration after the collision is no longer the same as it would have been had there been no collision.

—Weisskopf, 1933

Semi-empirical potential

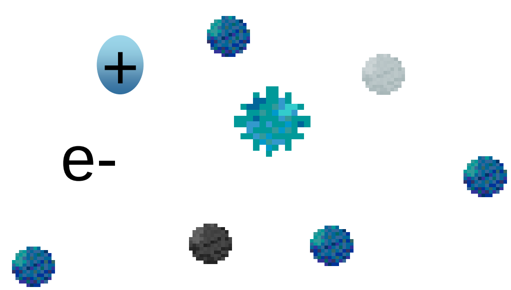
$$V(r) = \pm \frac{\hbar C_p^{\omega}}{r^p} = \pm \frac{h C_p^{\nu}}{r^p}$$

2π

$m^p s^{-1}$

Stark (p=2,4)
Neutral (van der Waals) (p=6)
Resonant (p=3)

ab-initio potential



Laboratoire de Chimie et Physique Quantiques

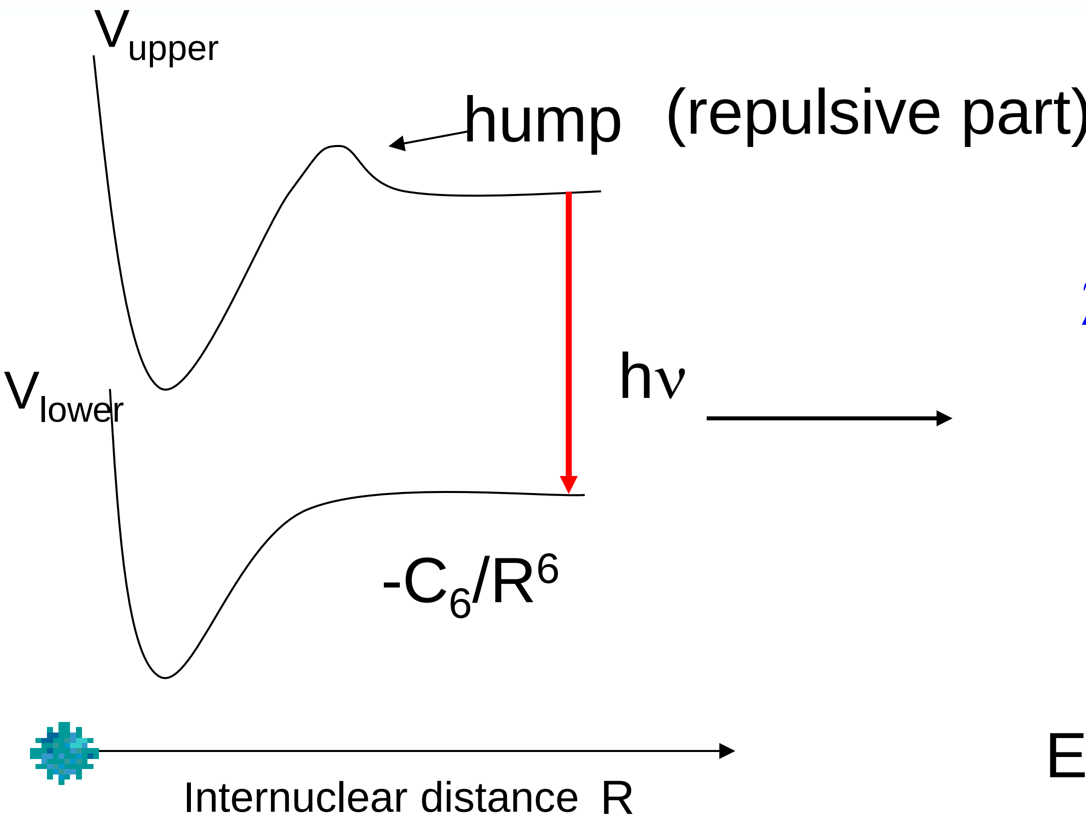
Systèmes ayant un faible nombre d'électrons

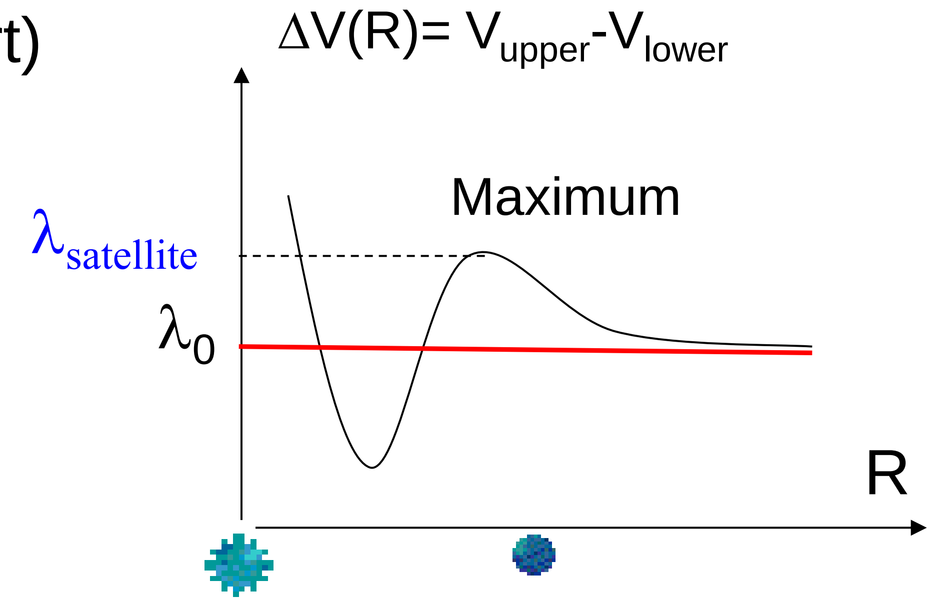
Semi-empirical Potential

Linear Stark	$V(r)=\pm\frac{\hbar C_2^{\omega}}{r^2}$	Literature
Quadratic Stark	$V(r)=\pm\frac{\hbar C_4^{\omega}}{r^4}$	Literature
Resonant	$V(r)=\pm\frac{\hbar C_3^{\omega}}{r^3}$	$C_3^{\omega}=\frac{e^2 f_r \lambda_r}{16\pi^2\varepsilon_0 m_e c}$
van der Waals	$V(r)=-\frac{\hbar C_6^{\omega}}{r^6}$	$C_6^{\omega}=\frac{1}{2h\varepsilon_0}e^2\alpha\left\|\langle r^2\rangle\right\|$ $\mathrm{m^6s^{-1}}$ $C_6^{\omega}=e^2\alpha\left\|\langle r^2\rangle\right\|$ ergcm^6 α atomic polarizability m^3 $\langle r^2\rangle = a_0^2\frac{n^{*2}}{2z_i^2}\langle 5n^{*2}+1-l(l+1)\rangle$ $n^*=\sqrt{z_i\frac{E_H}{E_i-E_u}}$
~~L-J~~	$V(r)=\hbar\left(\frac{C_{12}}{r^{12}}-\frac{C_6^{\omega}}{r^6}\right)$	W. Behmenburg J. Quant. Spectrosc. Radiat. Transfer 4, (1964) 177 W. R. Hindmarsh, A. D. Petford, G. Smith, Proc Roy Soc A 297 (1967) 296 W. R. Hindmarsh, A. N. Du Plessis et J. M. Farr (1970) J. Phys. B: At. Mol. Opt. Phys. 3, L5-L8 Butaux, F Schuller, R Lennuier J de Phys, 33, (1972), 635. ab initio potential

ab initio potential

H G Kuhn : Does your treatment predict satellite line?
A Jablonski: The theory does not predict this mysterious effect.   1968

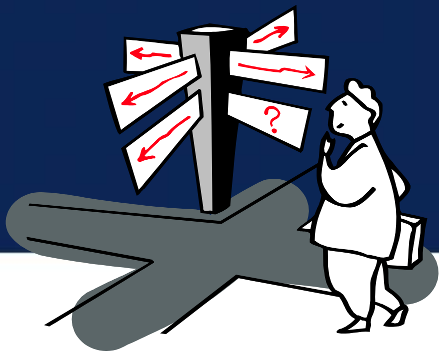




Extrema of ΔV → satellites

Maximum of ΔV → Blue satellites

MOLPRO 2009 package
http://www.molpro.net
Laboratoire de Physique et Chimie Quantique Toulouse



Interaction
Physical classification

Stark (Literature)
Van der Waals ($-C_6/r^6$)
Resonant ($\pm C_3/r^3$)

Potentiel ab initio

MOLPRO 2009 package
http://www.molpro.net

Spectral line Profile

Classical theory

?

?

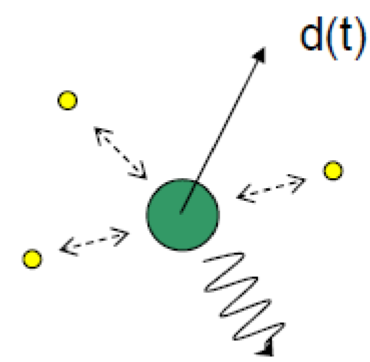
Quantum treatment

Stark

Spectral Line Profile

Quantum treatment

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^{\infty}dt\left\langle\vec{d}(0)\cdot\vec{d}(t)\right\rangle e^{i\omega t}$$



d is the dipole moment

U(t) evolution operator relative to the electrons

$$\vec{d}(t)=U^{+}(t)\vec{d}(0)U(t)$$

U-matrix

$$i\hbar\frac{dU}{dt}(t)=(H_0(t)+V(t))U(t)$$

H_0 is the Hamiltonian of the unperturbed emitter

time-dependent Schrödinger equation for the evolution operator U(t) ⟶ **Code**

PIIM Marseille
Weizmann Institute of Science, Israel;
Vallaloid Spain

Spectral Line Profile

Classical theory

Line shape formalism based on the Fourier transform of the autocorrelation function

$$P(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^{+\infty} \phi(\tau) \exp[i\omega\tau] d\tau \qquad \phi(\tau) = \int_{-\infty}^{+\infty} e^{i(\eta(t)-\eta(t-\tau))} dt$$

$$\phi(\tau) = \left\langle e^{-i\eta} \right\rangle_t = e^{-N_{pert} V_p(\tau)}$$

Autocorrelation function (wave train)

The autocorrelation function measures the average evolution of the wave train over a time interval τ from an initial time t

P. W. Anderson, Phys Rev 76 (1949) 647.
P. W. Anderson, Phys Rev 86 (1952) 809.

Spectral Line Profile

Classical theory

$$\phi(\tau) = \left\langle e^{-i\eta} \right\rangle_t = e^{-N_{pert} V_p(\tau)}$$

Perturber density N_{pert}

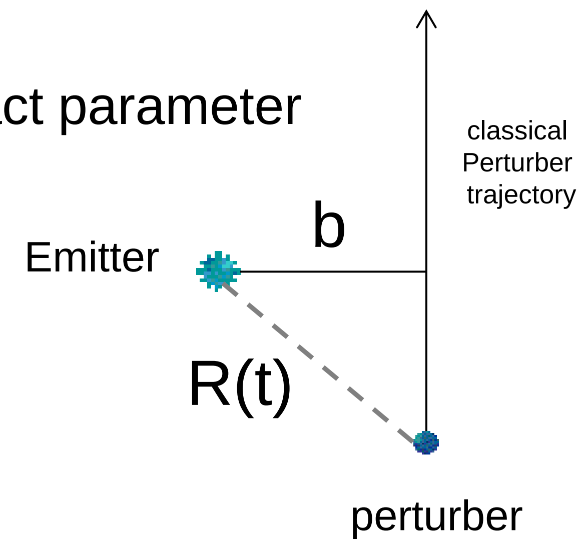
V_p: collision volume

$$V_p(\tau) = 2\pi[\int_0^{+\infty} b\,db \int_{-\infty}^{+\infty} dx \,\{ 1 - \exp(-i\frac{1}{\hbar}\int_0^{\tau} V(R(t'))dt')\}]$$

Rectilinear classical path

$$R(t) = \left[b^2 + (x_0 + \bar{v}t)^2\right]^{1/2}$$

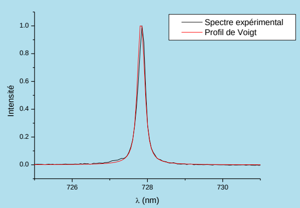
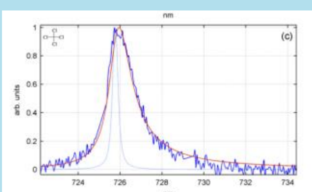
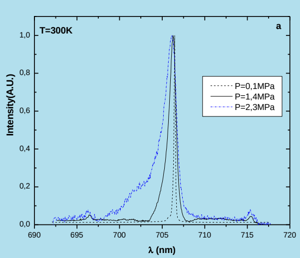
b is the impact parameter



Unified theory
Impact approximation N_{pert} <<<
Quasitatic approximation N_{pert} >>>

Spectral Line Profile

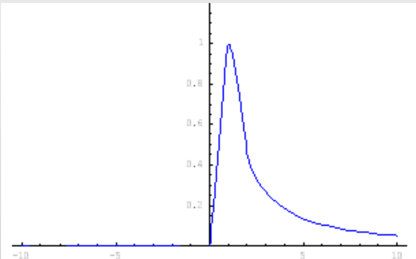
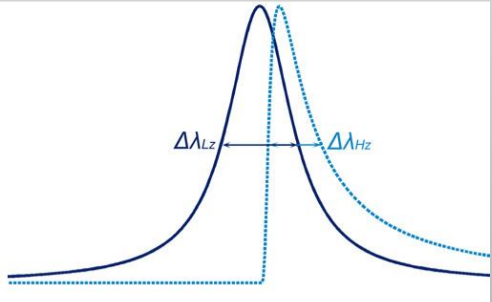
The quasistatic and impact approximations represent important theoretical limits that are in many cases sufficient for practical purposes and have been used to guide and develop new methods that are more generally applicable and, in fact, satisfactorily solve the line broadening problem in practically all cases. S. Alexiou / (2009)

Experimental profile			
	Lorenztian profile (Voigt profile)	Impact approximation	N<<, core
	Red Asymmetric profile	Quasi static approximation	N>>, wing
	Complex Satellite Blue wing	**Unified theory (ab initio potential)**	N, ω

Impact approximation

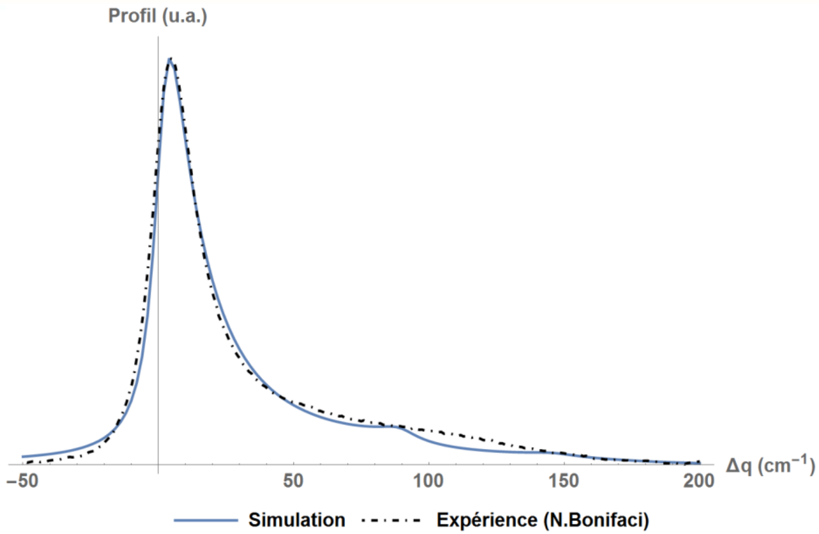
Stark	literature
Resonant	$$\Delta\lambda_{res} = K\frac{1}{\pi}\sqrt{\frac{g_0}{g_r}}\frac{e^2\lambda_{ul}^2 f_r\lambda_r}{4\pi\varepsilon_0 m_e c^2}N \propto \frac{P}{T}$$ K: 0,9-1,8 $$S_{\lambda res} \approx 0$$
van der Waals	$$\Delta\lambda_{vdw} = A\left(\frac{\lambda_{ul}^2}{2\pi c}\right)\Delta C_6^{2/5}\bar{v}^{3/5}N \propto \frac{P}{T^{0.7}}$$ A : 8.08 ou 8.16 $$S_{\lambda vdw} = \frac{\Delta\lambda_{VDW}}{2,75}$$ $$\bar{v} = \sqrt{8kT/\pi\mu}$$

Quasistatic Approximation

Stark	-------
Resonant	$\Delta\lambda_{resQS} = \Delta\lambda_{res}\left(1-\beta N\right)$ $\qquad S_{\lambda resQS} \approx \varepsilon\Delta\lambda_{resQS}$ H. R. Zaidi , Can. J. Physics 55, (1977) 1243.
Van der Waals	$\Delta\lambda_{QS} = 0.411\pi^2 C_6 \frac{\lambda_{ul}^2}{c} N^2$ $\begin{cases} P_{QS}(\lambda) = \frac{1}{2}\left(\frac{\Delta\lambda_{qs}}{(\lambda-\lambda_{ul})^3}\right)^{1/2} \exp\left(-\frac{\pi}{4}\frac{\Delta\lambda_{qs}}{(\lambda-\lambda_{ul})}\right) & \lambda > \lambda_{ul} \\ P_{QS}(\lambda) = 0 & \lambda \le \lambda_{ul} \end{cases}$  $P_T = \int_{-\infty}^{+\infty} P_{Lor}(\Delta\lambda-\zeta)P_{QS}(\zeta)d\zeta$  H. Margenau Phys. Rev. 48, (1935) 755. H. Margenau Phys Rev 82 (1951) 156.

