This set of slides consists of a collection of short presentations on different topics, all related to plasma diagnostics. During my presentation I will use the first 'introductory' presentation as a guideline. I will discuss some diagnostics in more detail, and make a selection of the applications of diagnostics, depending on the audience.

PLASMA & MATERIALS PROCESSING

Plasma Diagnostics

- how to study molecule formation in plasma ? -

Richard Engeln

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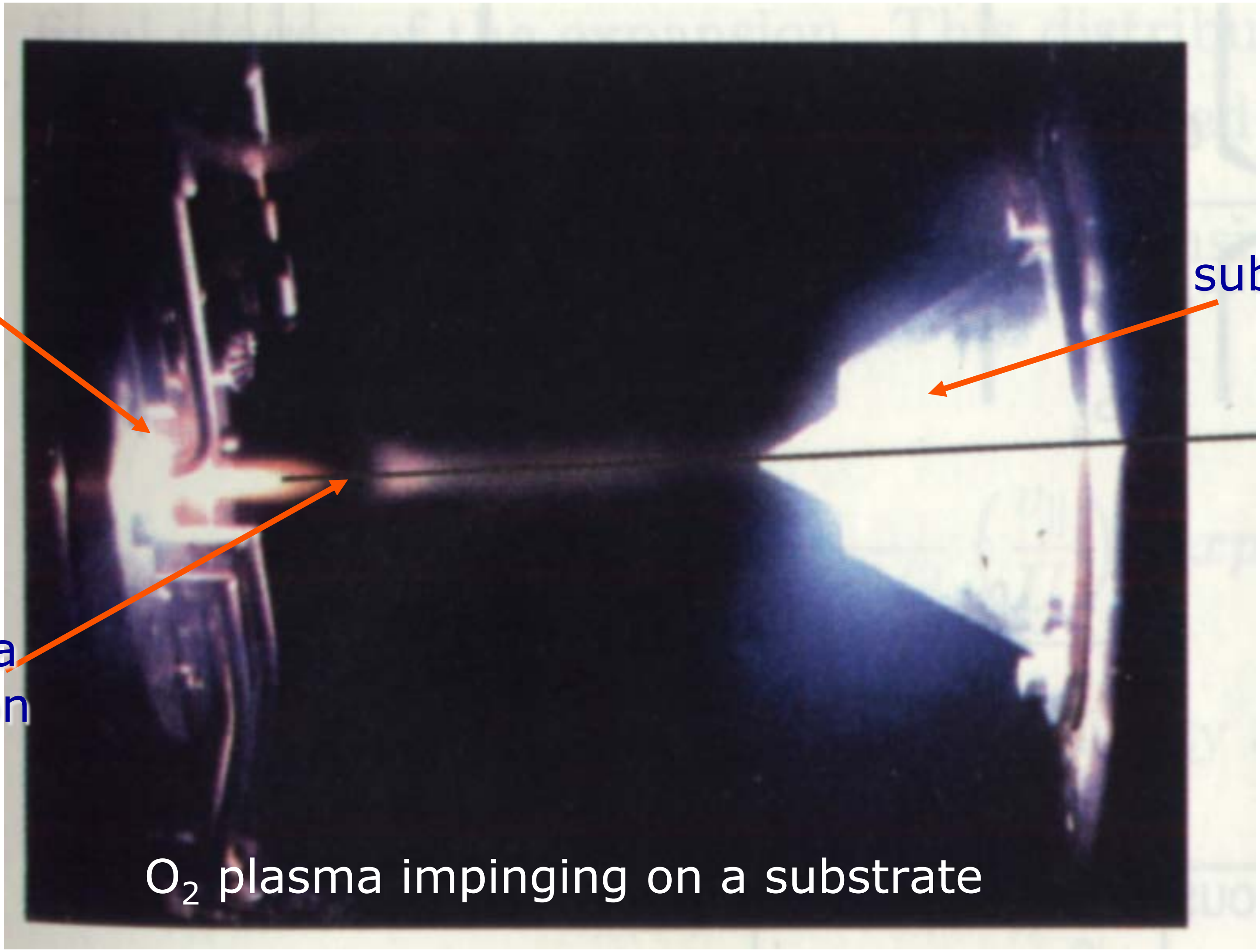
Where innovation starts

" your working gas mixture $\neq$ input gas mixture"

(at high dissociation degree)

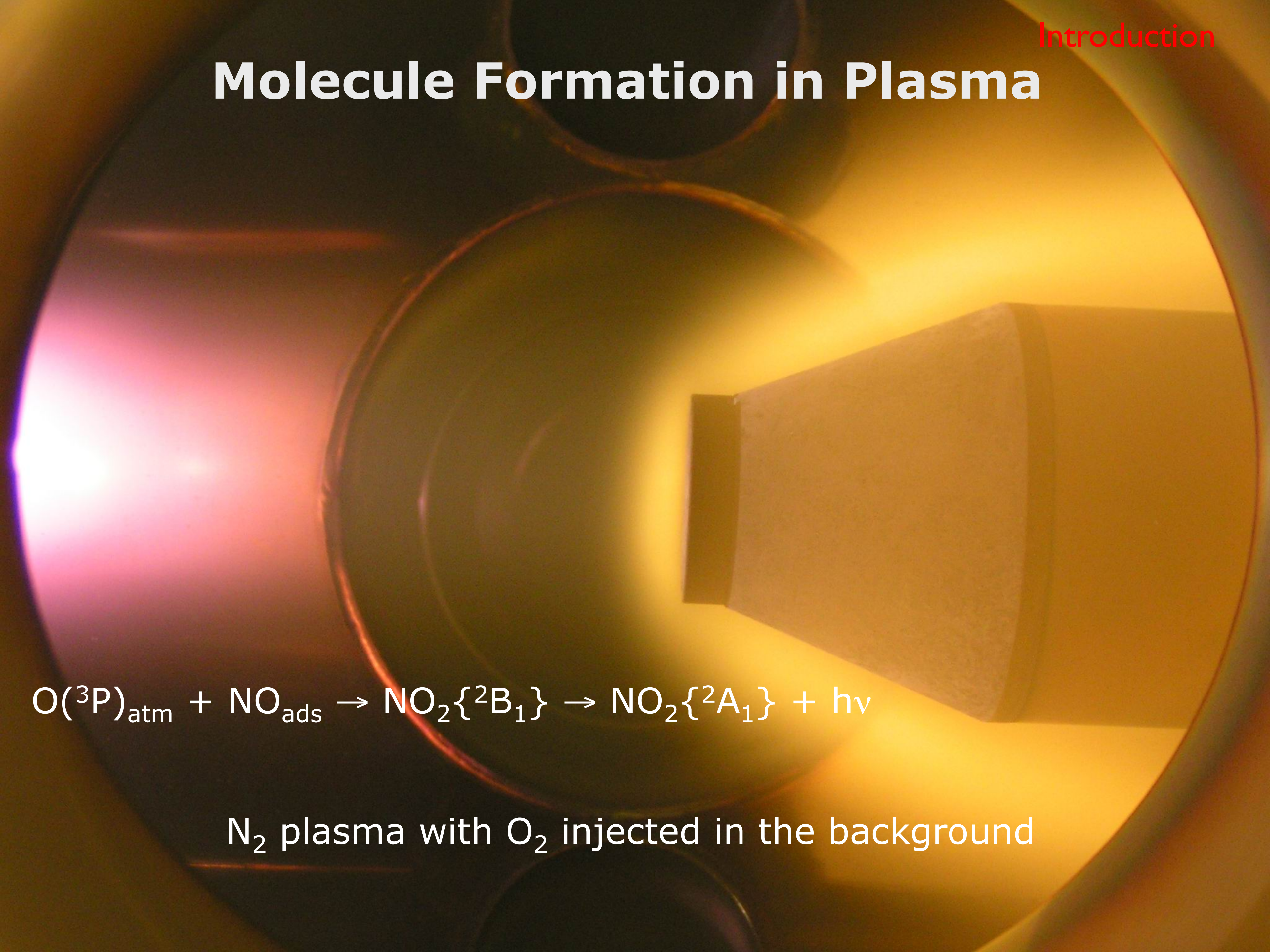
quote from Prof. J. Winter during his lecture during
the 2005 Summer School on
Low Temperature Plasma Physics: Basics and Applications

Molecule Formation in Plasma



taken from: A. Lebéhot *et al.* in ‘Atomic and Molecular Beams’, ed. R. Campargue

Molecule Formation in Plasma



$$O(^3P)_{atm} + NO_{ads} \rightarrow NO_2\{^2B_1\} \rightarrow NO_2\{^2A_1\} + h\nu$$

N_2 plasma with O_2 injected in the background

Molecule Formation in Plasma

VOLUME 60, NUMBER 4 PHYSICAL REVIEW LETTERS 25 JANUARY 1988

Vibrational Excitation of Hydrogen via Recombinative Desorption of Atomic Hydrogen Gas on a Metal Surface

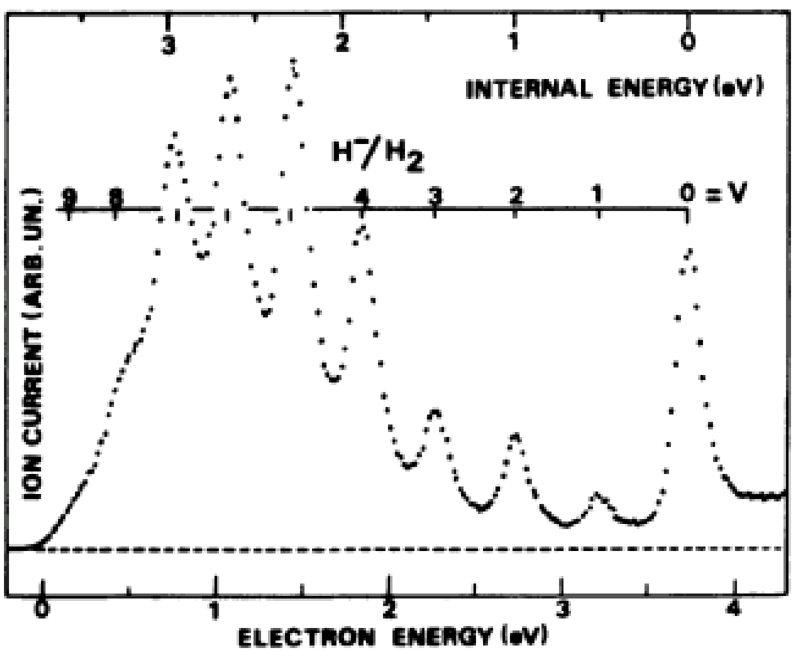
R. I. Hall, I. Čadež,[a] M. Landau, F. Pichou, and C. Schermann

Groupe de Spectroscopie par Impact Electronique et Ionique, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

(Received 20 July 1987)

Recombinative desorption of atomic hydrogen on the walls of a gas cell has been observed to populate vibrational levels up to $v = 9$. The vibrational populations follow a Boltzmann distribution near 3000 K up to $v = 3$ and for higher levels the populations are well in excess of this temperature. These observations bring to light a new mechanism for vibrational excitation of H_2 in volume H^--ion sources.