Spectral Line Profile

Classical theory



Unified theory N Allard

GEPI, Observatoire de Paris

Ab initio potential

$$g_{(i,f)}(\tau) = \frac{1}{\sum_{ee'}^{\alpha} |d_{ee'}|^2} \sum_{ee'}^{\alpha} \int_0^{\infty} 2\pi\rho d\rho \int_{-\infty}^{+\infty} dx d_{ee'}(R(0)) \left[e^{\frac{i}{\hbar}\int_0^{\tau} dt \mathbf{V}(R(t))} \tilde{d}^{*}_{e'e}(R(\tau)) - \tilde{d}_{ee'}(R(0)) \right]$$

modulated electric dipole transition moment

$$\tilde{d}_{ee'}(R(t)) = d_{ee'}[R(t)] e^{-\frac{1}{kT} V_e[R(t)]}$$

$d_{ee'}$ Dipole transition moment (ab initio calculation)

Allard N F, Royer A, Kielkopf J F and Feautrier N 1999 Phys. Rev. A 60 1021

Spectral Line Profile

Stark broadening

Linear Stark effect Hydrogen lines

H_α 656.2 nm, H_β 486.1 nm

H.R. Griem, Plasma Spectroscopy, Academic Press, New York, 1964.1964 H Griem Spectral line broadening by Plasmas London Academic 1974 H. Griem, Principles of Plasma Spectroscopy, Cambridge University Press, 1997.	$N_e=C(N_e,T)*\Delta\lambda^{3/2}$ Where $C(N_e,T)$ is in $A^{-3/2}$ cm^{-3}.
M. Gigosos et V. Gardeñoso, J. Phys. B: At. Mol. Opt. Phys., vol. 29, no 20, p. 4795, oct. 1996. M. Gigosos , M Gonzalez V. Gardeñoso Spectrochimica Acta Part B 58 (2003) 1489–1504	H_α { Table; full width at half area } H_β $\Delta\lambda_{stark}(nm) = 4.8\left(\frac{N_e}{10^{23}}\right)^{0.68116}$

Example : Helium Gas
Linear Stark effect + van der Waals

$$\Delta\lambda_{lor} = \Delta\lambda_{stark}\left(N_e, T_e\right) + \Delta\lambda_{vdw}\left(N\right)$$

H-β	C_6 [$m^6 s^{-1}$]	$\Delta\lambda_{vdw}$
4s-2p	$7.59*10^{-43}$	$2.20\times10^{-5}PT^{-7/10}$
4p-2s	$6.85*10^{-43}$	$2.12\times10^{-5}PT^{-7/10}$
4d-2p	$5.82*10^{-43}$	$1.98\times10^{-5}PT^{-7/10}$

H-α	C_6 [$m^6 s^{-1}$]	$\Delta\lambda_{vdw}$
3s-2p	$2.75*10^{-43}$	$2.40\times10^{-5}PT^{-7/10}$
3p-2s	$1.696*10^{-43}$	$2.20\times10^{-5}PT^{-7/10}$
3d-2p	$1.18*10^{-43}$	$1.93\times10^{-5}PT^{-7/10}$

H_β quadratic Stark, H_α self –absorption

Quadratic Stark Effect

Impact Approximation

electrons

Quasistatic Approximation

ions

$$J(x) = \frac{1}{\pi}\int_0^{\infty} \frac{W(\beta)d\beta}{1+\left(x - A^{4/3}\beta^2\right)^2}$$

Holtsmark distribution

$$W(\beta) = (2/\pi)\beta\int_0^{\infty} \chi \sin(\beta\chi)\exp\left(-\chi^{3/2}\right)d\chi$$

$$\Delta\lambda_{Stark} = \left(1+1.75\alpha(1-0.75r)\right)2\omega$$

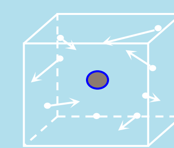
$$S_{\lambda(Stark)} = d \pm 2A(1-0{,}75r)\omega$$

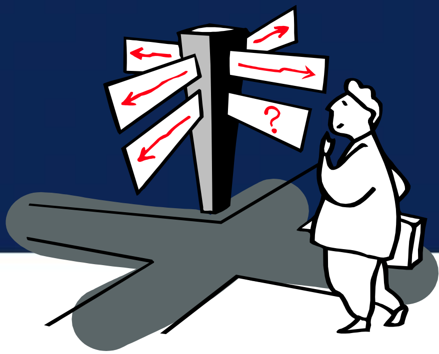
$\Longrightarrow$ N_e, T_e p. 97 Griem 1974

- H. R. Griem (1964) Plasmas Spectroscopy , McGraw-Hill Book Compagny, New York.
- H .R. Griem (1974) Spectral Line Broadening by Plasmas , New York : Academic Press.
- H. R. Griem (1997) Principles of Plasma Spectroscopy , Cambridge.

Stark : Line shape Code

Quantum treatment, Numerical calculation

Simulation code	**LSNS**	PIIM Rosato, J. et al J. Quant. Spectrosc. Radiat. Transfer **2015**, 165, 102–107	**computer simulation method** The particle motion is simulated and the Schrödinger Eq. is solved numerically it is time consuming	
	SimU	Stambulchik, E. et al Phys. Rev. E **2007**, 75, 016401		
	.....			
Models	**PPP**	PIIM Calisti, A et al Phys. Rev. A **1990**, 42, 5433–5440.	Frequency Fluctuation Model Rapid calculations for neutral and charged emitters	
	QC-FFM	Stambulchik, E.et al Phys. Rev. E **2013**, 87, 053108.	Frequency Fluctuation Model	
	Zest	Gilleron, F et al Atoms **2018**, 6, 11	Quasi-static description of ions and impact approximation for electrons	
	......			



Interaction
Physical classification

Stark (*literature*)
Van der Waals ($-C_6/r^6$)
Resonant ($\pm C_3/r^3$)

Potentiel ab initio
Code MOLPRO
http://www.molpro.net

Spectral line Profile

Classical theory

- Unified theory
- Impact approximation
- Quasitatic approximation

Quantum treatment

Stark

PIIM Marseille
Weizmann Institute of Science, Israel;
Vallaloid Spain

Examples

Positive streamers in liquid nitrogen

Streamers in chlorinated alkane and alkene liquids

→ Approximation quasi static

vdw

Corona discharge in Helium 300 K

→ Unified theory — Ab initio potential

→ Quantum treatment — Stark

Cold helium jet

→ 2 T model

Corona discharge in Helium 4 K → ?

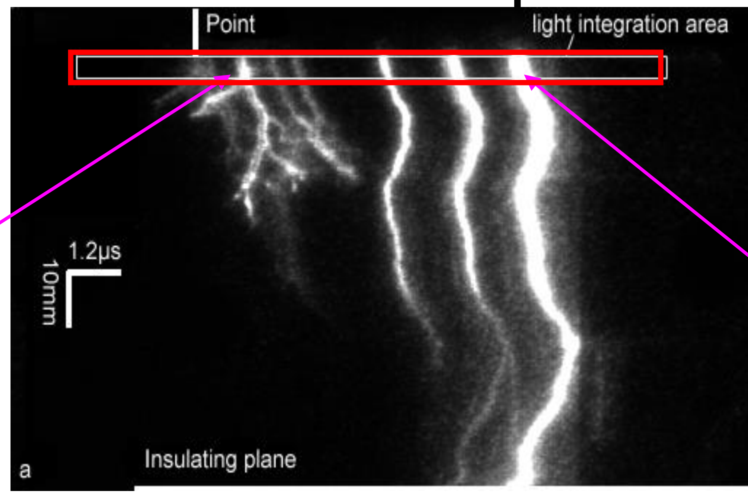
Positive filamentary streamers in liquid nitrogen

Two distinct phases

0,4/1400µs
100-200 mA

80mm, 102kV

d



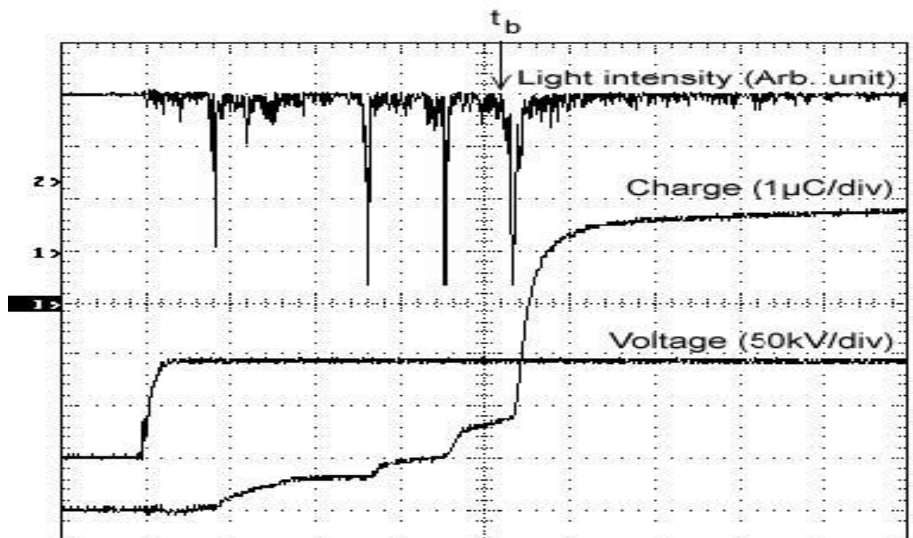
Streak photograph of filamentary streamer propagating up to plane

The streamer propagation

Streamer reaches the plane
Re-illumination

Weak emitted light

Intense emitted light



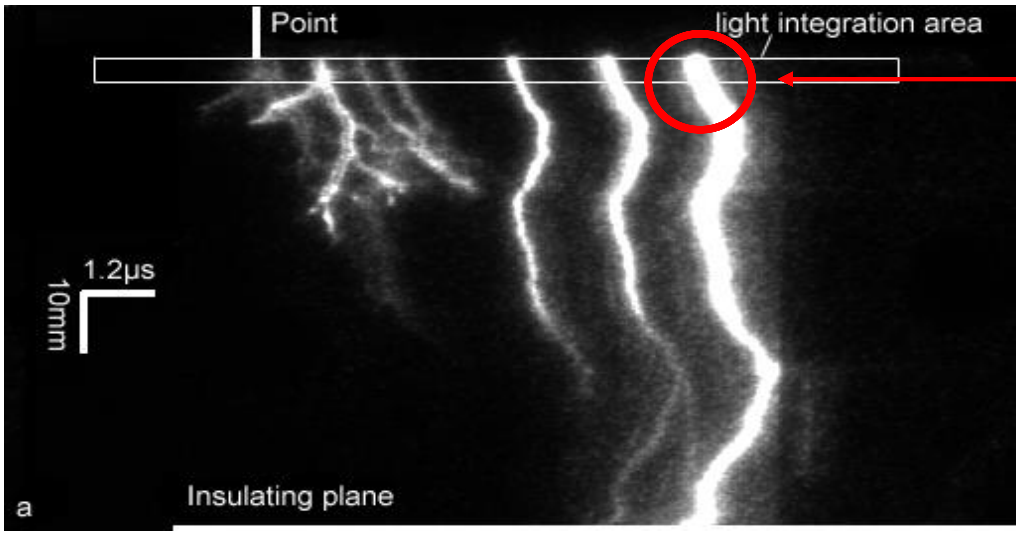
~100 streamers

1 streamer

Positive filamentary streamers in liquid nitrogen

Experimental Results

Re-illumination



T=0 — $T_{breakdown}$ → time

Light emitted by one positive streamer in LN_2 when it stops on the insulating plane

Intense NI Atomic line

($3s^4P$-$3p^4S^0$ and $3s^4P$-$3p^4P$ transition)

↓

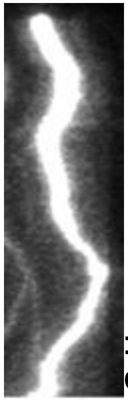
No N_2 emission

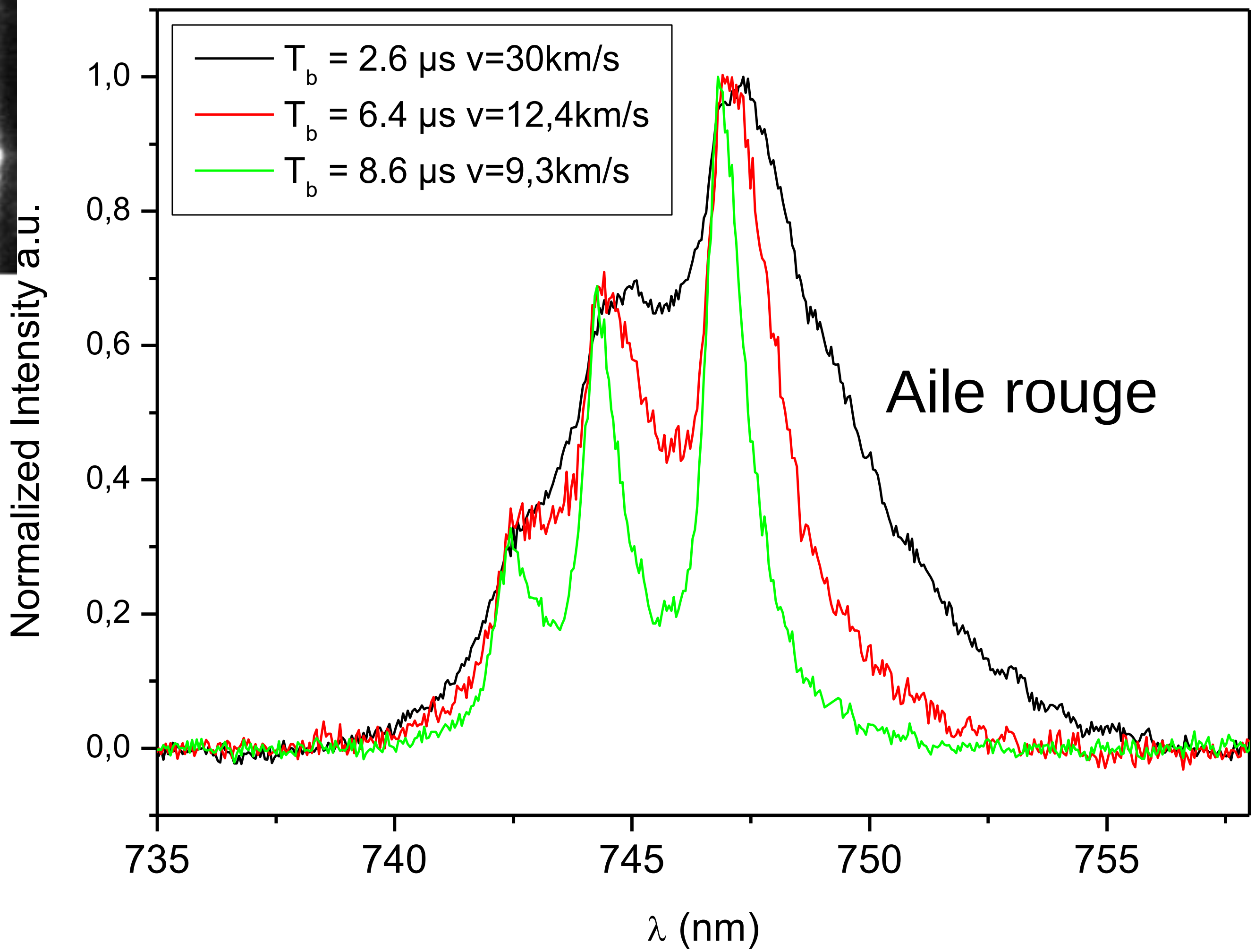
When one positive streamer stops on the insulating plane,
a large current pulse and a bright emitted light are recorded at t_b