PACS numbers: 79.20.Nc, 34.80.Gs, 52.40.Hf



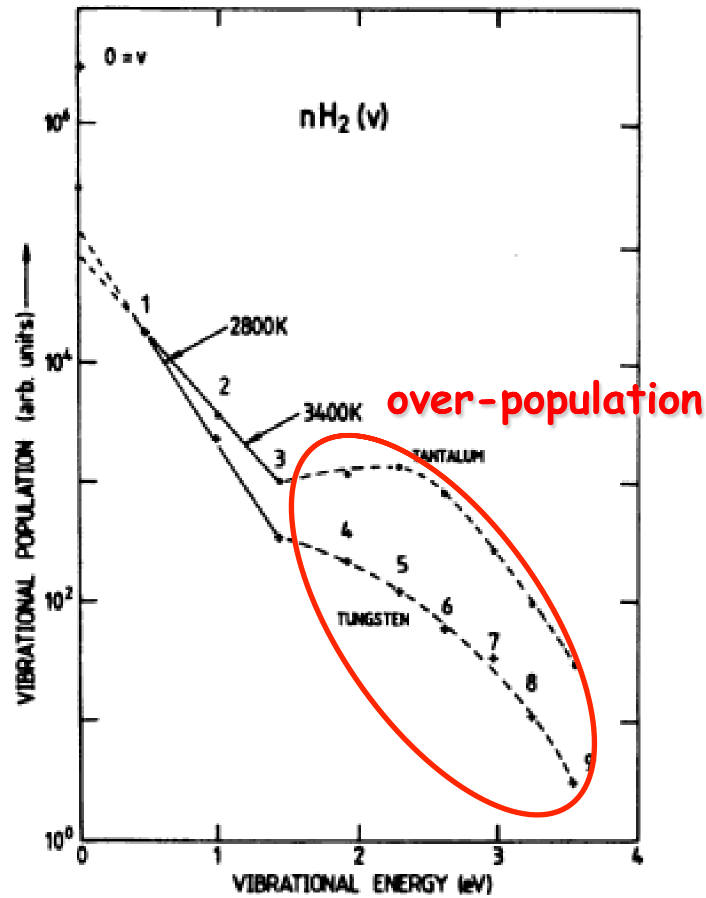


FIG. 3. Vibrational populations against vibrational energy on a semilog scale for tungsten and tantalum filaments.

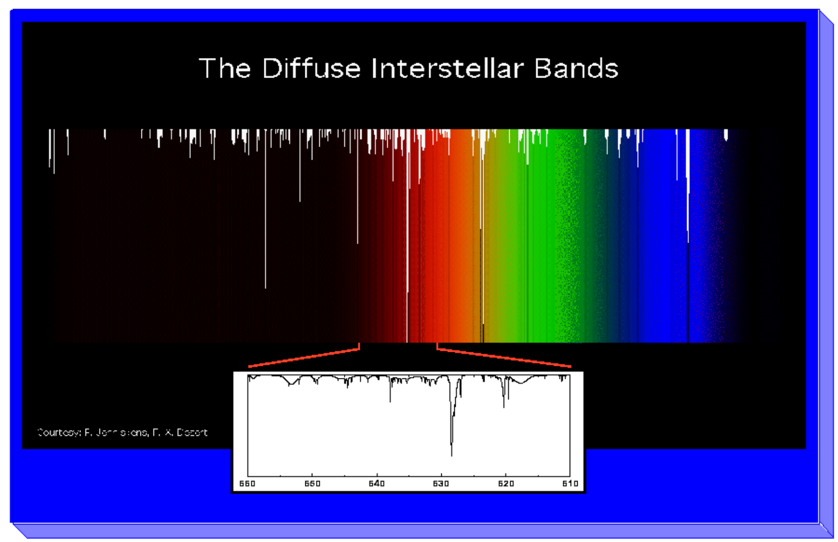
$H_2^{r,v}$ detection via QMS detection of H^-

$H_2 + e \rightarrow H^- + H$

Molecule Formation in Plasma

Diffuse (translucent) clouds

- ✓ 40-100 K / 100 part./cm^3
- ✓ Unknown absorption features



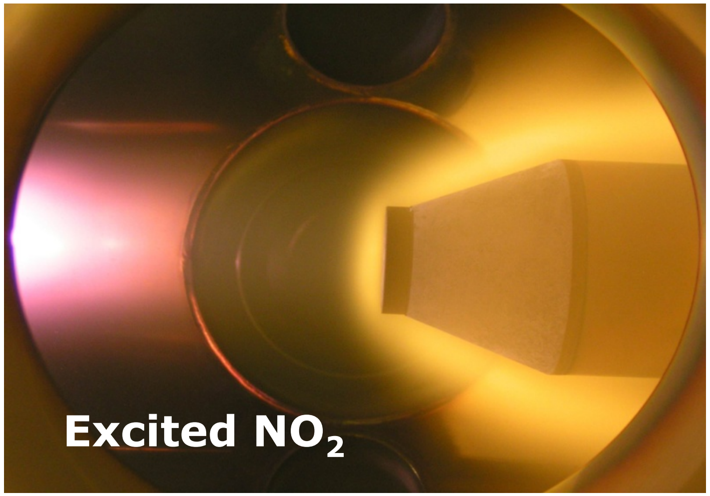
Dark (dense) clouds

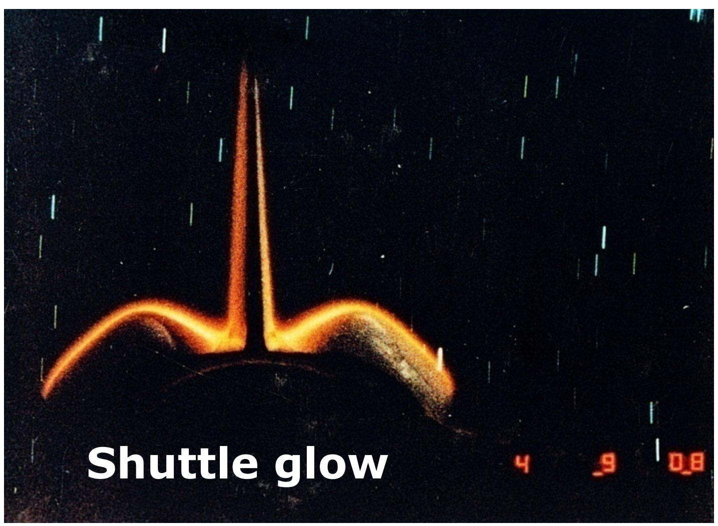
- ✓ 10-30 K / 10^4-10^8 part./cm^3
- ✓ Universal molecule factory

(from: H. Linnartz, CRD meeting (2004))

Questions when studying molecule formation in plasma ?

(when in contact with a surface)

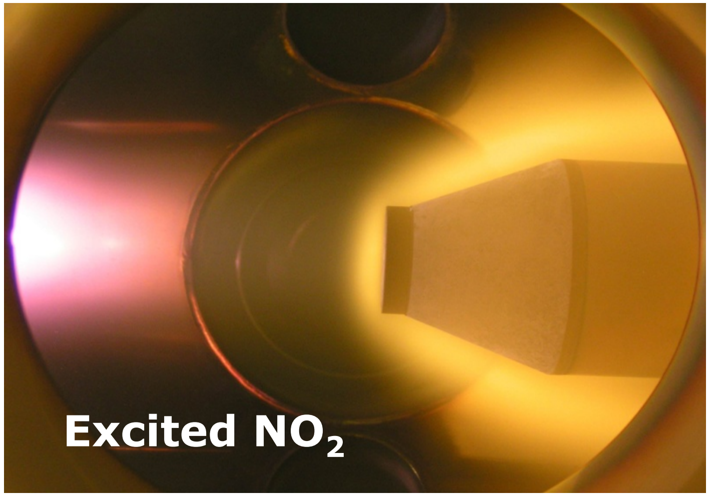


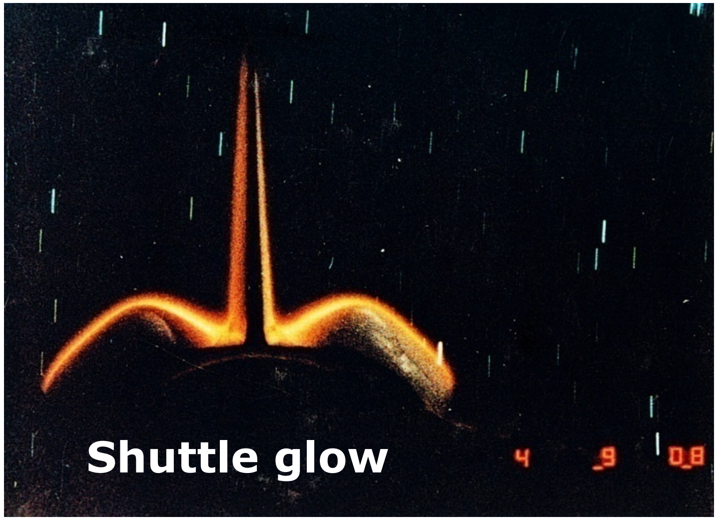


- What particles are arriving at the surface ?
- In which state are the particles arriving ?
- New molecules are generated:
  - electronically and/or ro-vibrationally excited ?
  - substrate material and temperature dependence ?
- Is there flux dependence on the generation process ?

Questions when studying molecule formation in plasma ?

(when in contact with a surface)





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What is needed to answer these questions ?

Gas-phase optical diagnostics for the detection of stable molecules and atomic/molecular radicals

- (VUV) Laser Induced Fluorescence

    - relative densities, + spatial resolution

- Fourier Transform IR/UV absorption

    - line of sight, + absolute densities, + large λ-range (overview spectrum)

- (Cavity Ring Down) absorption

    - line of sight, + (very) high sensitivity

- (spontaneous) Raman spectroscopy

    - ‘low’ sensitivity, + every molecule Raman active, + spatial resolution

Plasma Diagnostics (optical)

Optical diagnostic	Parameters	Examples
Doppler LIF	w, T, n	Ar-metastable
Two-photon LIF	w, T, n	H atom
VUV LIF	n(v,J), T	$H_2^{r,v}$
IR absorption	n(v,J), T	NO, N_2O, NO_2
Cavity Ring Down absorption	n(v,J), T	NH, NH_2, NH_3

All diagnostics are complimentary

Literature

On diagnostics (general):

✓ H R Griem, *Plasma Spectroscopy* (McGraw-Hill Book Company, New York, 1964)

✓ W Demtröder, *Laser Spectroscopy,Basic Concepts and Instrumentation* edited by F P Schäfer (Springer-Verlag, Berlin, Heidelberg, New York, 1981)

✓ K Muraoka, K Uchino, M D Bowden, Plasma Physics and Controlled Fusion **40**, 1221 (1998)

✓ J-P E Taran, *CARS spectroscopy in Applied Laser Spectroscopy*, edited by W Demtröder and M Inguscio (Plenum, New York, 1990)

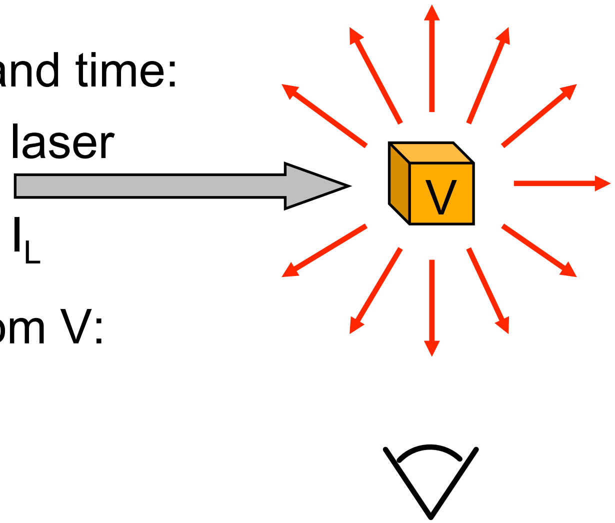
✓ G Berden, R Peeters, G Meijer, Int. Rev. Phys. Chem. **19**, 565 (2000)

✓ G. Berden and R. Engeln, *Cavity Ring-Down Spectroscopy, Techniques and Applications*, Blackwell Publishing Ltd, United Kingdown (2009)

Laser Induced Fluorescence spectroscopy

Laser Induced Fluorescence (LIF)

- number of laser photons n_a absorbed in unit volume and time:

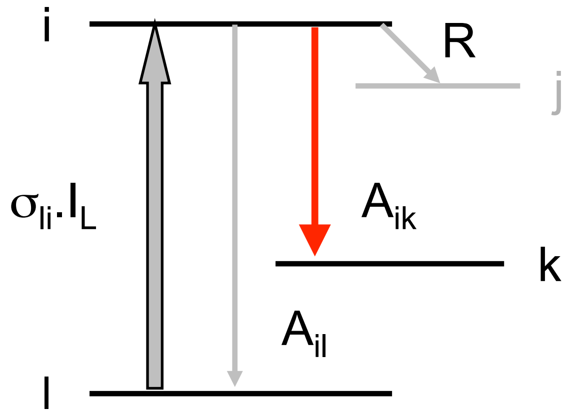


$$n_a = \sigma_{li}\, I_L\, n_l$$

- number of fluorescence photons $N_f\,(\lambda_{ik})$ originating from V:

$$N_f = n_a V q_f = \sigma_{li}\, I_L\, n_l V \cdot \frac{A_{ik}}{A_i + R}$$

- signal S_f:



$$S_f = N_f \cdot \Omega / 4\pi \cdot T \cdot q_{ph}(\lambda) \cdot G_{ph}$$

$$S_f \propto n_l$$

Advantages

- sensitive
- extra info from time behaviour
- experimentally straightforward
- possibility of 2D-imaging

Disadvantages

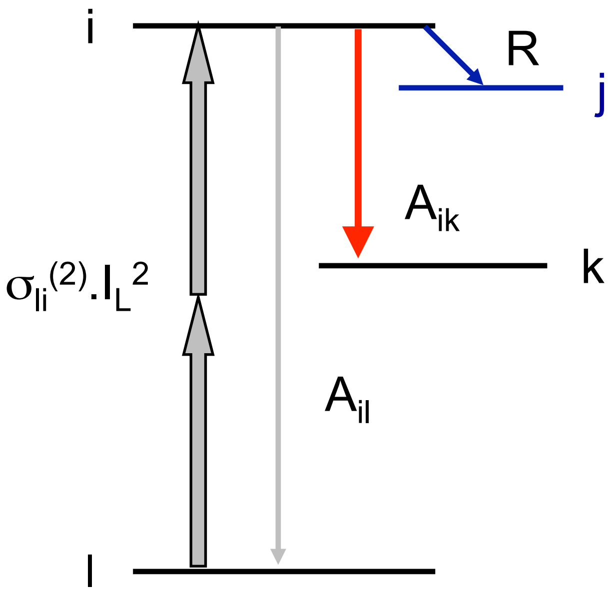
- not quantitative
- depending on gas composition (quenching)

How to detect the hydrogen atom

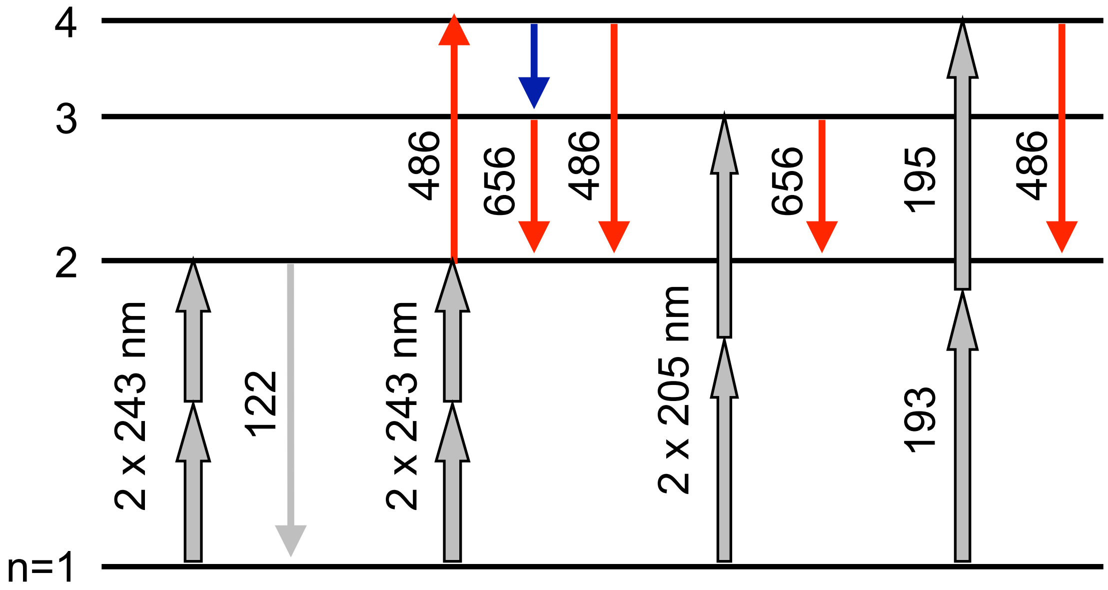
in the growth state with LIF ?

with LIF ?

2 photon LIF



H excitation schemes



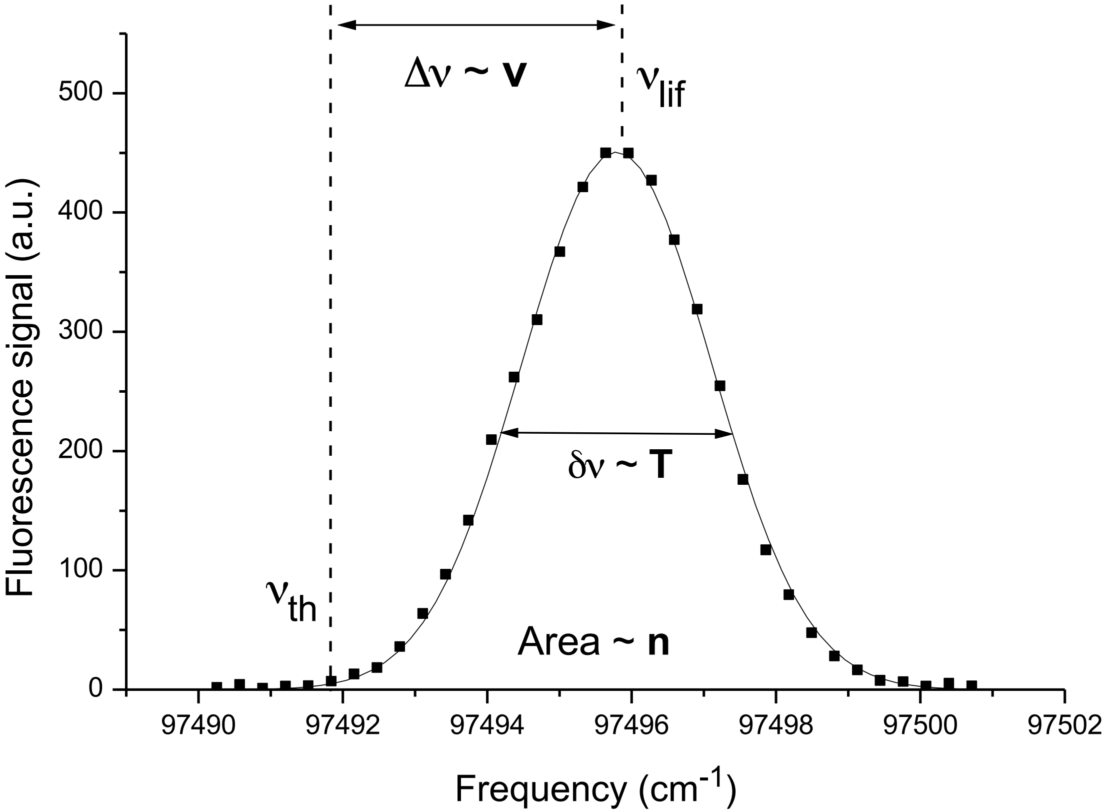
Advantages

- no demanding VUV-generation
- non-resonant fluorescence detection possible
- self-absorption can be avoided

Disadvantages

- low 2-photon cross sections require high laser intensities
- 2-photon cross sections often not known