Positive filamentary streamers in liquid nitrogen

Re-illumination

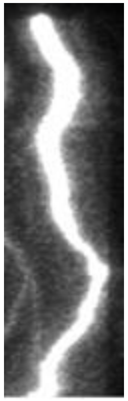
Propagation velocity : 10-30 km/s

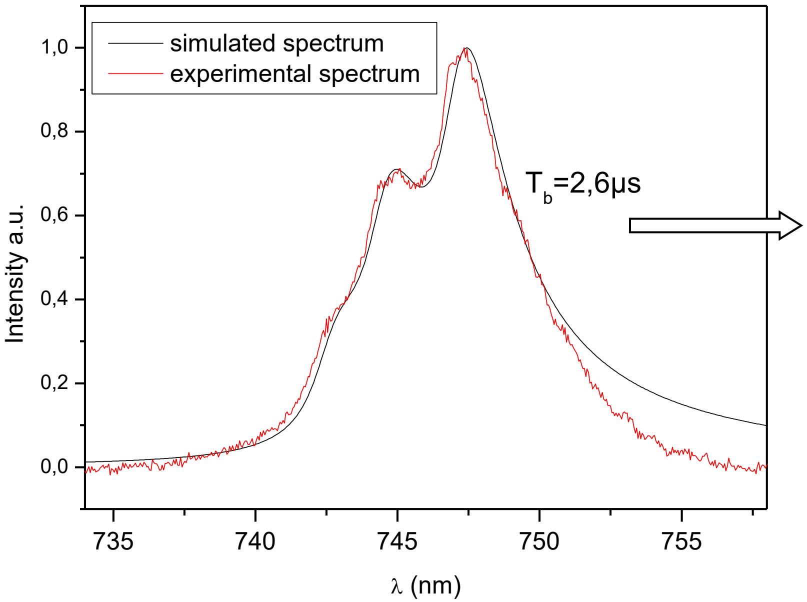




Broadening of Atomic line of NI ($3s^4P$-$3p^4P$)

Positive filamentary streamers in liquid nitrogen

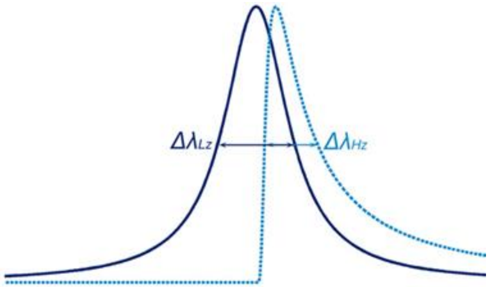


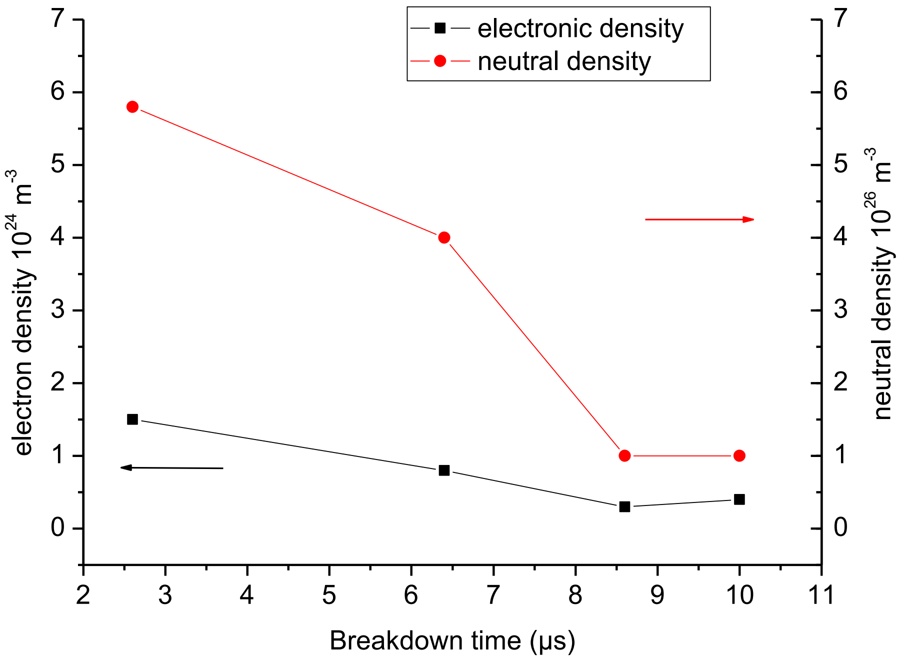


Quasi static approximation

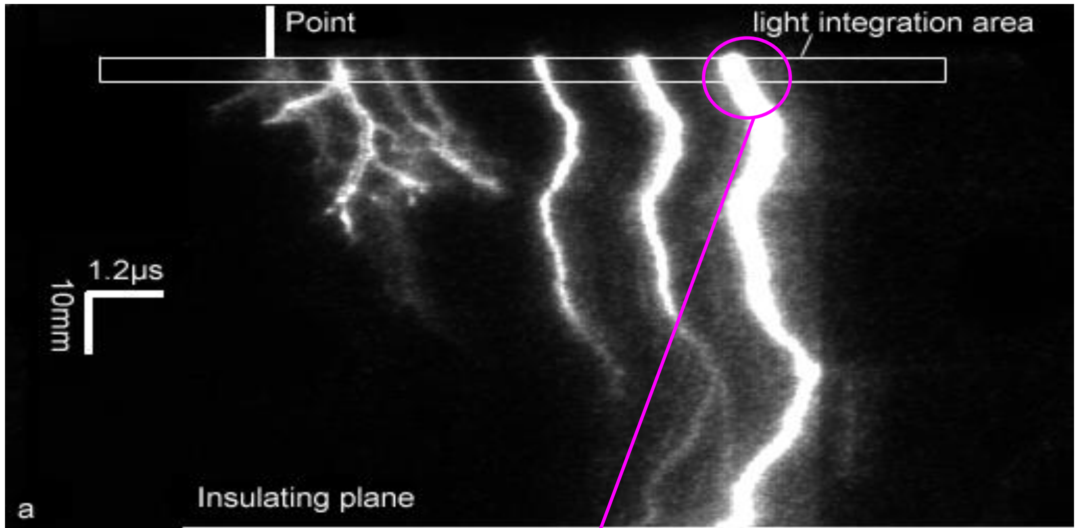
N_e~1,5x10^{24} m^{-3}

N_g~6x10^{26} m^{-3}





Positive filamentary streamers in liquid nitrogen

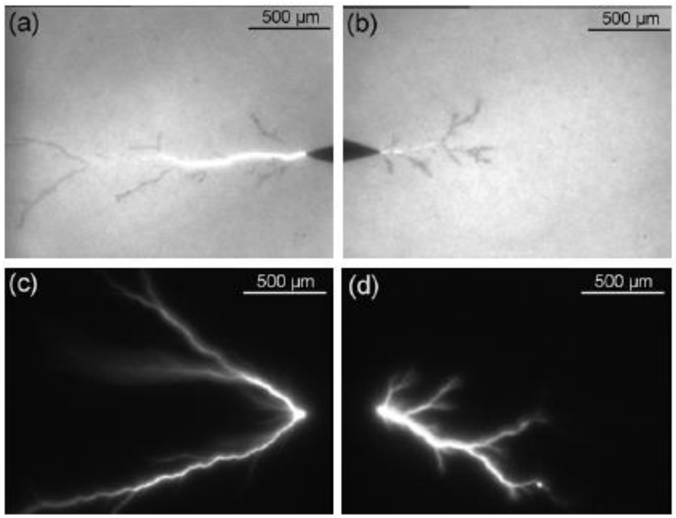


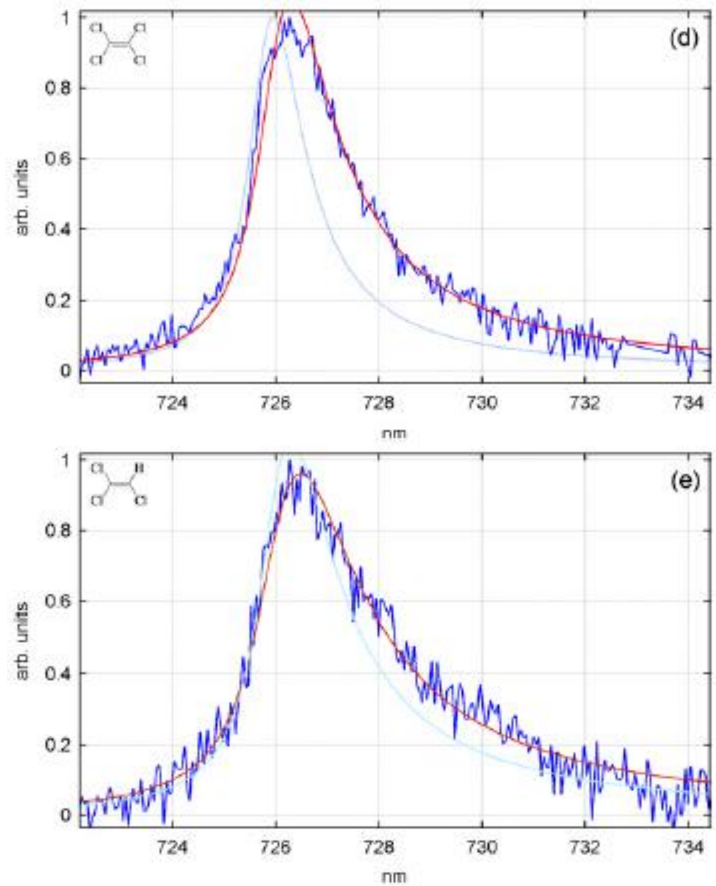
2000 K- 3000 K

Internal Pressure of the gas ~200 B   V=30 km/s
Internal Pressure of the gas ~30 B   V=10 km/s

N_e=0,5-1,5 10^{24} m^{-3}

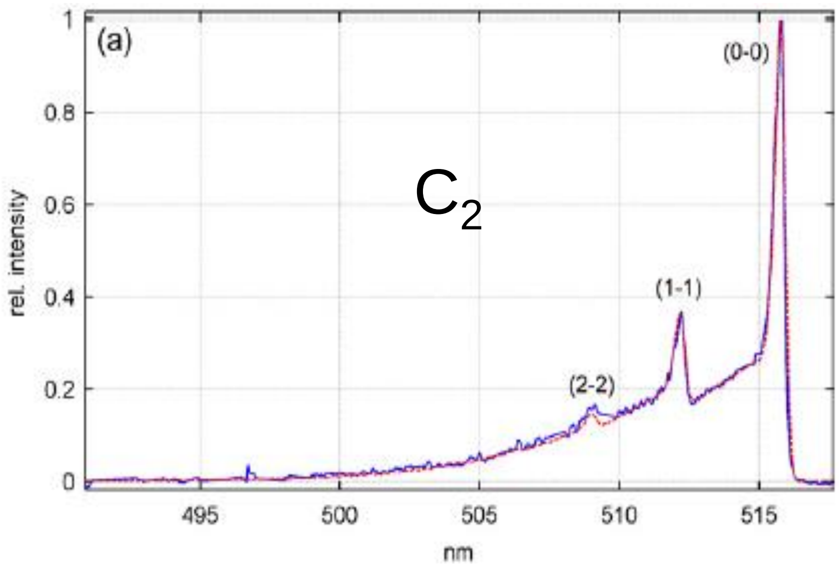
Streamers in chlorinated alkane and alkene liquids





725,6 nm

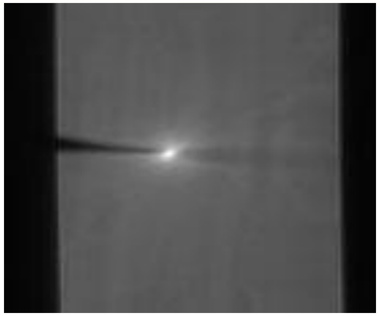
20-30 km/s



T_{rot} = 3000-4000 K
P = 86-136 bar
N_e= 4-8 10^{23} m^{-3}

Optical Emission from Helium Cryoplasma

Discharge in dense fluids (liquids or high-pressure gases :1-100 bar)



V ~ kV DC, I ~ 0,1-50µA

P=0,1-100mW,

gap distance~5-8 mm

R_{tip} ~ 0,1-2µm

Corona-discharge

Gas → liquid

T ↘

Temperature: 300 K → 4.2 K

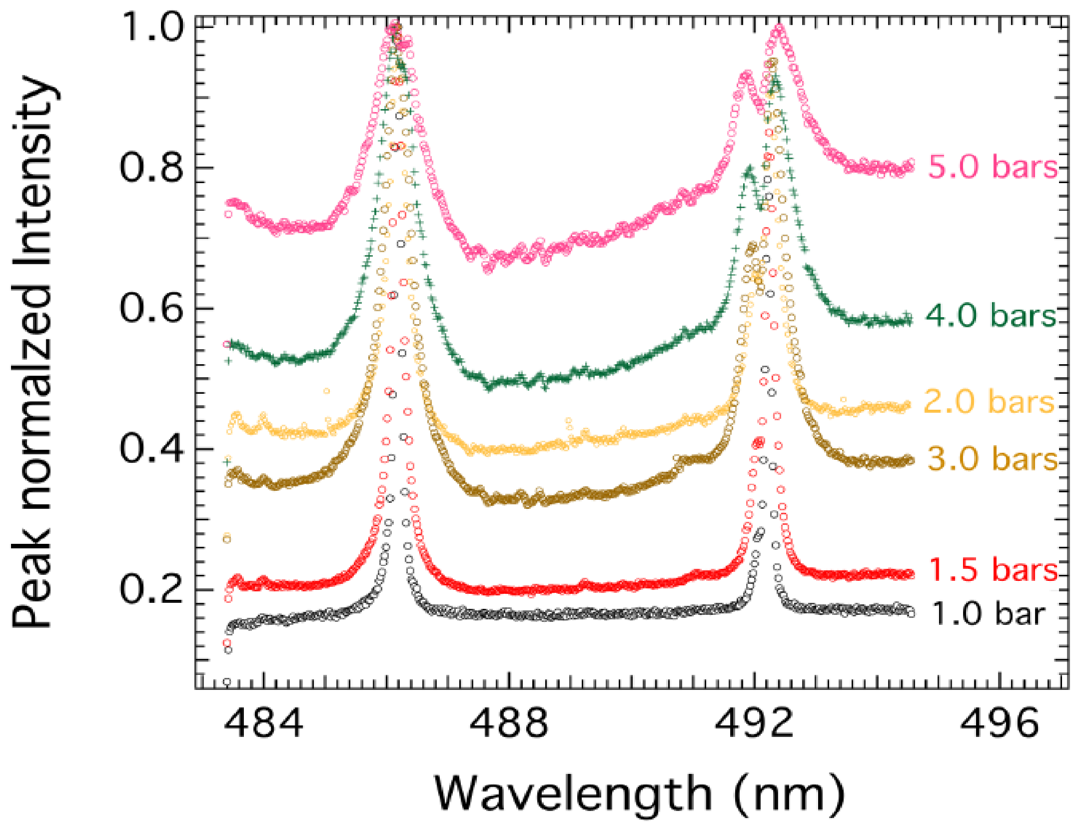
Density N: $2\ 10^{19}$ cm^{-3} → $2\ 10^{22}$ cm^{-3}