Quantities deduced from LIF



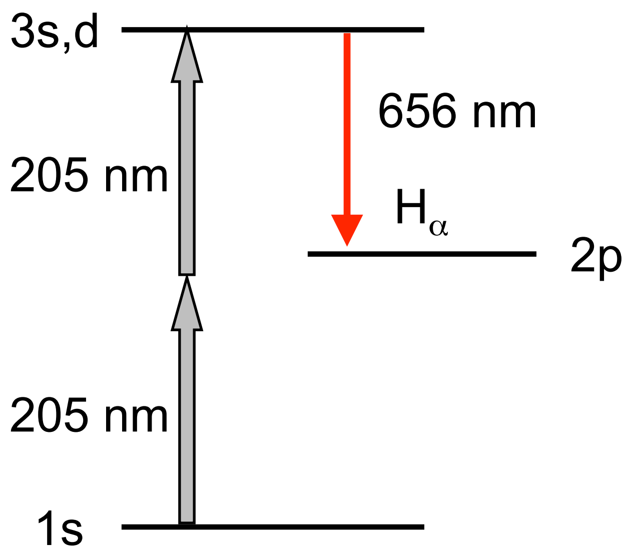
- integrated intensity: n
- Doppler width: T

$$\frac{\Delta \nu_D}{\nu} = \frac{1}{c}\sqrt{\frac{8\ln 2 \cdot kT}{M}}$$

- Doppler shift $\nu - \nu_0$: **v**

2 photon LIF on atoms

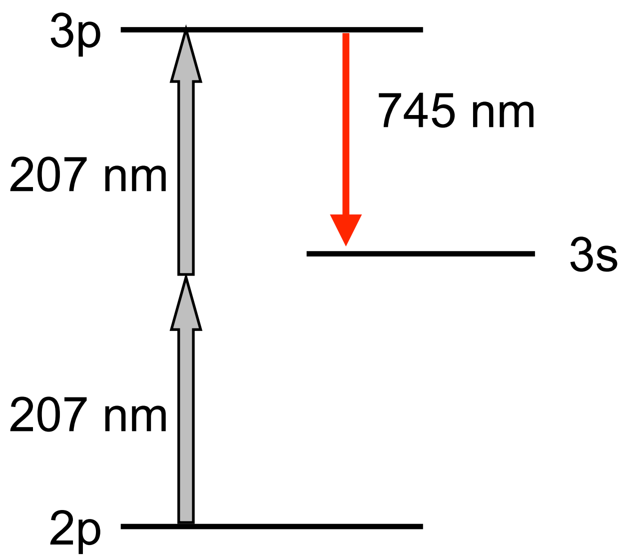
monitoring H



Applications:

- fast deposition of a-Si:H
- H-source
- surface passivation

monitoring N



Applications:

- deposition of a-C:N
- plasma etching (photo-resist)

450 *Molecular spectra*

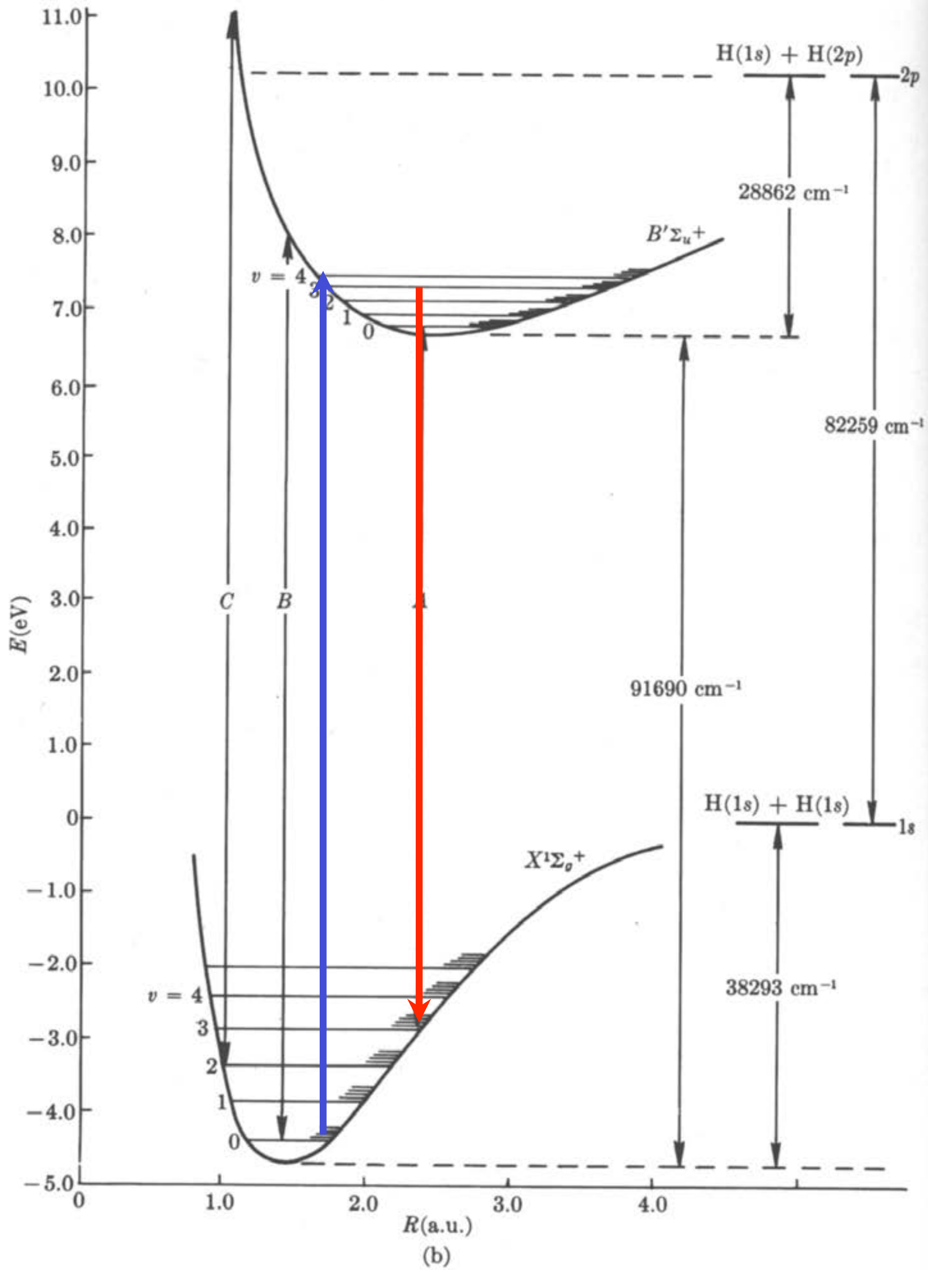


Fig. 7.2 (b). Vibration-rotation levels shown.,

(VUV) LIF on H_2 molecules

Excitation from H_2(X, v=0) to H_2(B)

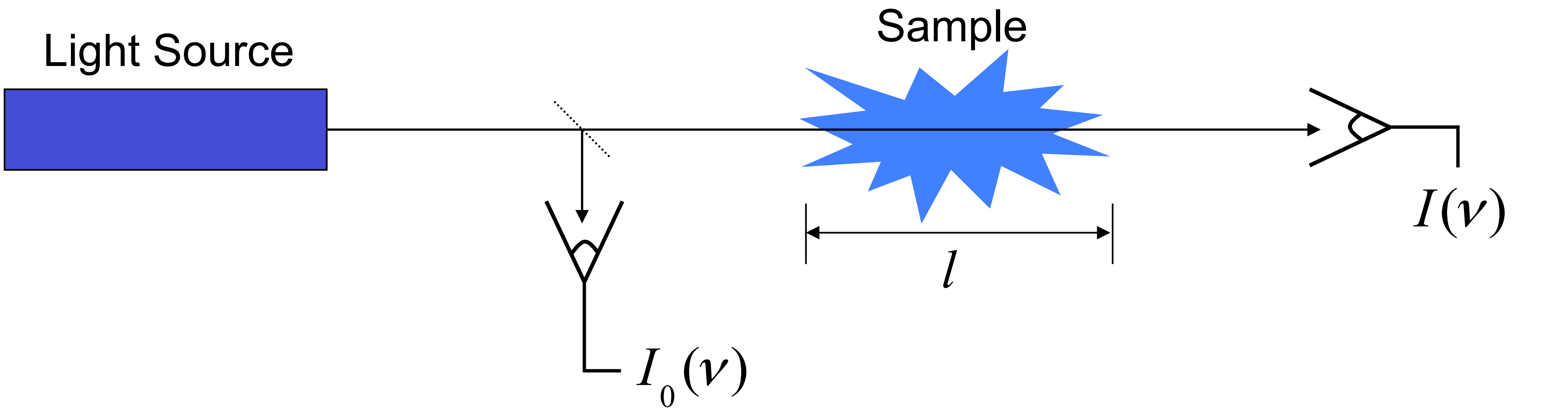
Photons with energy ≅ 11 eV
(λ ≅ 110 nm, Vacuum UV)

Fluorescence of H_2 in B-state

λ in the Vacuum UV

Absorption spectroscopy

Absorption spectroscopy

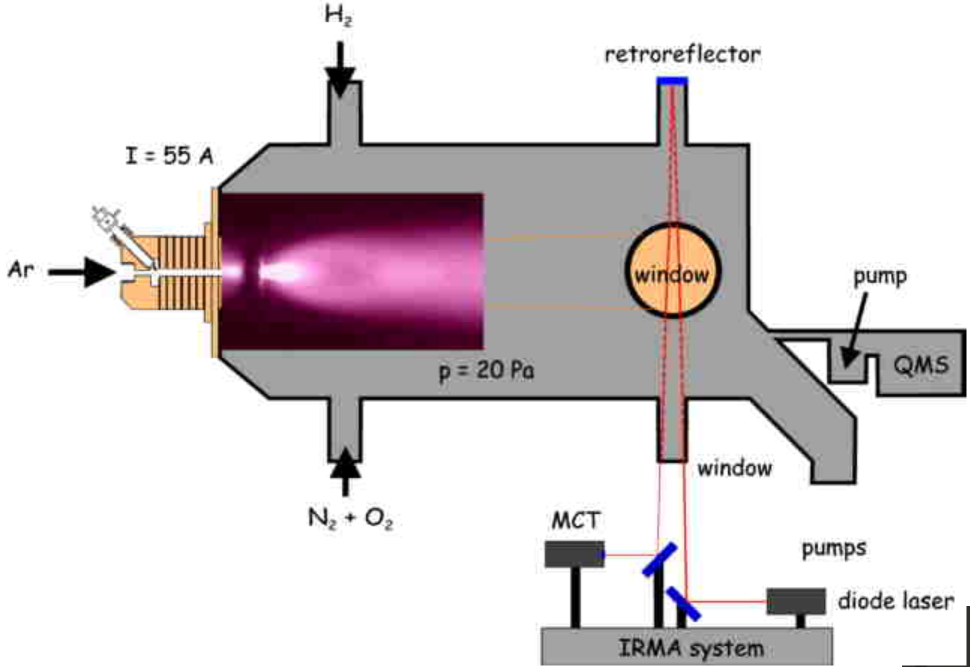


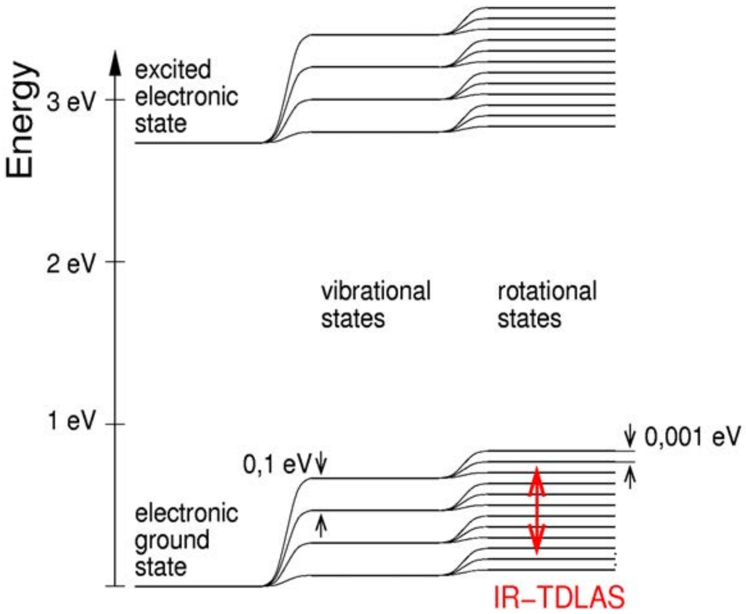
Lambert-Beer : $I(\nu) = I_0(\nu)\exp[-\kappa_\nu l]$

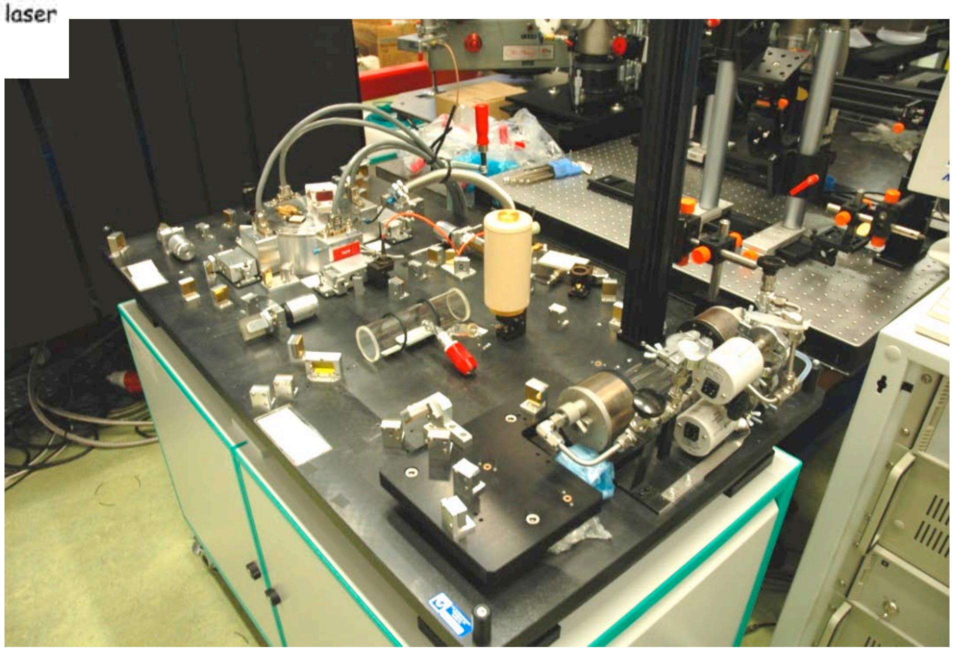
Absorption: $\kappa_\nu = n(v, J)\sigma_\nu$