Goal:

Determine N_e ,T_e, T, N_{He}

The 4th Spectral Line Shapes in Plasmas code comparison workshop– Baden – March 20th to 24th, 2017

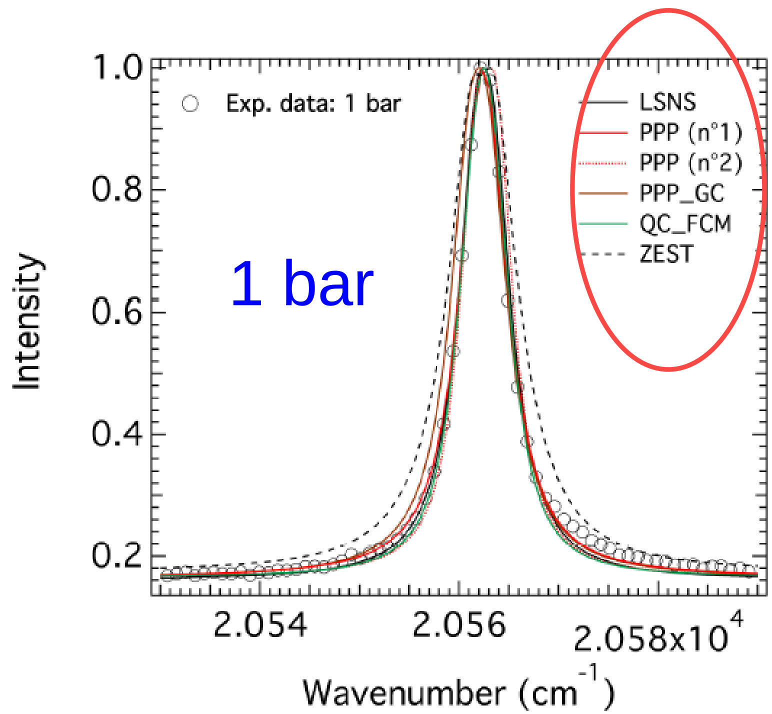
Corona discharge in helium 300 K

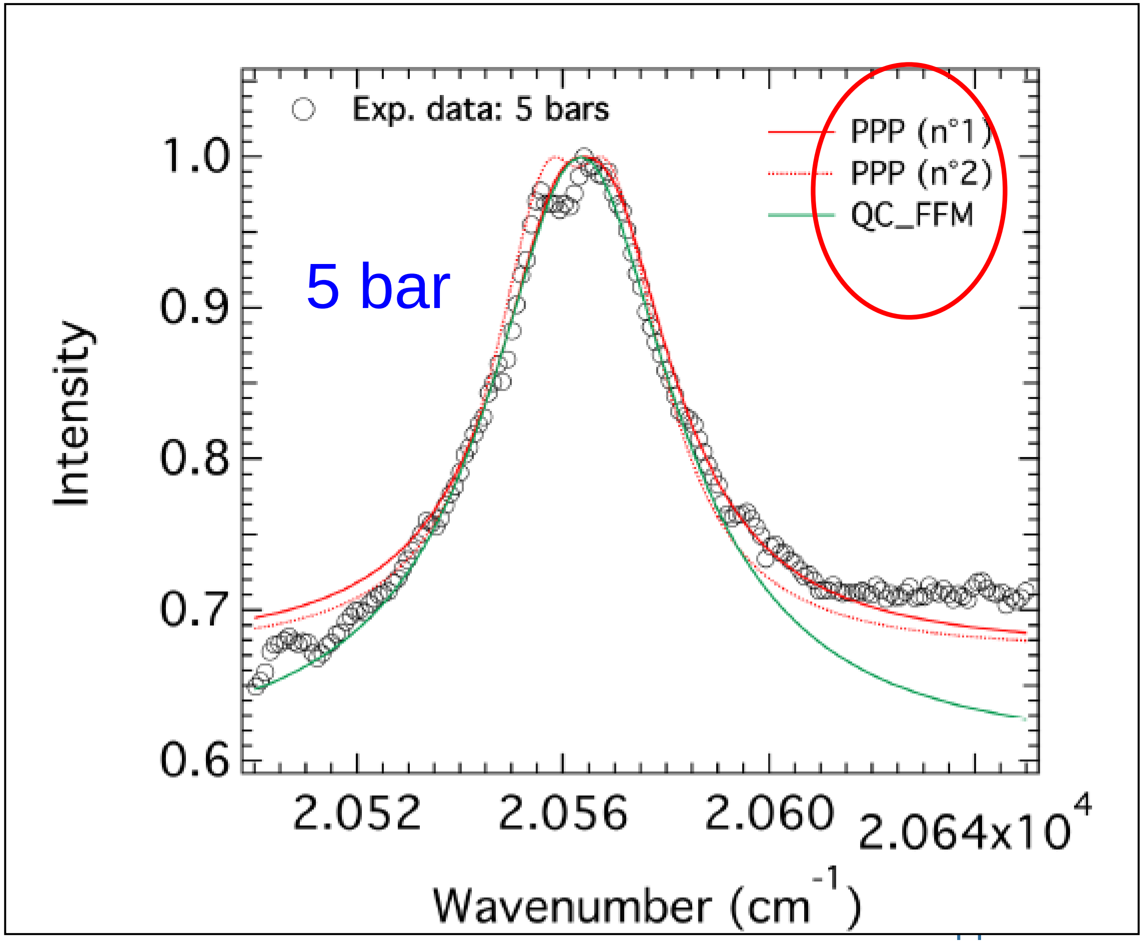


Code comparison code workshops
http://plasma-gate.weizmann.ac.il/slsp

Comparison of the FWHM of the H-β Line

300 K





H-β Line in a Corona Helium Plasma: A Multi-Code Line Shape Comparison

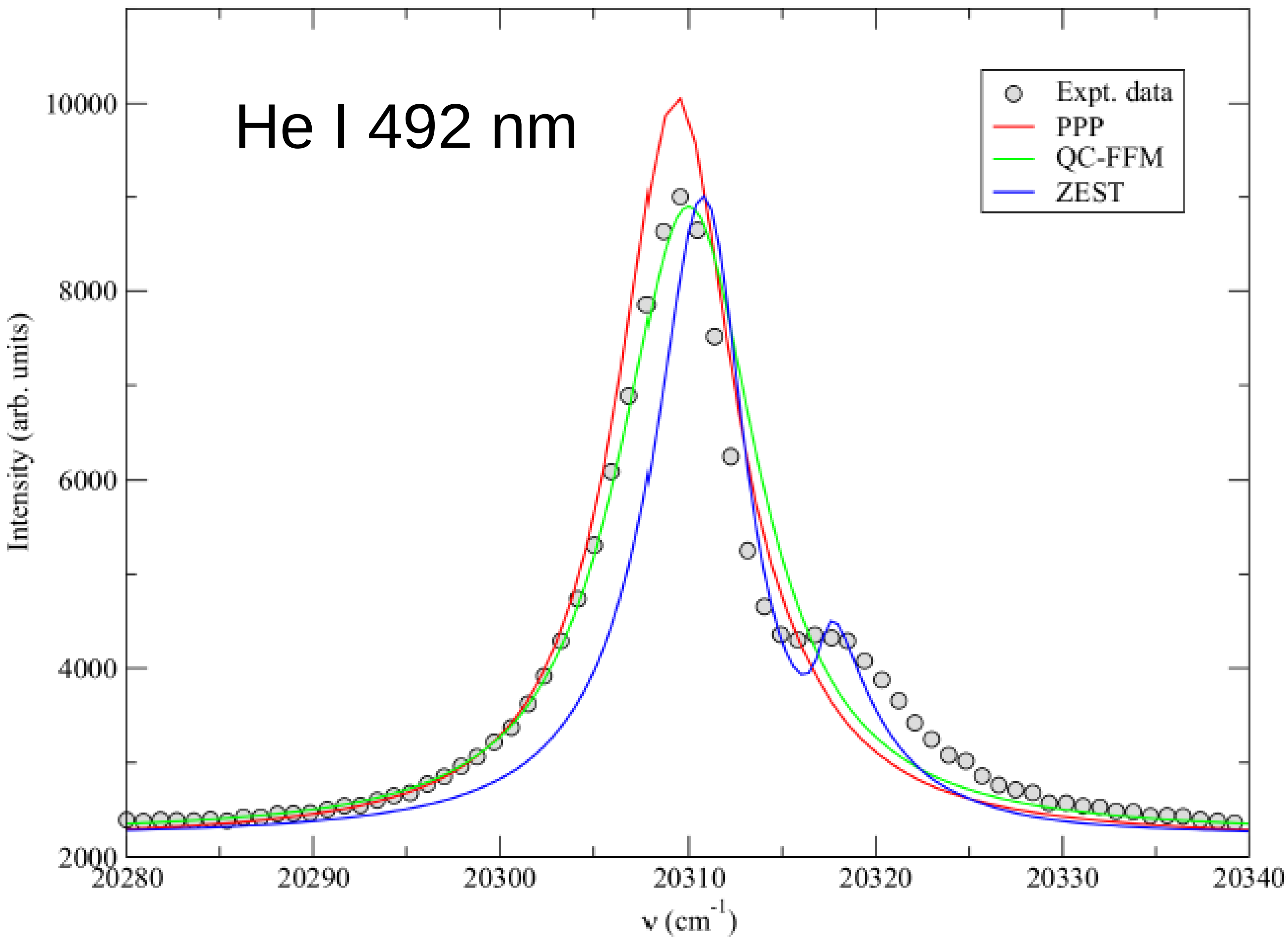
Table 3. The electron densities (in units of 10^{15} cm^{-3}) as inferred from the fit of the experimental H-β spectra by the contributing codes. P is the pressure in units of bars.

Case n°	P	LSNS	PPP (n°1)	PPP (n°2)	PPP_GC	QC_FFM	ZEST
1	1	0.5	0.15	0.26	0.18	0.8	1.2
2	1.5	1.1	0.3	0.58	0.38	2.2	2.7
3	2	-	0.55	1.0	1.3	4.7	-
4	3	-	0.9	2.0	-	10.0	-
5	4	-	1.3	2.8	-	15.0	-
6	5	-	1.9	3.8	-	27.0	-

RR Sheeba, M Koubiti, N Bonifaci, F Gilleron, C Mossé… - *Atoms* **2018**, *6*(2), 29; https://doi.org/10.3390/atoms6020029

Broadening of the Neutral Helium 492 nm Line in a Corona Discharge: Code Comparisons

1.5 bar 300 K



RR Sheeba, M Koubiti, N Bonifaci, F Gilleron, JC Pain… - *Atoms* **2018**, *6*(2), 19; doi:10.3390/atoms6020019

A New Procedure to Determine the Plasma Parameters from a Genetic Algorithm Coupled with the Spectral Line-Shape Code PPP

Table 5. Results of the fitting GA analysis of the H-β line. n_e: electron density; T_e: electron temperature; $\Delta\lambda_{VDW}$: van der Waals width; $\Delta\lambda_{ins}$: Gaussian width.

Hβ

Pressure (bar)	n_e (cm^{-3})	T_e (10^4 K)	$\Delta\lambda_{VDW}$ (nm)	$\Delta\lambda_{ins}$ (nm)
1	10^{14}	1.23	7.2×10^{-2}	8.0×10^{-2}
2	8×10^{14}	1.17	15.2×10^{-2}	8.0×10^{-2}
3	1.85×10^{15}	1.21	24.2×10^{-2}	8.0×10^{-2}

≠

Table 6. Results of the fitting GA analysis of the He I 492 nm line.

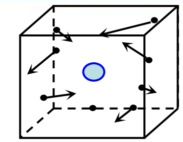
492 nm

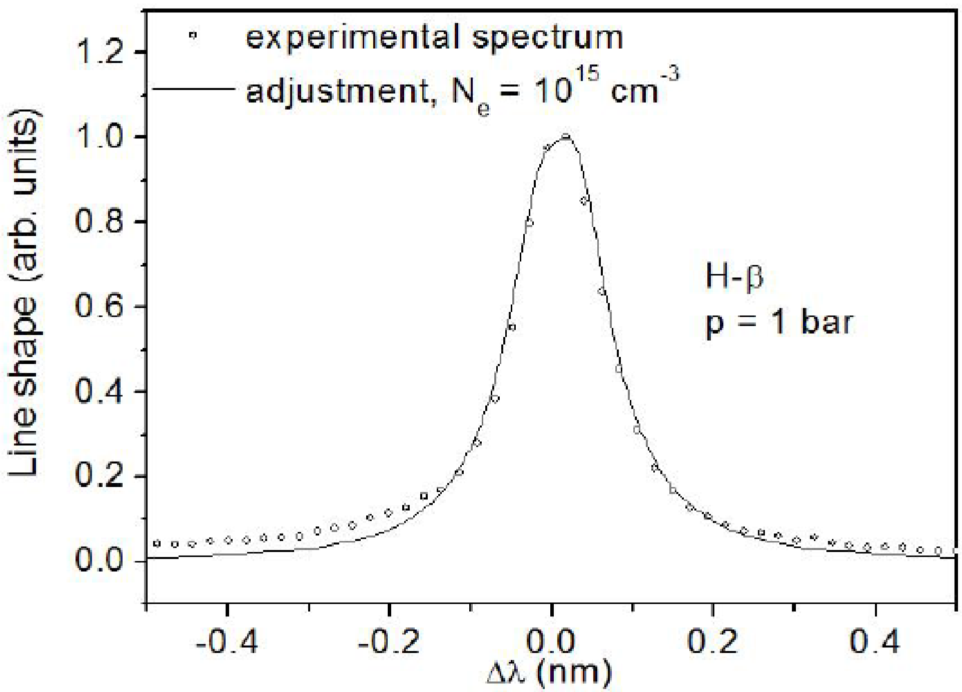
Pressure (bar)	n_e (cm^{-3})	T_e (10^4 K)	$\Delta\lambda_{VDW}$ (nm)	$\Delta\lambda_{ins}$ (nm)
1	10^{15}	1.21	2.93×10^{-2}	8.0×10^{-2}
2	3.96×10^{15}	1.16	5.82×10^{-2}	8.0×10^{-2}
3	8×10^{15}	1.16	9.7×10^{-3}	8.0×10^{-2}