If $\kappa_\nu l$ is small: $\dfrac{\Delta I}{I_0} = \kappa_\nu l$

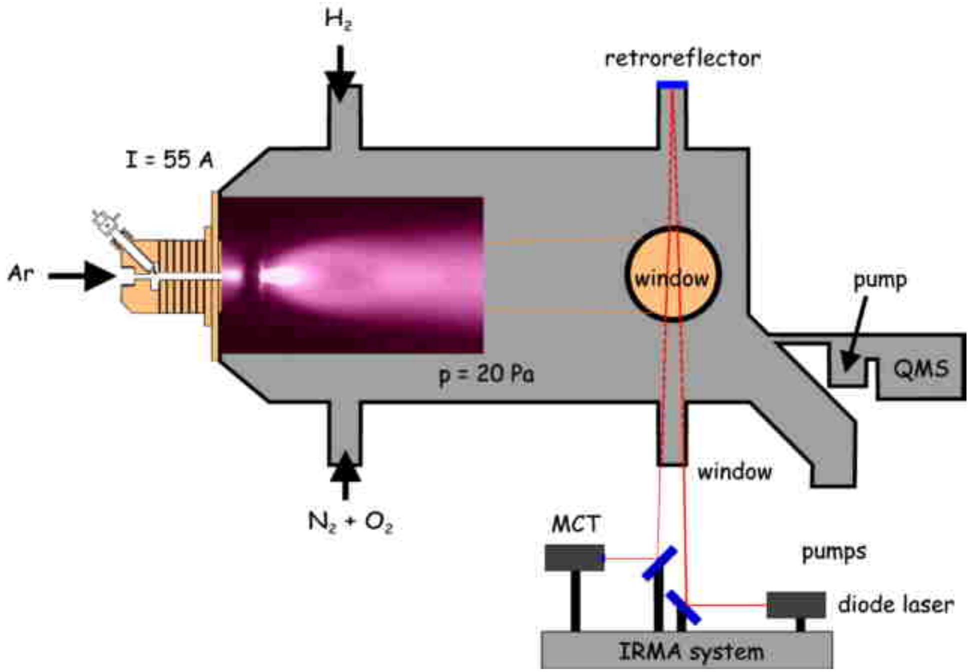
IR laser absorption spectroscopy

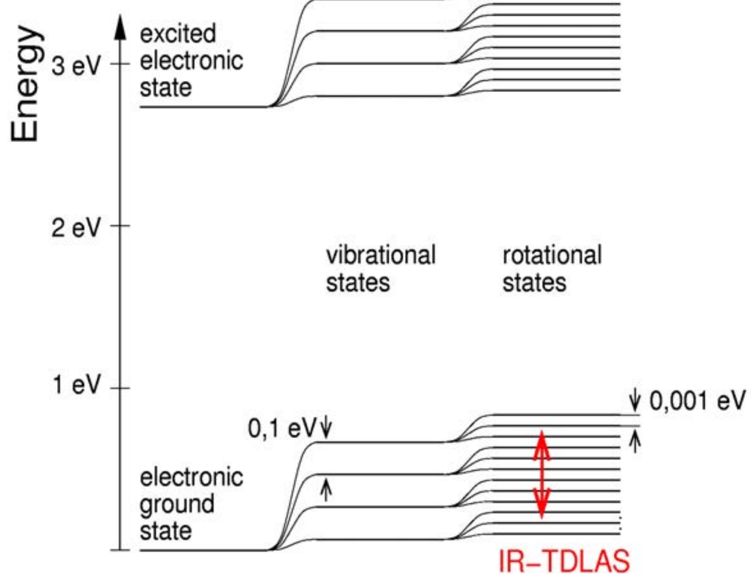




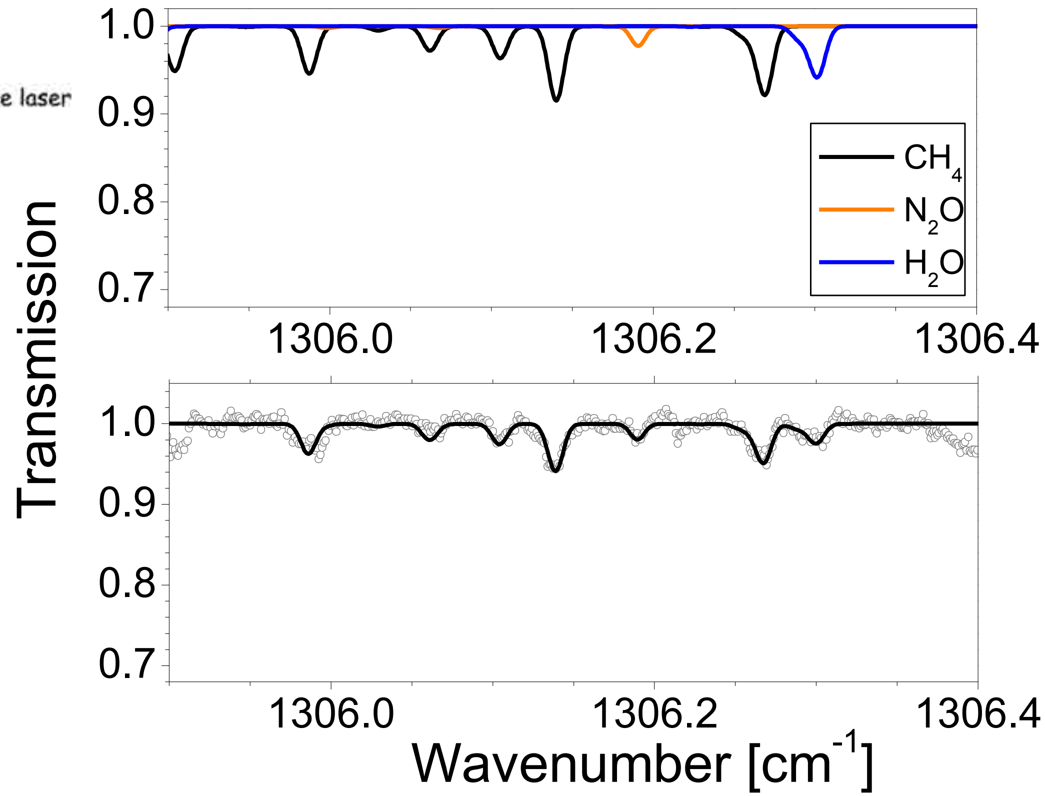


IR laser absorption spectroscopy

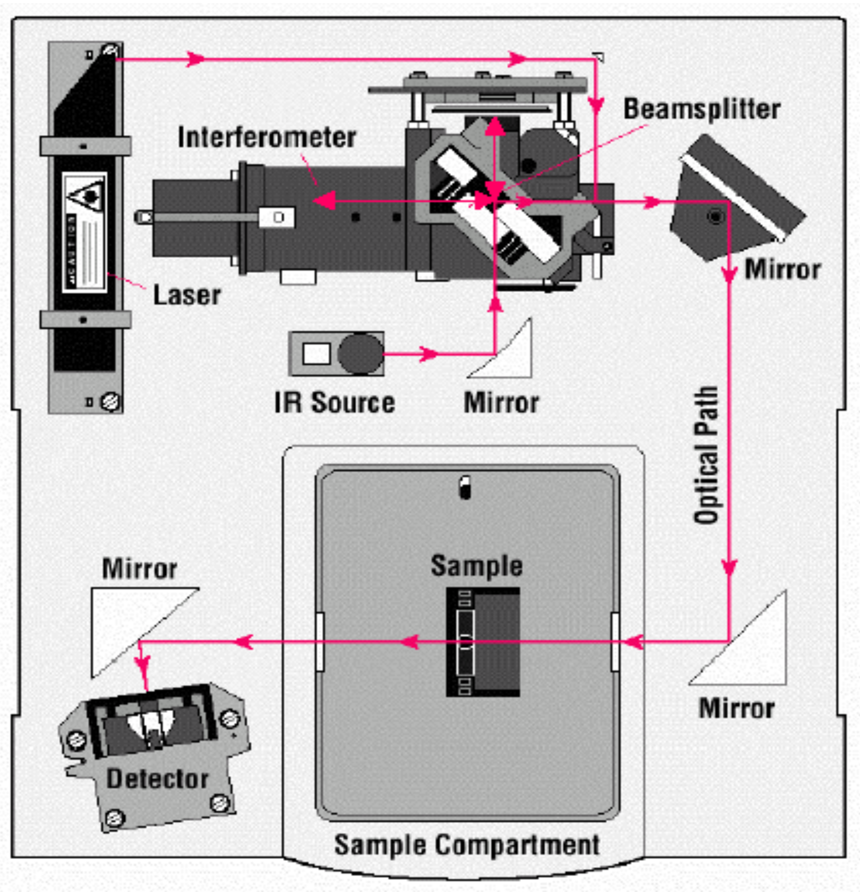




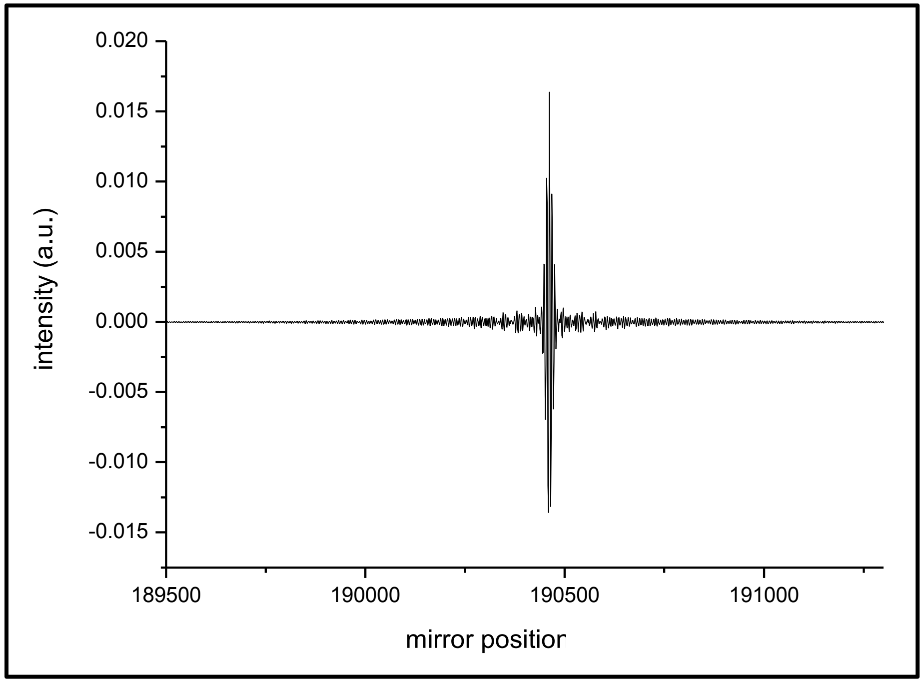
Trace gas detection



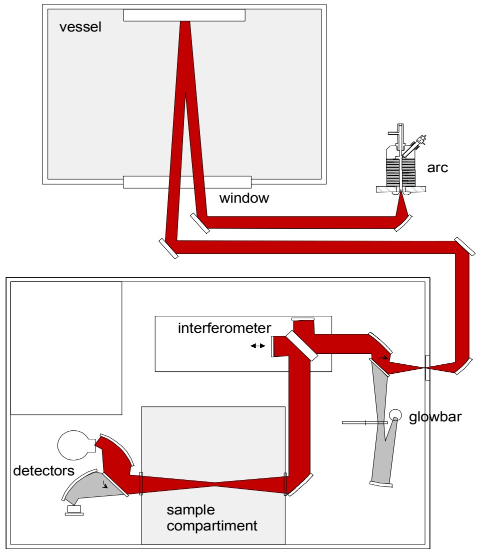
Fourier Transform absorption spectroscopy