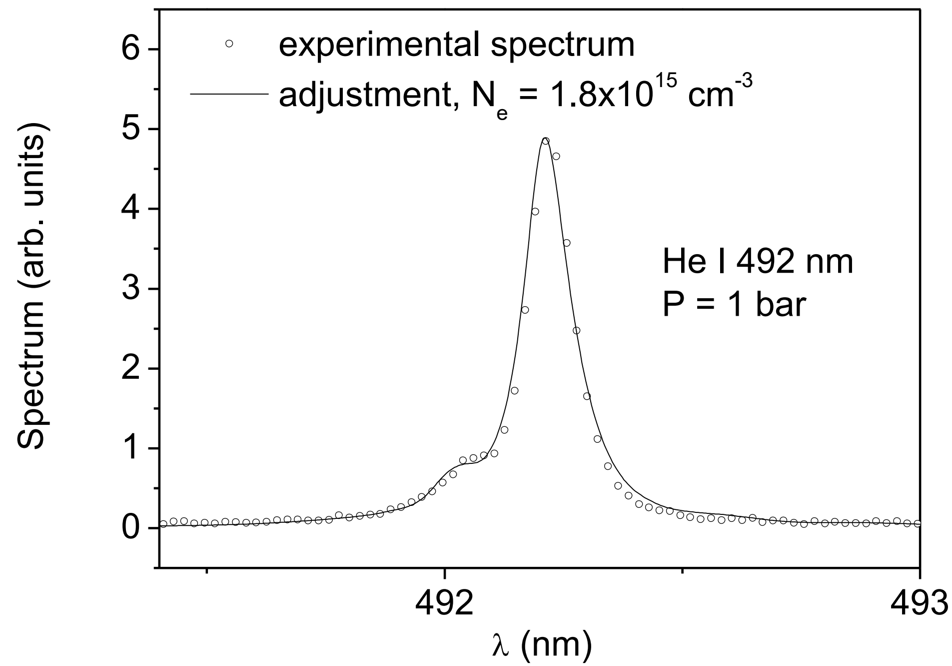
Electron number density : N_e

Computer simulation method

P= 1 Bar







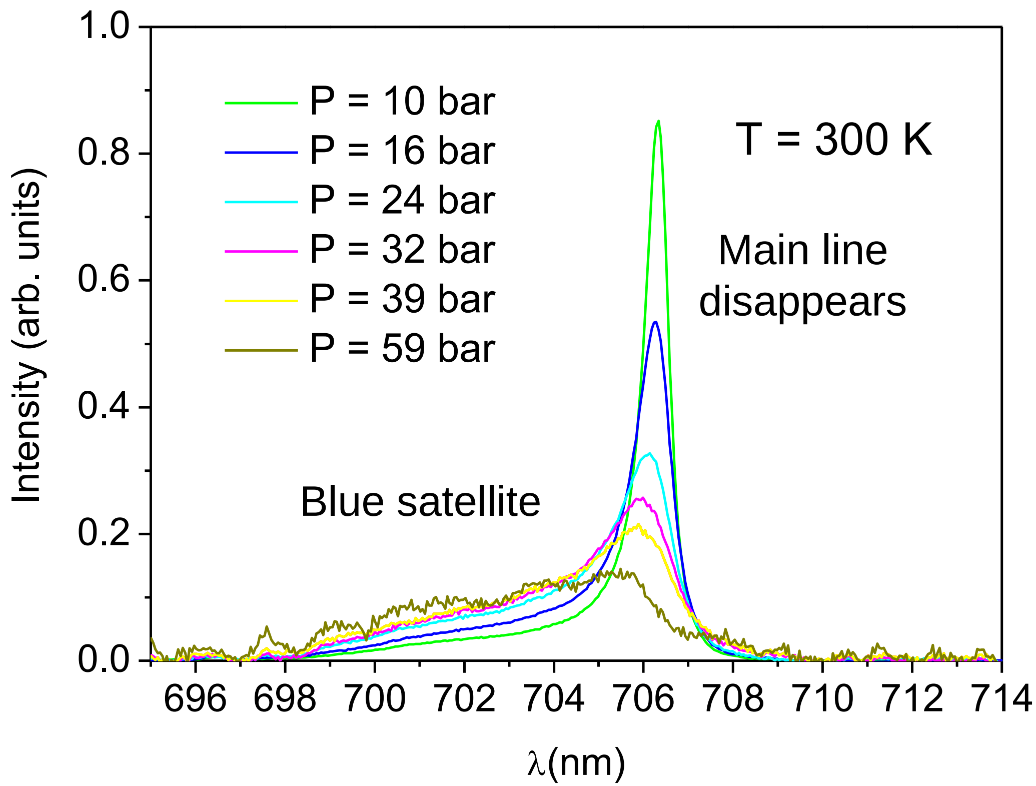
$T_e = 10^4$ K

Line Shape Modeling for the Diagnostic of the Electron Density in a Corona Discharge

J Rosato, N Bonifaci, Z Li, R Stamm - **Atoms**, 2017

Neutral Perturbers Density : N_{He}

300 K (P) 706 nm (^3S-^3P)



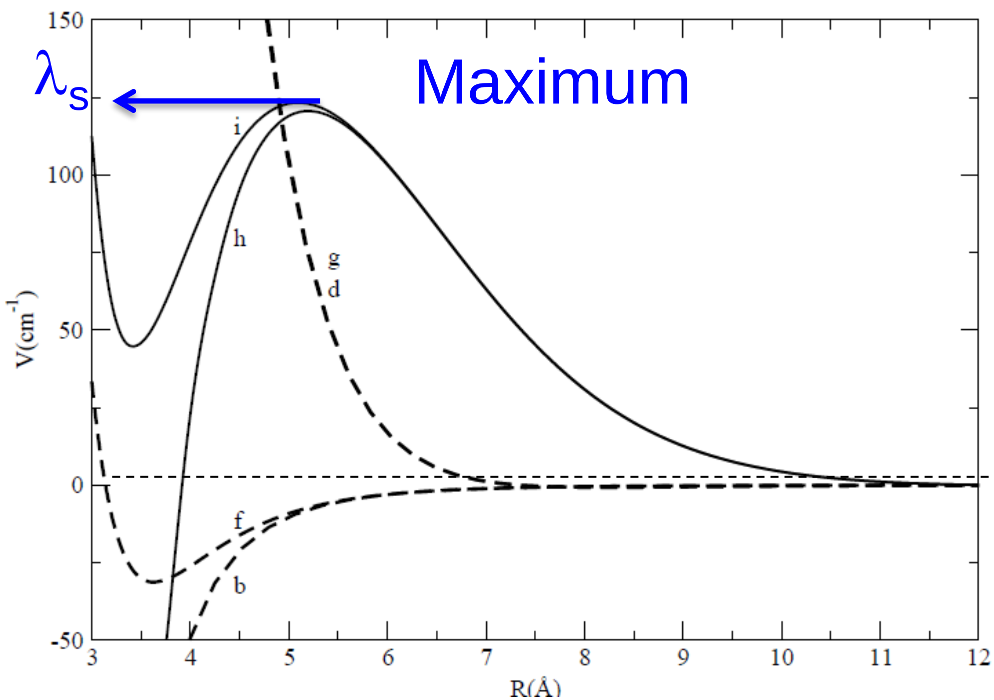
Fourier Transform of the dipole autocorrelation function

$$\phi(\tau) = e^{\left(-N_{He} g_{\alpha}(s)\right)}$$

$$g_\alpha(s) = \frac{1}{\sum_{e,e'}{}^{(\alpha)} |d_{ee'}|^2} \sum_{e,e'}^{(\alpha)} \int_0^{+\infty} 2\pi\rho d\rho \int_{-\infty}^{+\infty} dx \, \tilde{d}_{ee'}[R(0)] \left[e^{\frac{i}{\hbar}\int_0^s dt \, V_{e'e}[R(t)]} \, \tilde{d}^*_{ee'}[R(s)] - \tilde{d}_{ee'}[R(0)] \right]$$

Neutral Perturbers Density : N_{He}

He*-He Potential

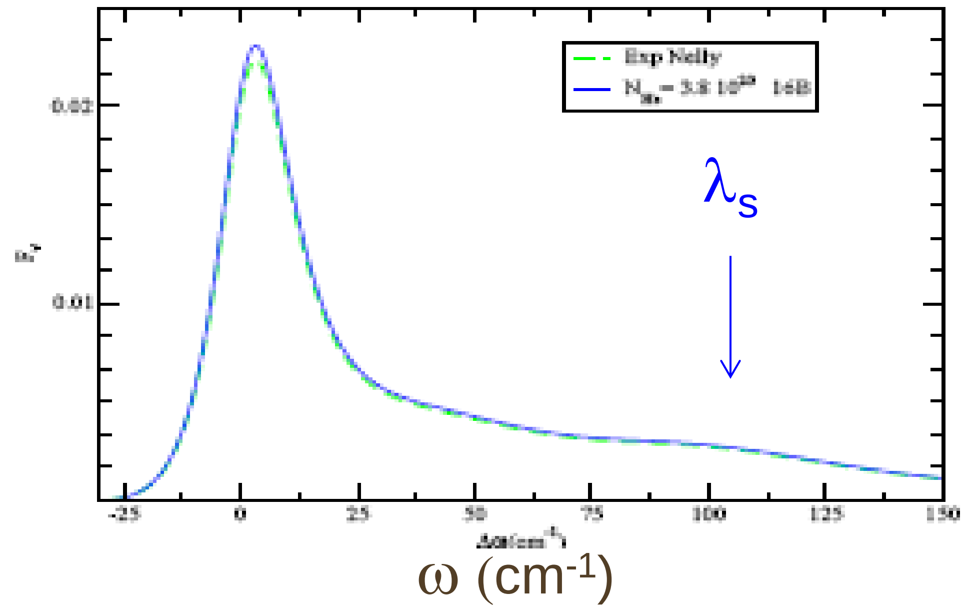


N ALLARD, et al EPL 88 (2009) 53002

N ALLARD, et al EPJ D 61 (2011) 365-372

Comparison between experiment and theory

16 Bar



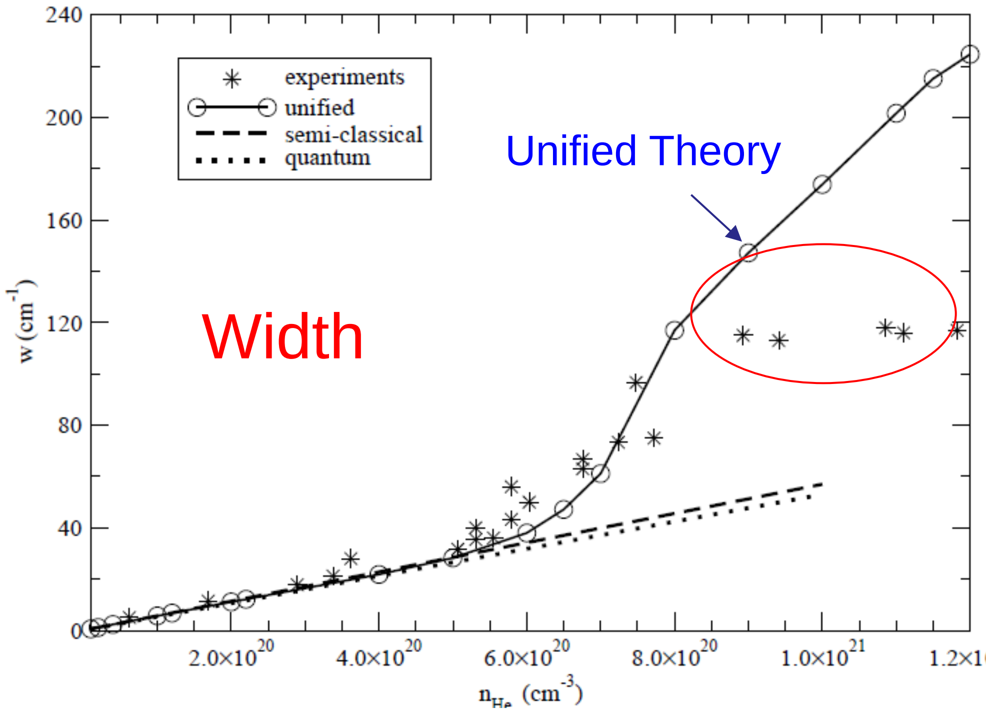
N_{per}=3.8 10^{20} cm^3

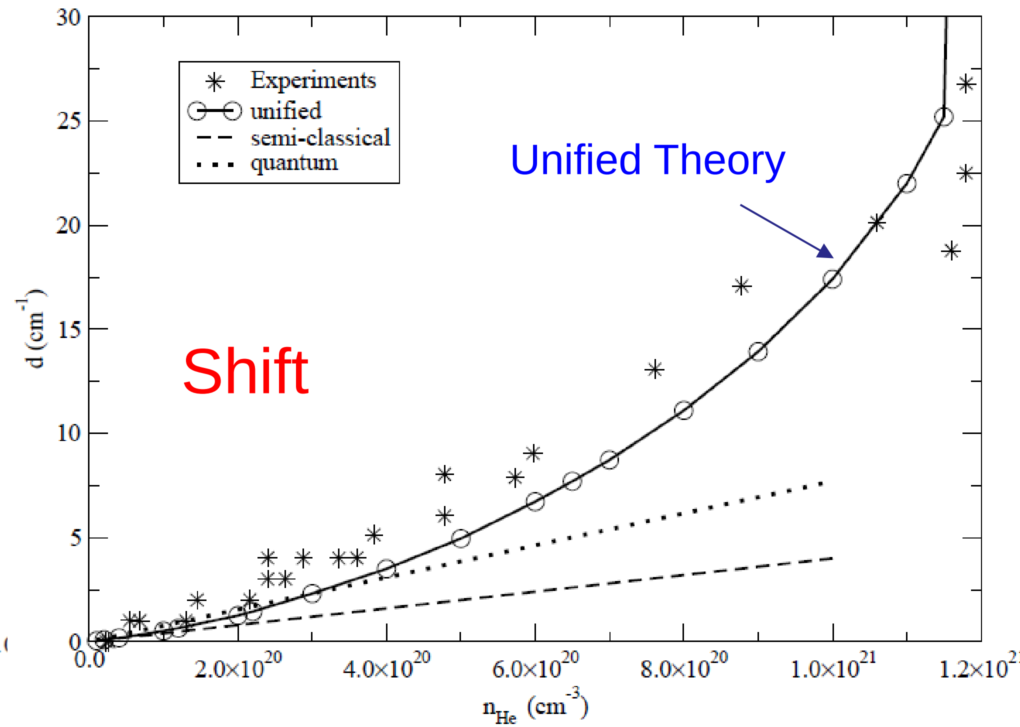
Results for He line 706 nm (^3S-^3P) at 300 K

Neutral Perturbers Density : N_{He}

300 K (P)
706 nm

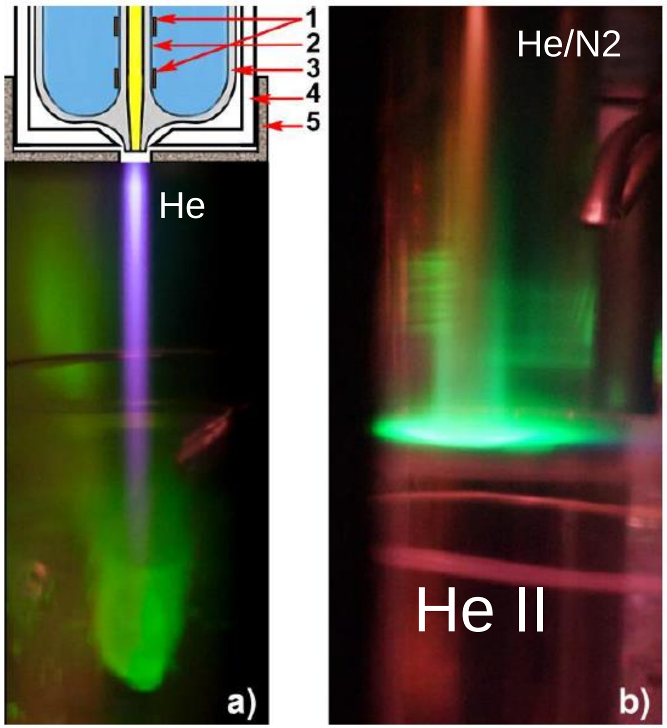
Comparison between experiment and theory