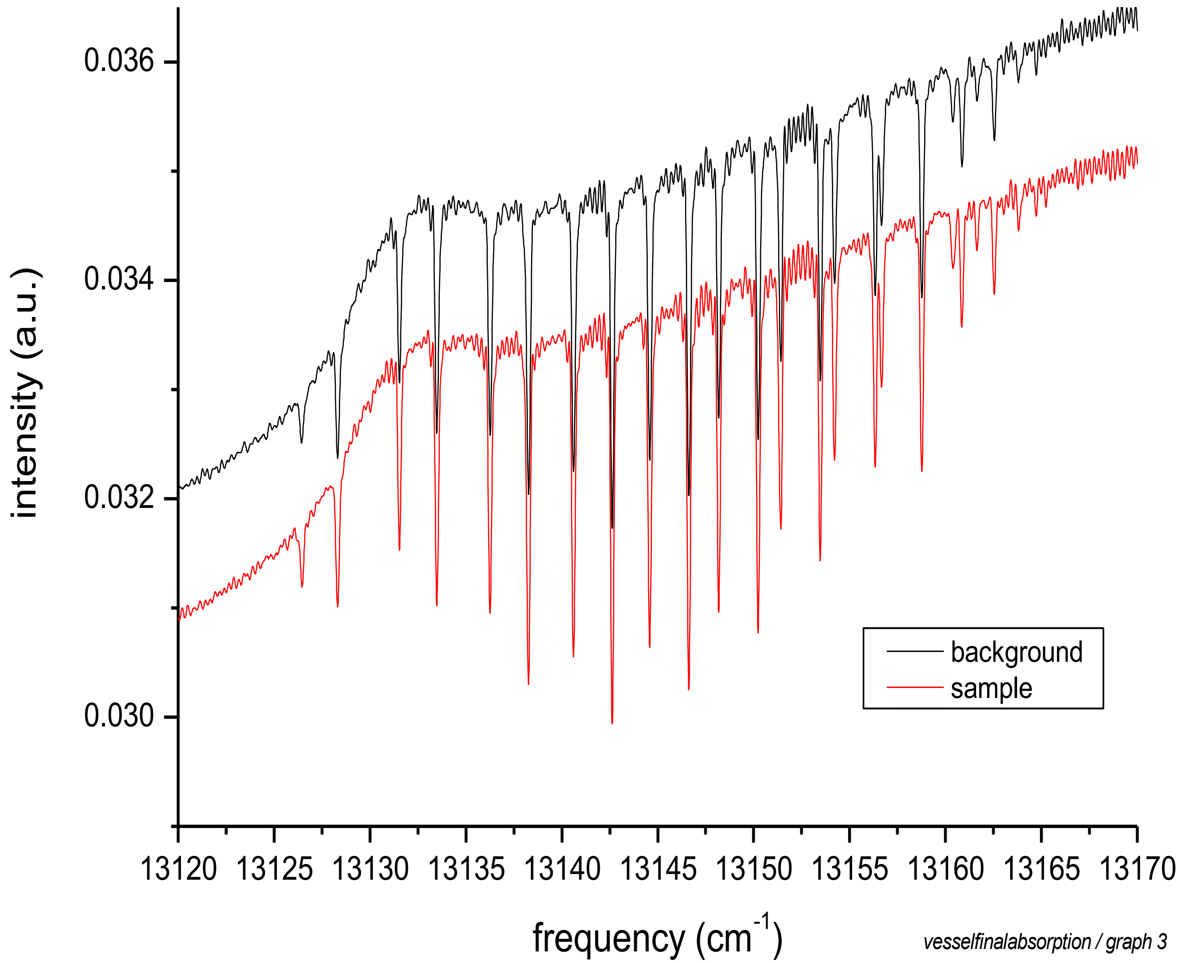


interferogram



O_2 FTIR measurement in a vessel





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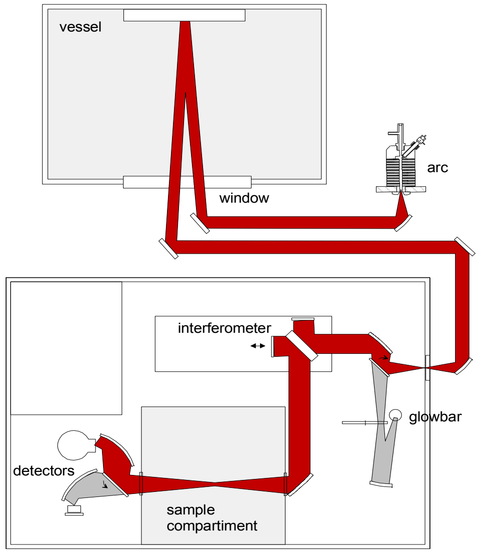
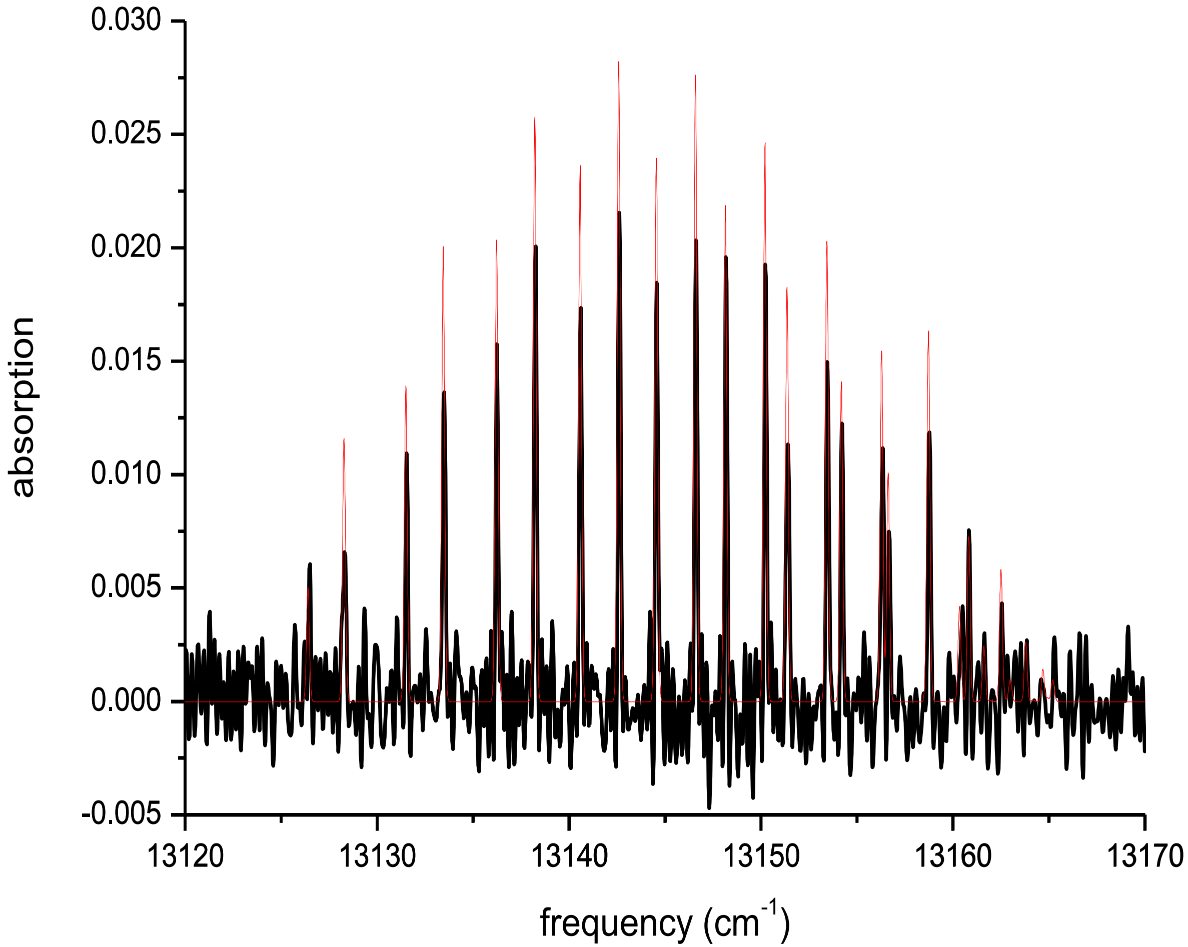
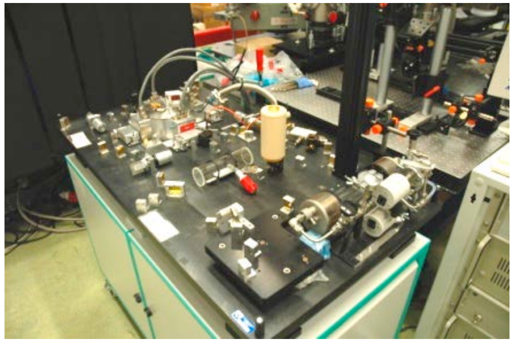
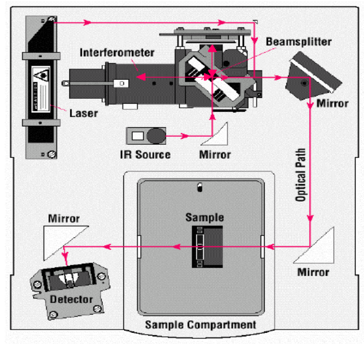








IR laser absorption

FT IR absorption

+ (IR laser absorption)
- ✓ Very high wavelength resolution
- ✓ High sensitivity

+ (FT IR absorption)
- ✓ Multiplex advantage
- ✓ Very large wavelength range

– (IR laser absorption)
- ✓ Very small wavelength range

– (FT IR absorption)
- ✓ Low wavelength resolution
- ✓ Sensitivity

Homo-nuclear diatomic species **not** detectable in IR

Sensitivity

$$\frac{\Delta I}{I_0} \geq 10^{-3}$$ (pulsed lasers)

➔ $\kappa_\nu l \geq 10^{-3}$

Example: $l = 0.1\ \text{m}$

$\sigma = 10^{-18}\ \text{m}^2$

➔ $n(v, J) \geq 10^{16}\ \text{m}^{-3}$

$$N_{tot} = \sum_{v,J} n(v, J) \geq 10^{18}\ \text{m}^{-3}$$

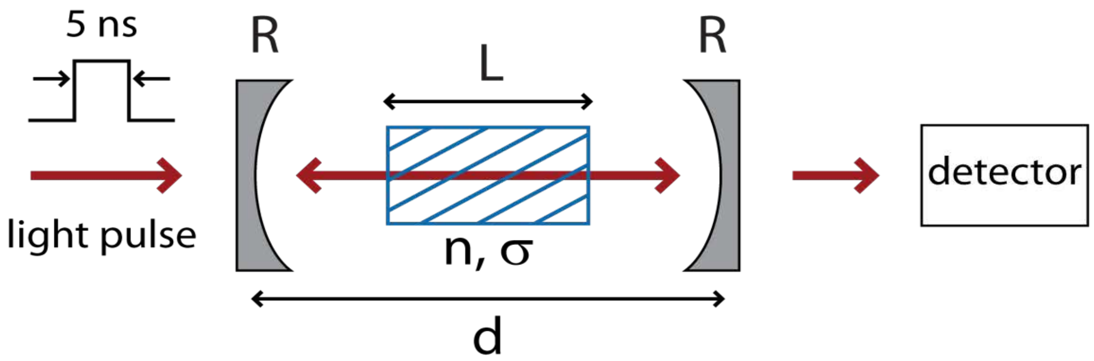
Alternative schemes:

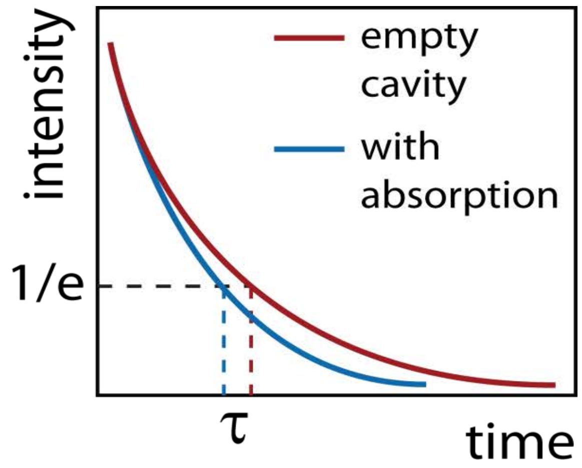
Fourier Transform spectroscopy (multiplex, but low sensitivity)

Cavity Ring Down spectroscopy (high sensitivity)

Sensitive direct absorption technique

(A. O'Keefe and D.A.G. Deacon, Rev. Sci. Instrum. **59** (1988) 2544)

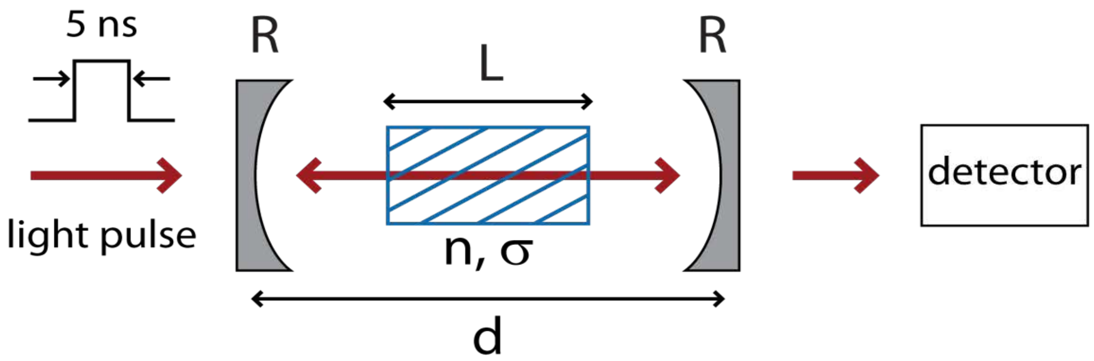


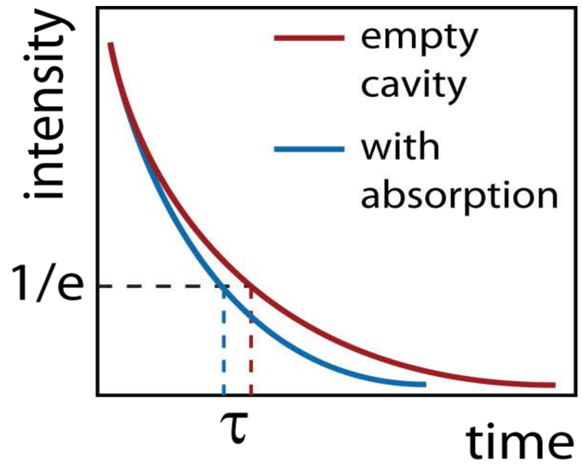


- ✓ absorption per unit of pathlength (cavity loss): $1/c\tau = (1 - R + n\sigma L)/d$
- ✓ non-intrusive and remote
- ✓ high sensitivity due to effective multipassing
- ✓ direct absorption –> line of sight measurement