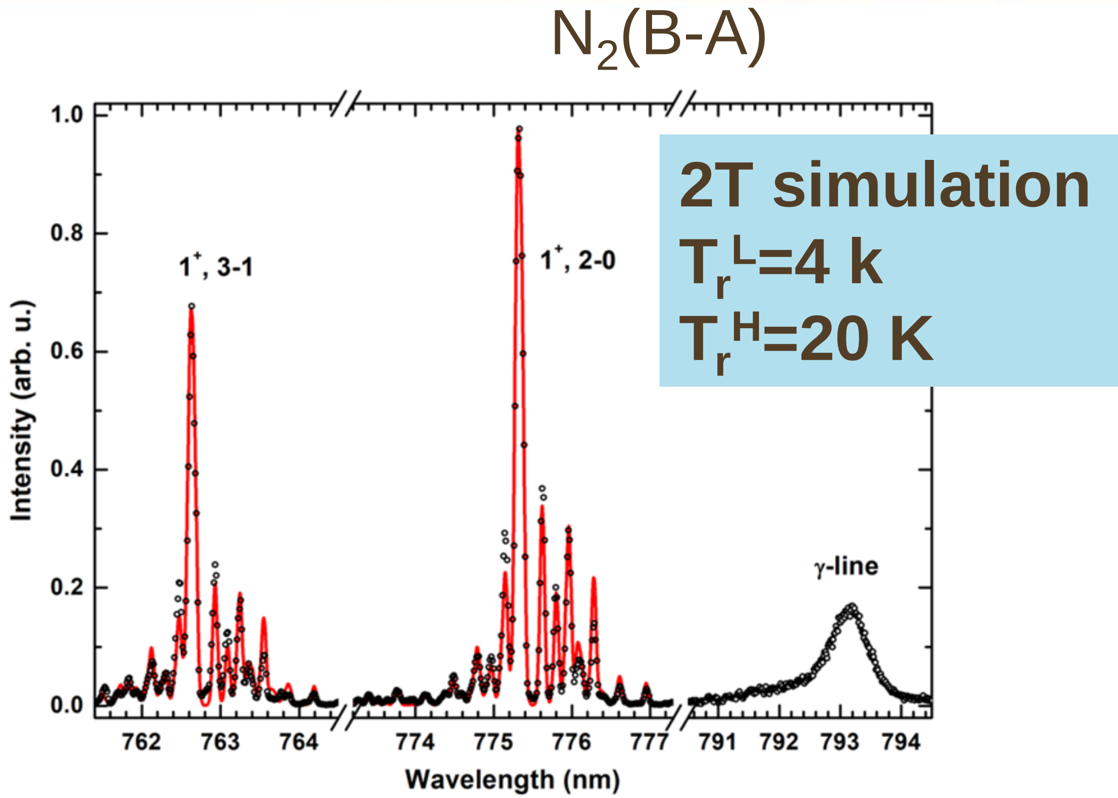




Discrepancy observed at high pressures

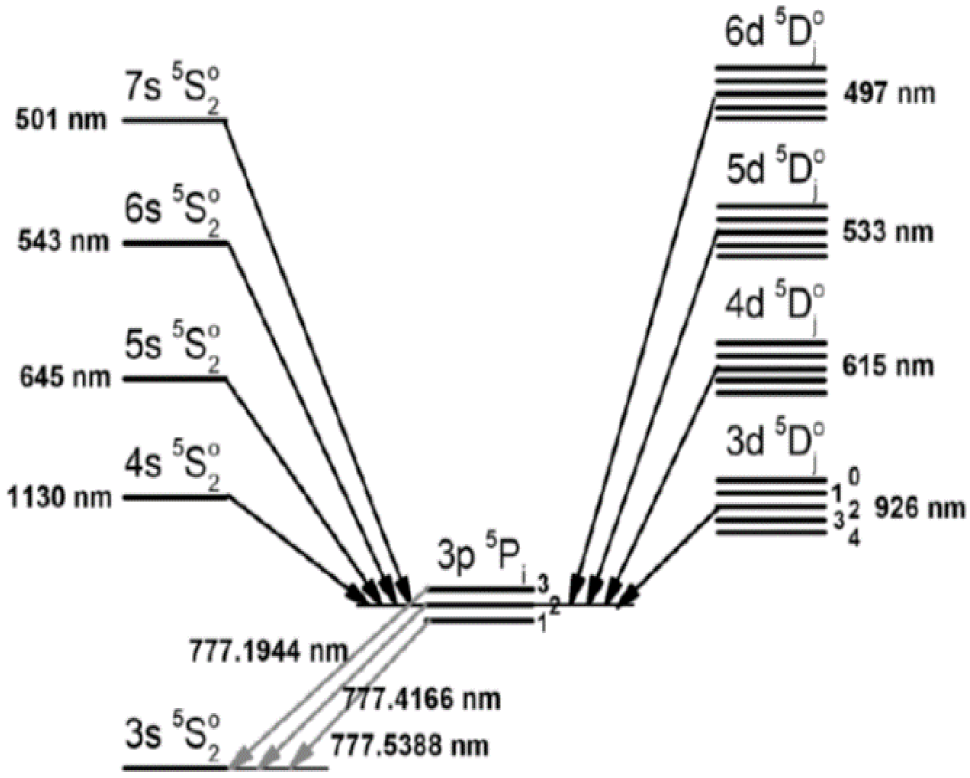
Cold helium jet excited by electrical discharges

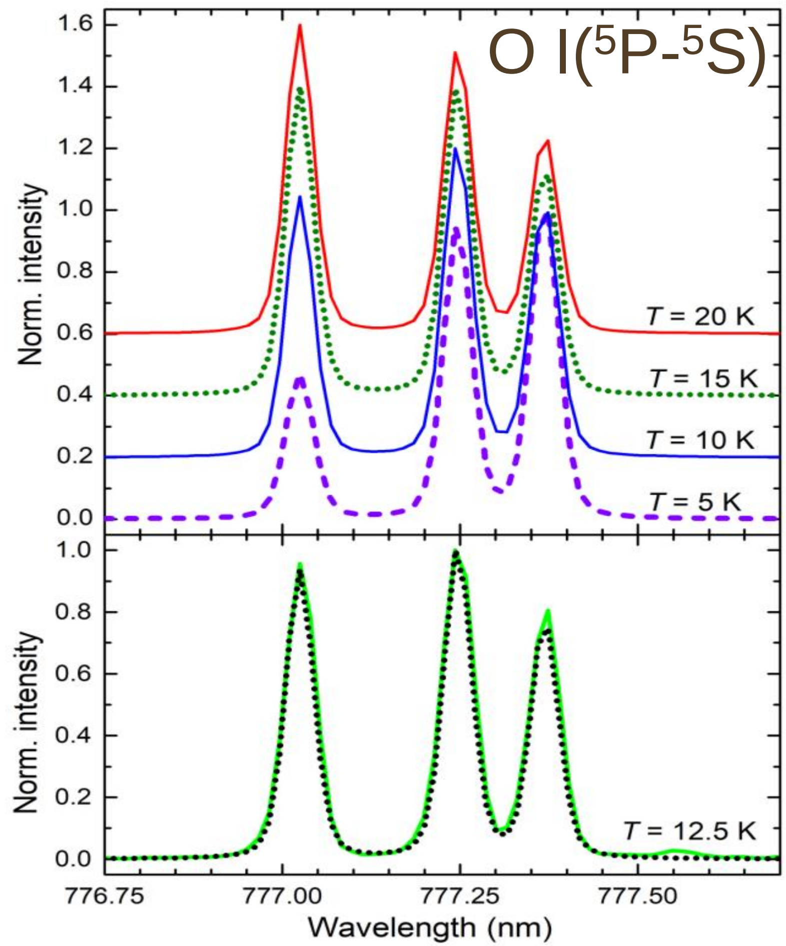




$$[N_J] \propto (2J+1)\left[\exp\left(-\frac{E_J}{kT_r^L}\right) + R\left(\frac{T_r^L}{T_r^H}\right)\exp\left(-\frac{E_J}{kT_r^H}\right)\right]$$

Cold helium jet excited by electrical discharges





Cold helium jet excited by electrical discharges

gas	probe	top	middle	bottom
pure He	O atom			12.5
$[N_2]/[He] = 1/10000$	O atom	70	36	23
	$N_2(1^+, 2\text{-}0)$ PGOPHER	42±10.5	30±7.5	18±4.5
	$N_2(1^+, 2\text{-}0)$ 2-T*	20-100	18-70	8-70
$[N_2]/[He] = 1/400$	$N_2(1^+, 2\text{-}0)$ 2-T			4-20
	$N_2(1^+, 2\text{-}0)$ PGOPHER			13.2±2
	$N_2(1^+, 3\text{-}1)$ 2-T			4-25
	$N_2(1^+, 3\text{-}1)$ PGOPHER			14±2.1
$[N_2]/[He] = 1/200$	$N_2(IRA, 8\text{-}3)$ PGOPHER		33±6.6	10.5±2.1
	$N_2(1^+, 2\text{-}0)$ PGOPHER	67±6.7	39±3.9	13.6±1.4
	$N_2(1^+, 2\text{-}0)$ 2-T	30-120	14-60	5-20

R E Boltnev et al **Plasma Sources Sci. Technol.2021**

Conclusion

Interaction
Physical classification

Stark (*literature*)
Van der Waals ($-C_6/r^6$)
Resonant ($+-C_3/r^3$)

Potentiel ab initio
Code MOLPRO
http://www.molpro.net

Spectral line Profile

Classical theory

- Unified theory
- Impact approximation
- Quasitatic approximation

Quantum treatment

PIIM Marseille
Weizmann Institute of Science, Israel;
Vallaloid Spain

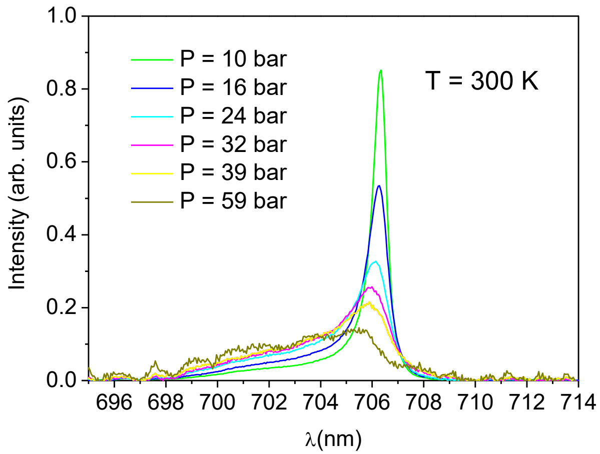
Spectral Line Shapes in Plasmas code comparison workshop

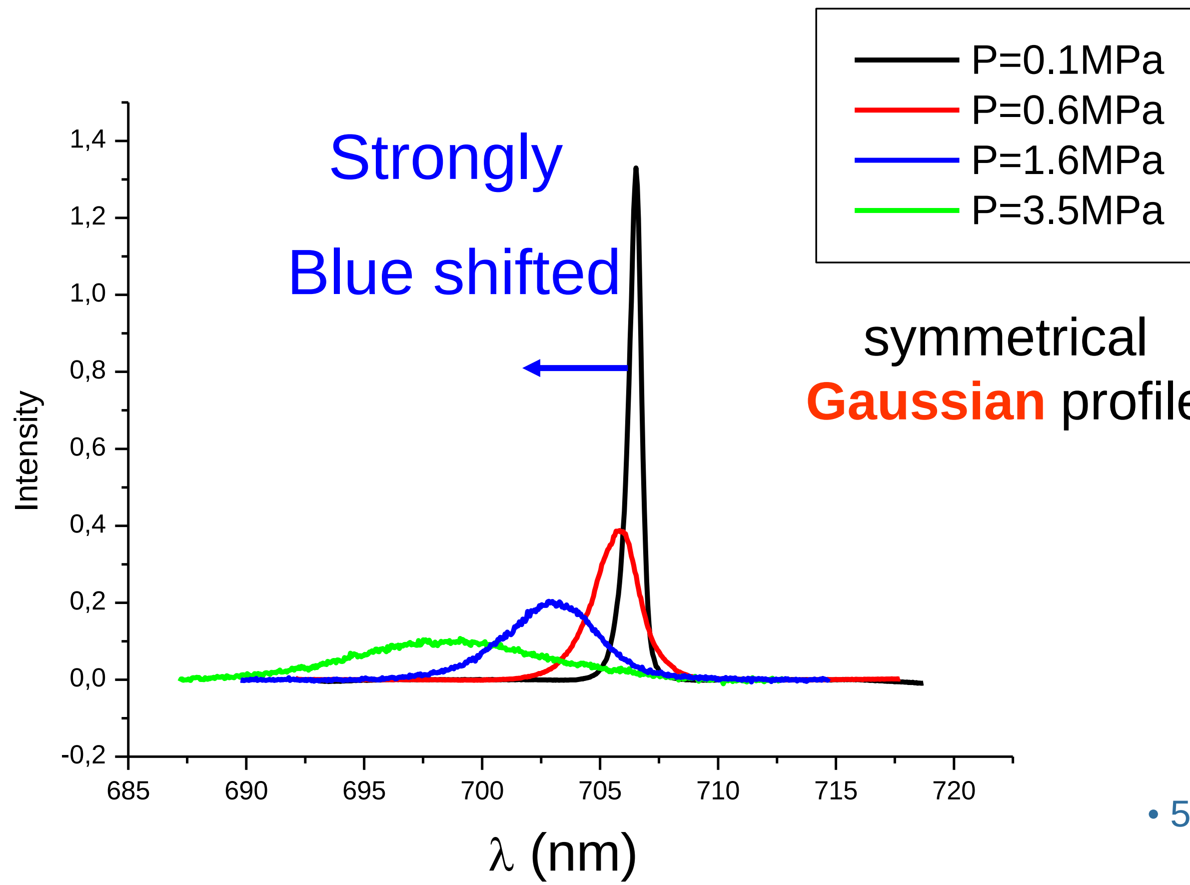
Thank you for your attention

Neutral Perturbers Density : N_{He}

4.2 K

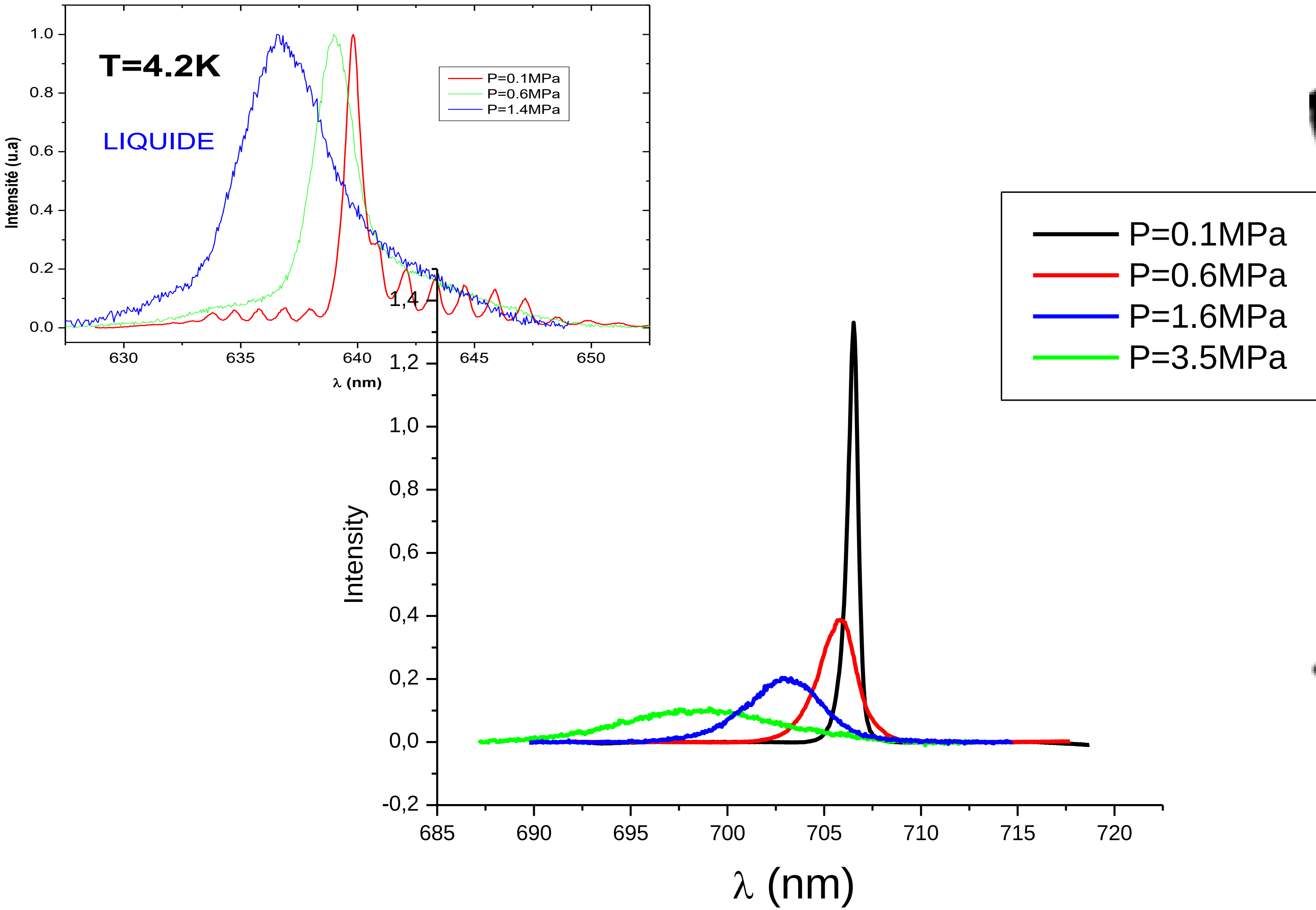
706 nm



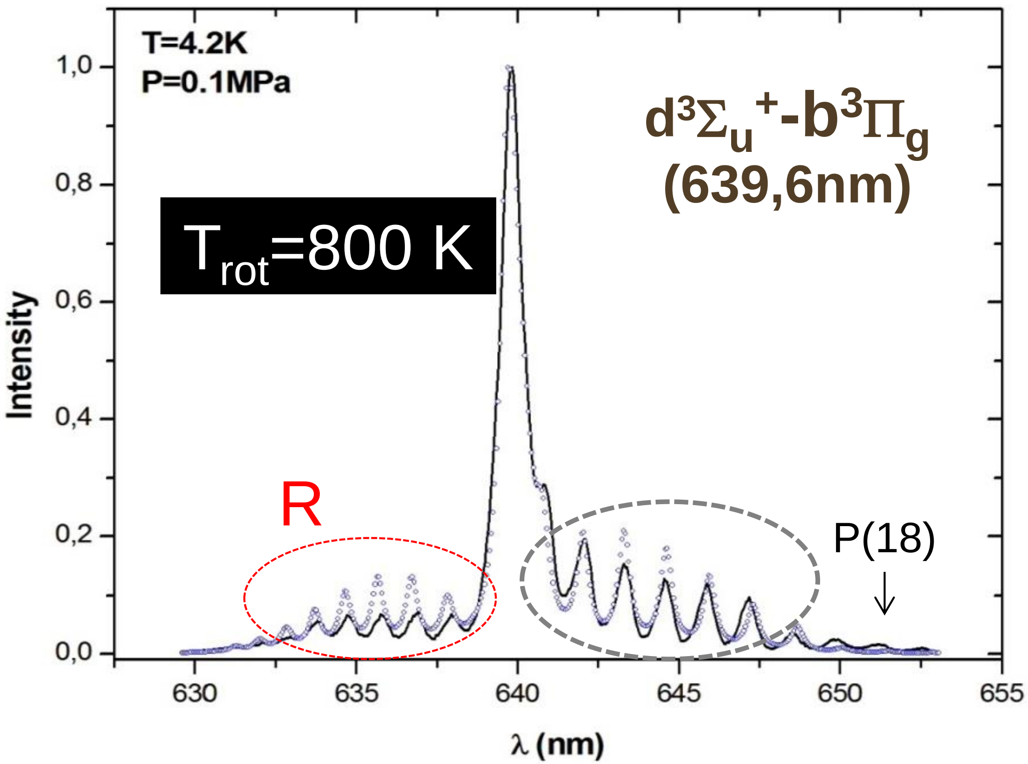


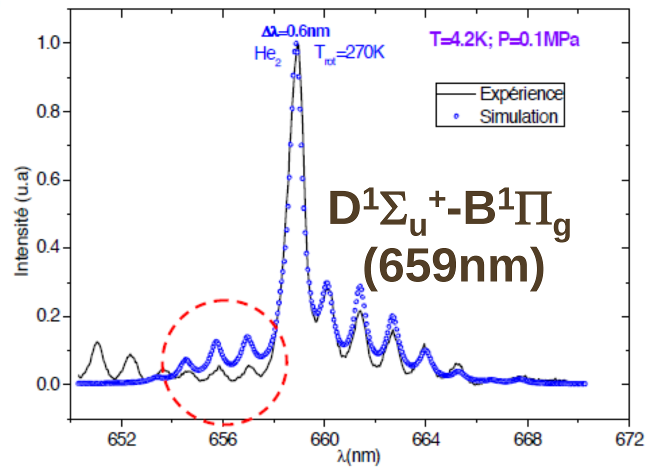
symmetrical
Gaussian profile

Interpretation ? 4.2 K

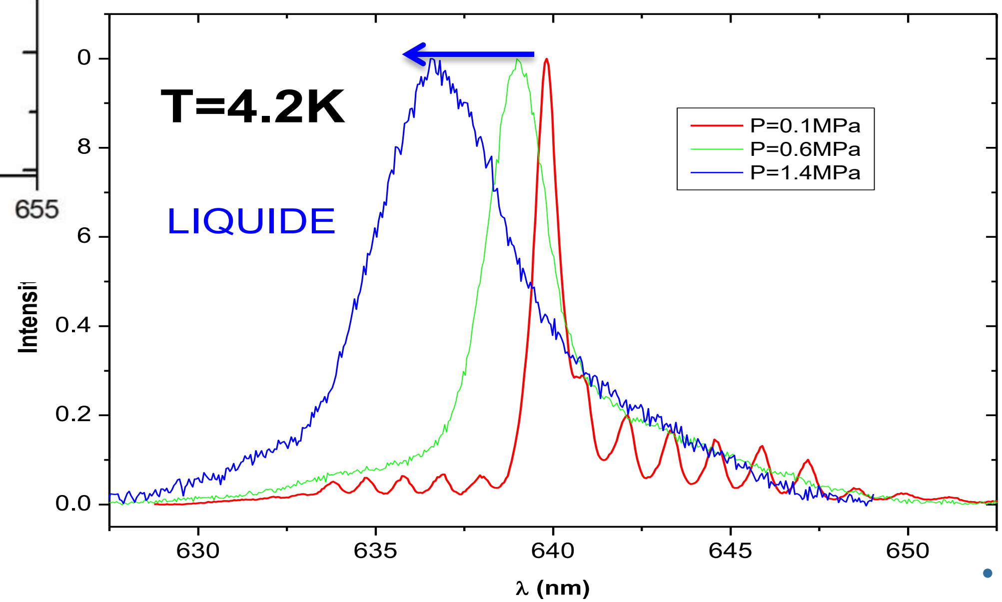


Temperature :
Rotational temperature measurements



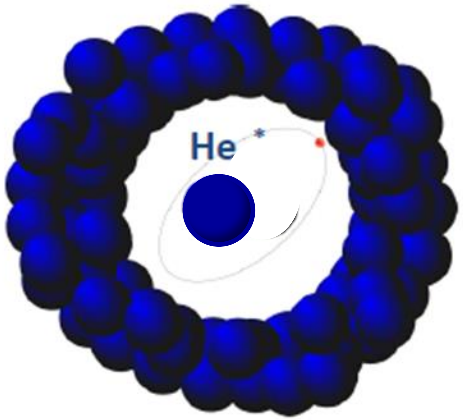


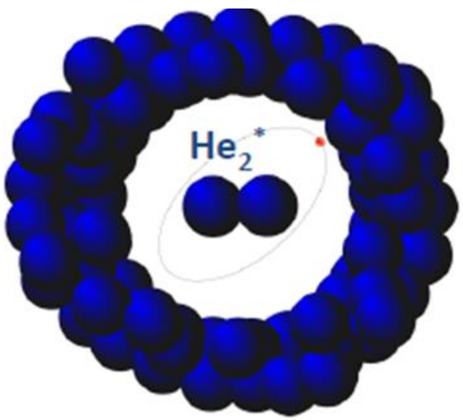
Strongly Blue Shifted



No boltzmann distribution
High degree of rotational excitation

He* He_2* Rydberg electron





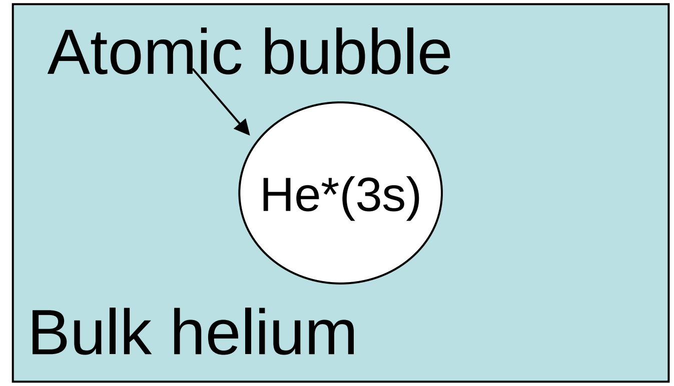
Interpretation:

Microscopic void around the He*3s and He_2*3d

?

Repulsion between Rydberg e^- and surrounding atoms in the ground state forms bubble

New autocorrelation function with « bath » interaction



$$\Phi(\tau) = \exp\left(-\int \left(1 - e^{-i\Delta V_{fi}(r)t/\hbar} \right) \rho_i(r) d^3 r \right)$$

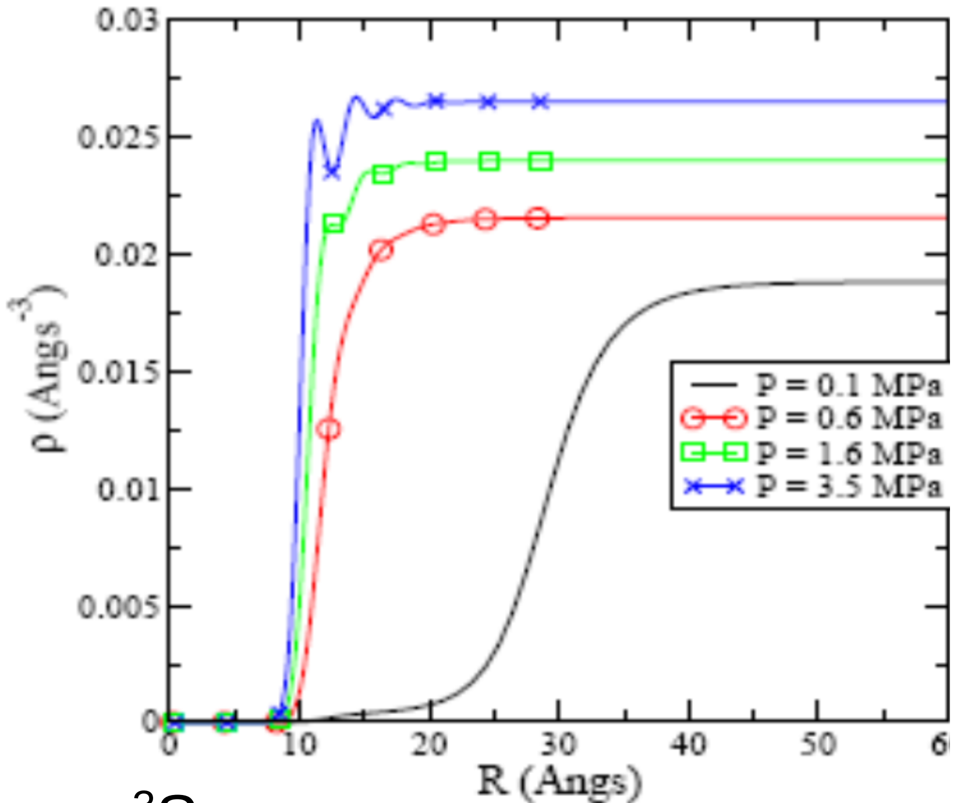
Difference pair potential between the states corresponding to the emission line

Liquid density in the electronic ground state around 3s calculated using Bosonic Density Functional Theory DFT

Molpro code

Liquid density around He*(3s^{3}S)

Liquid density around 3s^{3}S calculated using DFT



35 bar Phys. Rev. A 85 042706 (2012).

1 bar

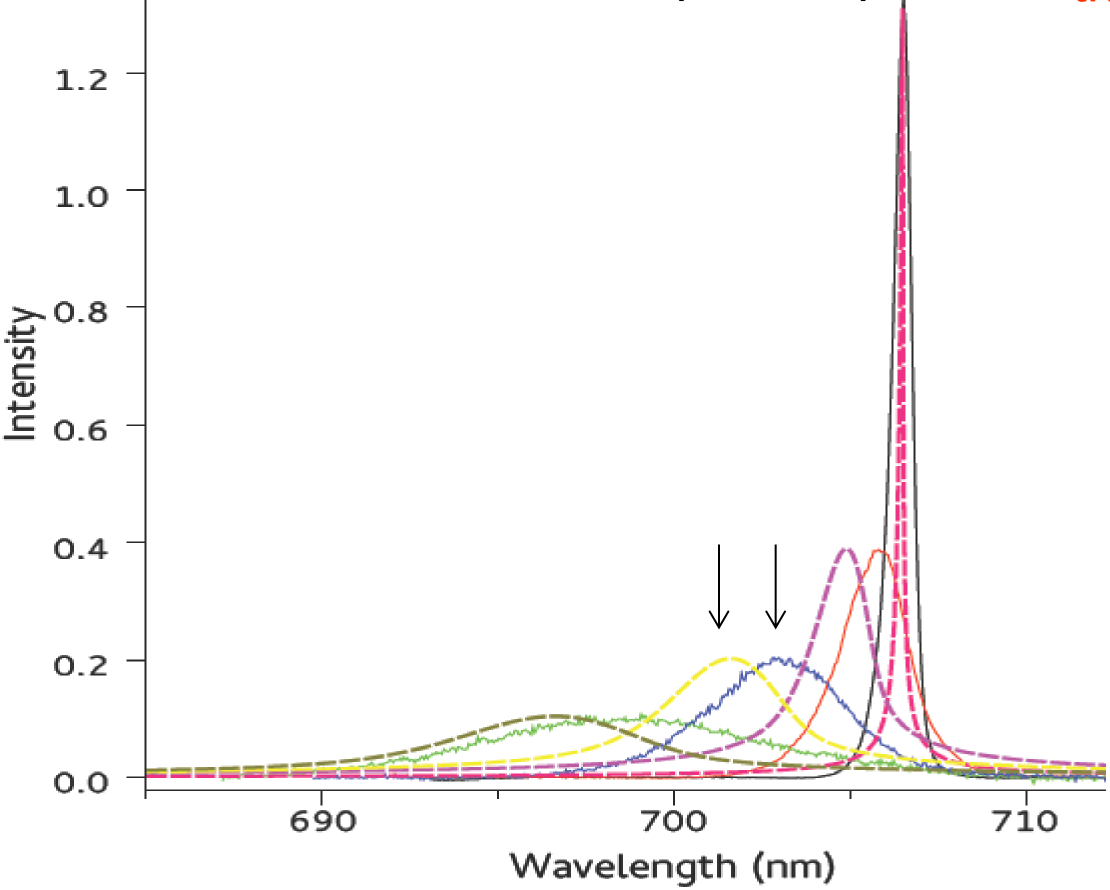
Bubble Radius (R_b) depends on applied pressure (**P**).

^{3}S

Empty cavity around excited atom (emitter)

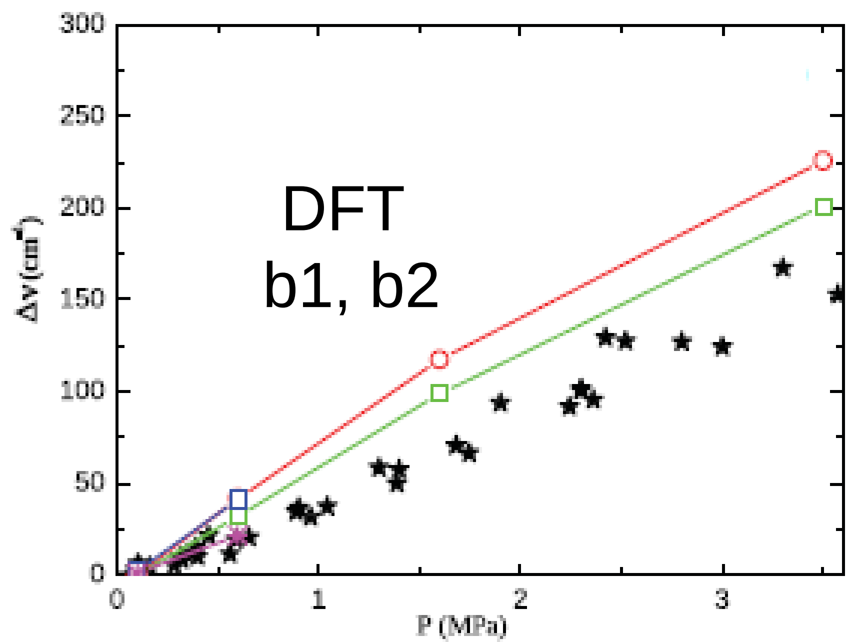
706.5 nm He* line (^3S-^3P)

Experimental (continuous) vs theoretical (dashed)



the line position is extremely sensitive to the He*(3s) - He pair potential

Line shift



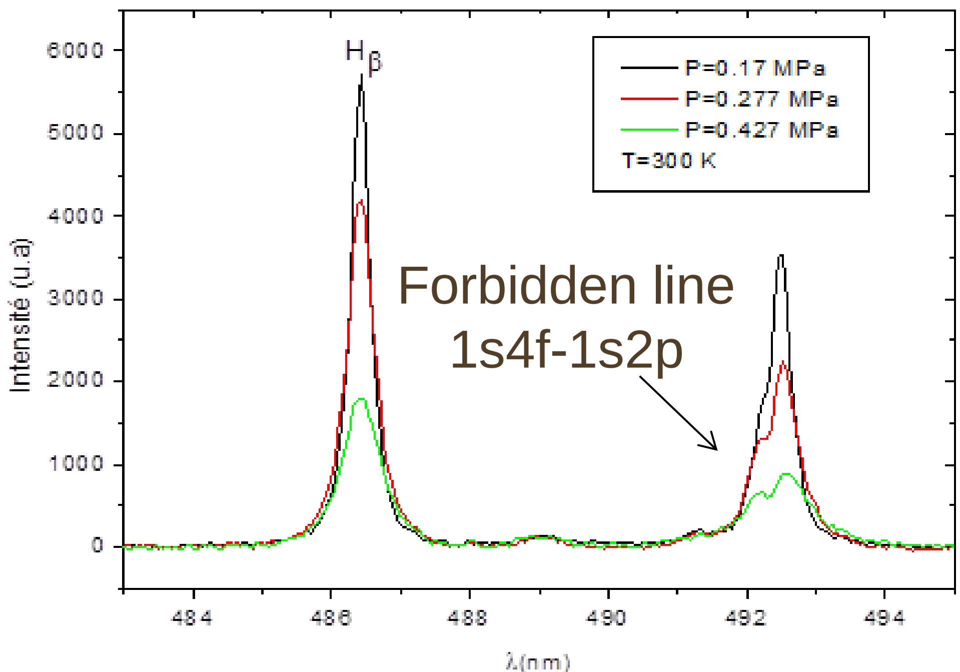
Electron number density : N_e

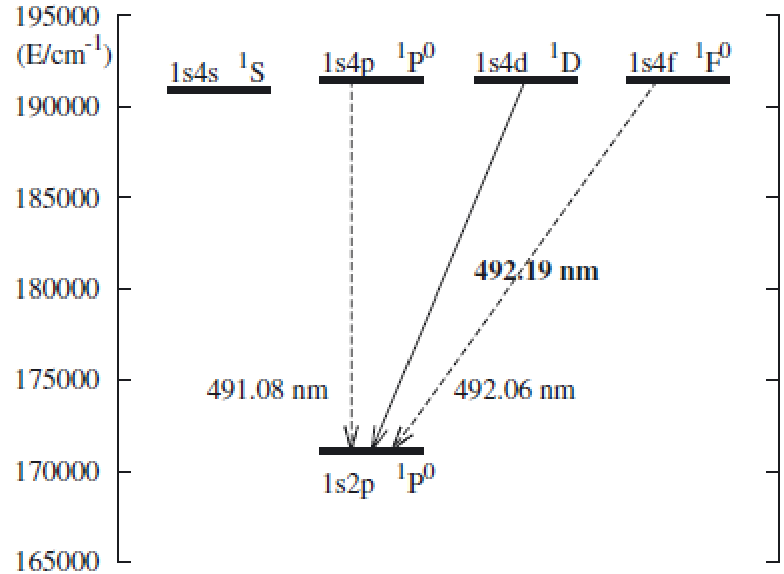
300 K (P) — 150 K — 11 K — 4.2 K(P)

- Hα : 656 nm
- Hβ : 486 nm
- He I : 492 nm

He 492 nm

300 K





Historical development

Impact approximation Phase shift

Weisskopf (1932), Lindholm (1941), Foley (1946)

$$\omega(t) = \omega_0 + \frac{d\eta}{dt}$$

Quasistatic approximation

Holtsmark (1919), Kuhn and Margenau (1937),

$$\omega = \omega_0 + \frac{\Delta V(r)}{\mathrm{h}}$$

Line shape formalism based on the Fourier transform of the autocorrelation function

$$P(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^{+\infty}\phi(\tau)\exp[i\omega\tau]d\tau \qquad \phi(\tau) = \int_{-\infty}^{+\infty} e^{i(\eta(t)-\eta(t-\tau))}dt$$

Autocorrelation function (wave train)

Voigt profile

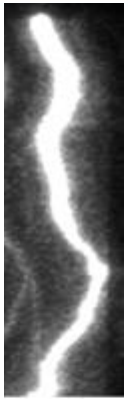
The width of the Voigt profile $\Delta\lambda_V$ is approximated by equation where $\Delta\lambda_G$ and $\Delta\lambda_L$ are the Gaussian and Lorentzian FWHMs, respectively

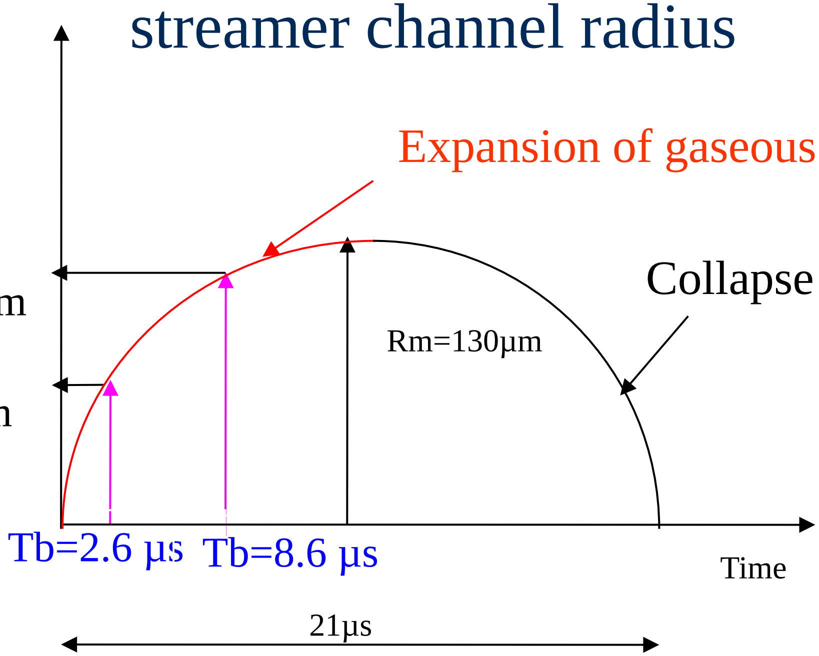
$$\Delta\lambda_V \approx \frac{\Delta\lambda_L}{2} + \sqrt{\frac{\Delta\lambda_L^2}{4} + \Delta\lambda_G^2}$$

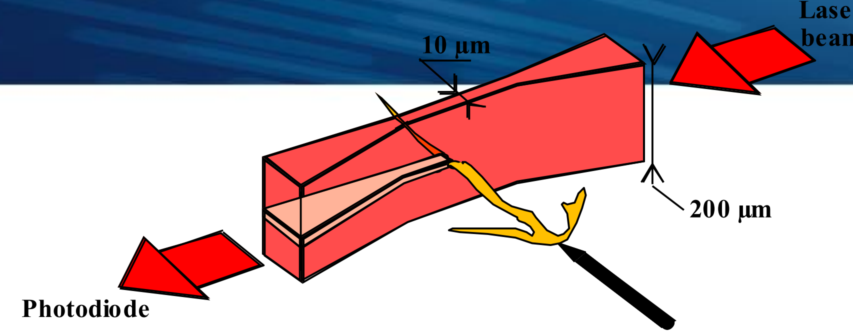
Positive filamentary streamers in liquid nitrogen

Re-illumination

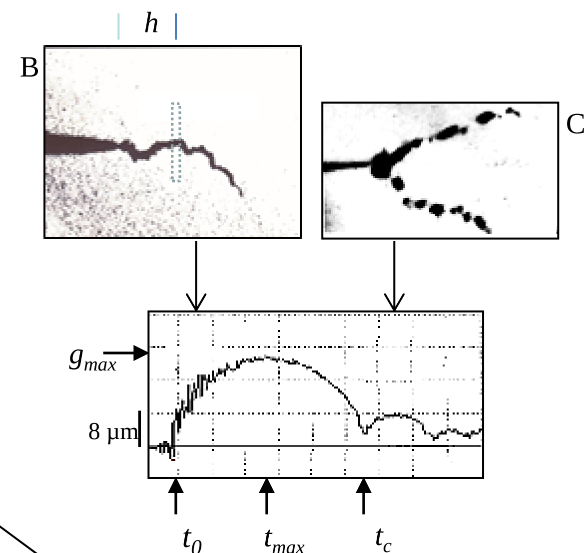
N_g (2.6µs) > N_g (8.6µs) ?







P Gournay and O Lesaint 1994

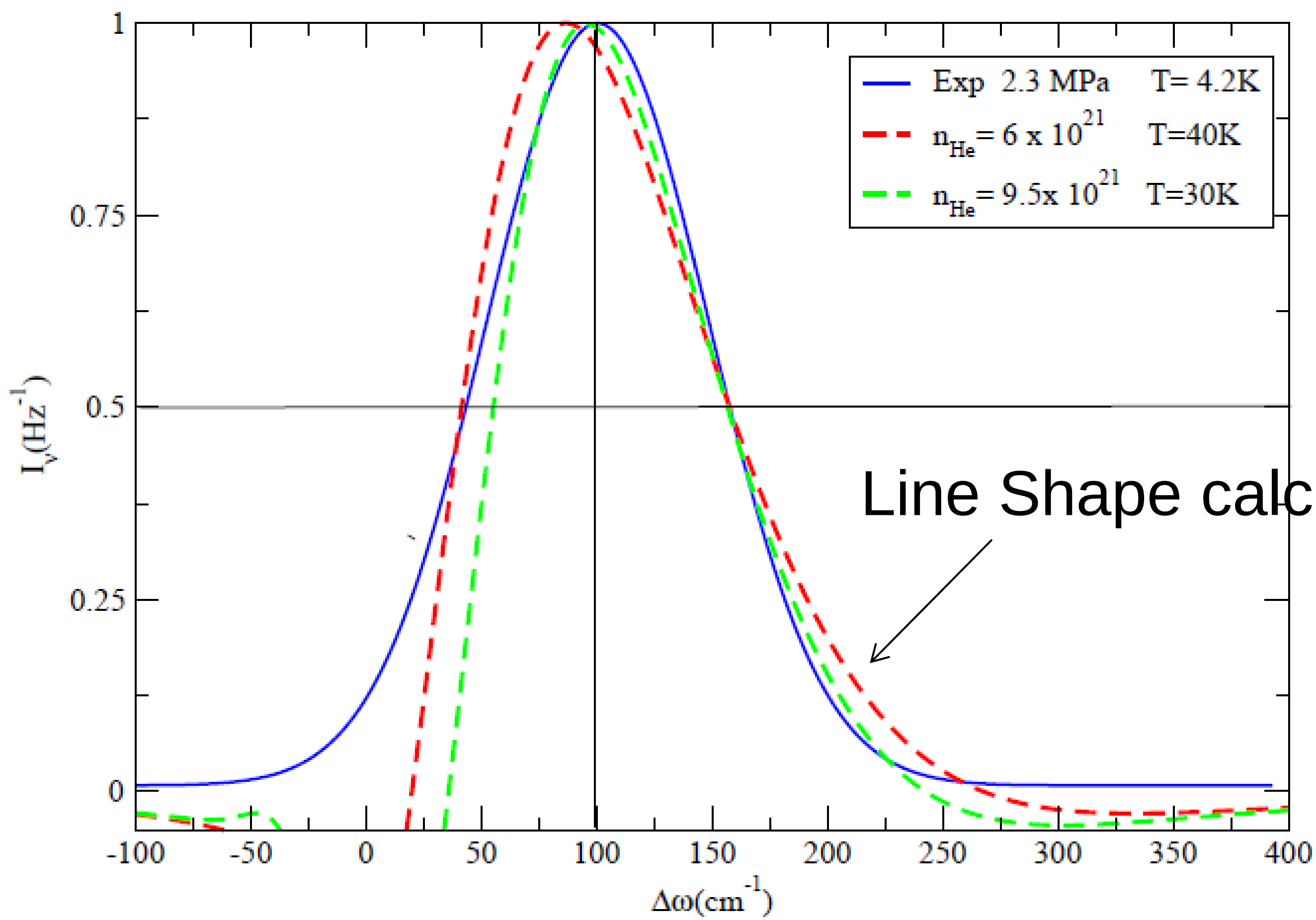


T_b ↗ The plasma column has expanded N_g ↘

Neutral Perturbers Density : N_{He}

Unified semiclassical theory

4. 2 K
706 nm



Line Shape calculations

Allard, N. F. 2012, J. Phys. Conf. Ser., 397, 012065