✓ absorption per unit of

Basic scheme of the pulsed CRD spectrometer





Ring-down time

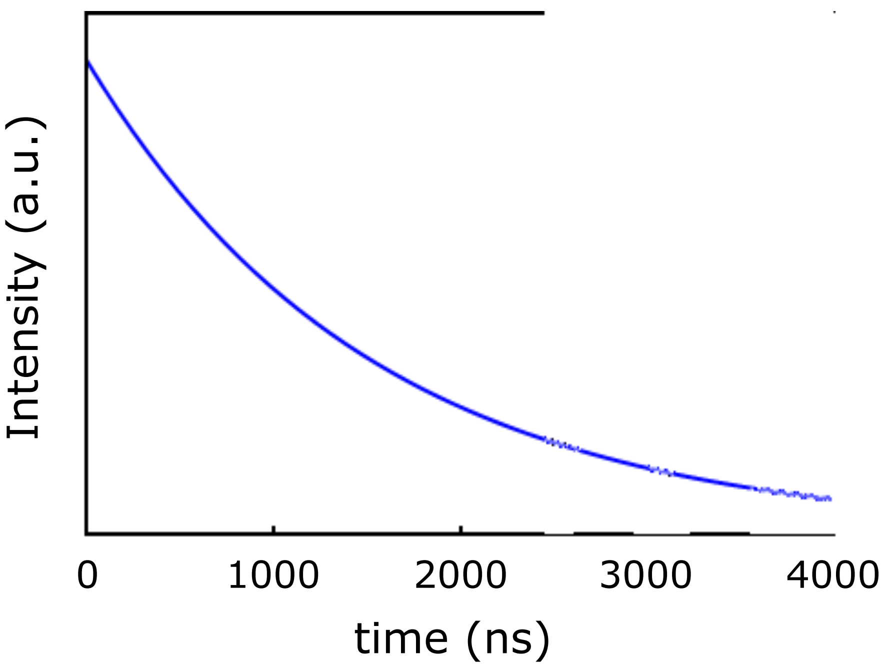
$$\tau = \frac{d}{c(1 - R + n\sigma L)}$$

Cavity loss

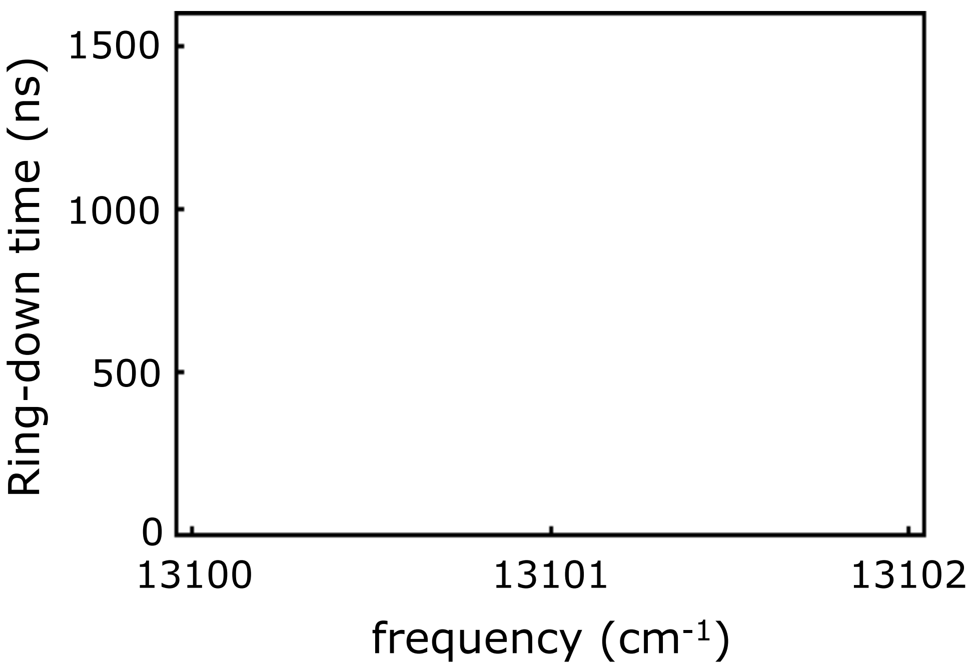
$$\frac{1}{c\tau} = \frac{1-R}{d} + \frac{n\sigma L}{d}$$

Performing a pulsed CRD experiment

Ring-down transient



CRD spectrum



Performing a pulsed CRD experiment

Cavity loss (1/cm)

$$\frac{1}{c\tau} = \frac{1-R}{d} + \frac{n\sigma L}{d}$$

baseline

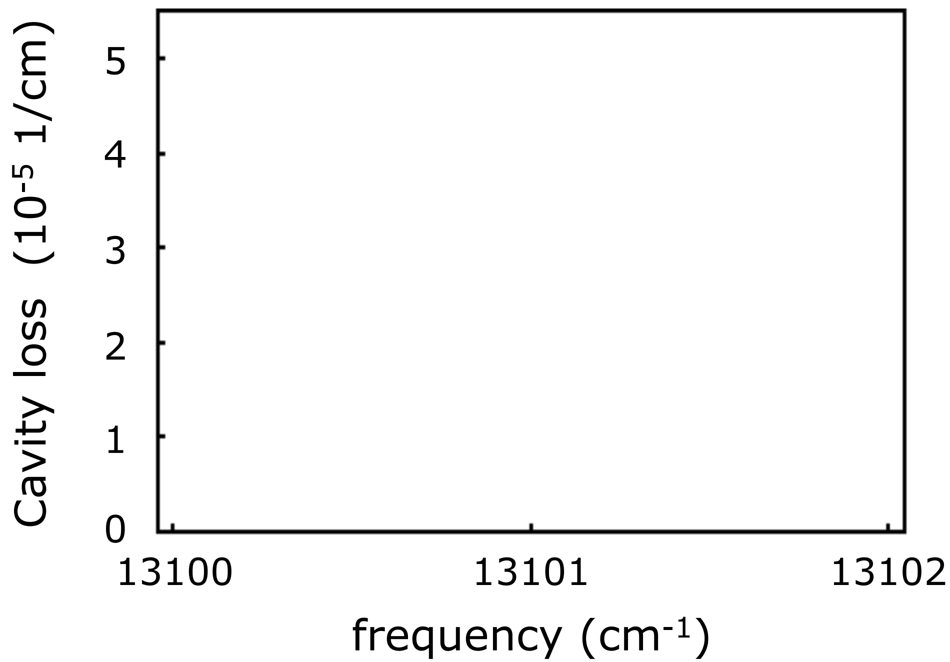
absorption spectrum

If cavity length is 5 cm, determine R:

1. R = 99 %
2. R = 99.9 %
3. R = 99.99 %
4. Not enough information

?

CRD absorption spectrum



+ optical technique

+ independent of intensity

+ direct absorption measurement:

    -- but: line-of-sight

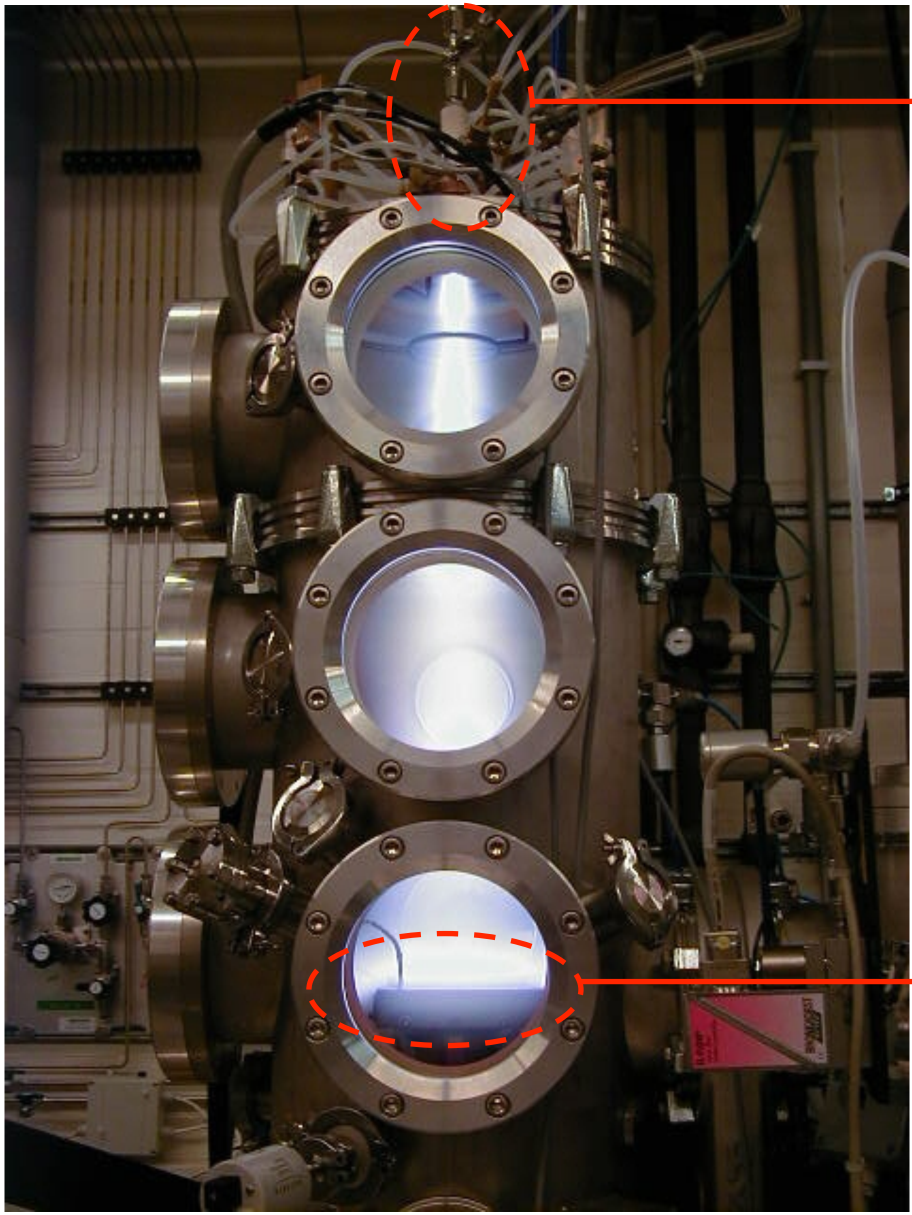
+ high sensitivity due to effective multipassing

+ pulsed light sources: spectral range into the UV

+ experimentally straightforward (tunable laser, highly reflecting mirrors, PMT, ‘fast’ and ‘deep’ digitizer)

high potential for diagnostics in plasmas

ETP setup



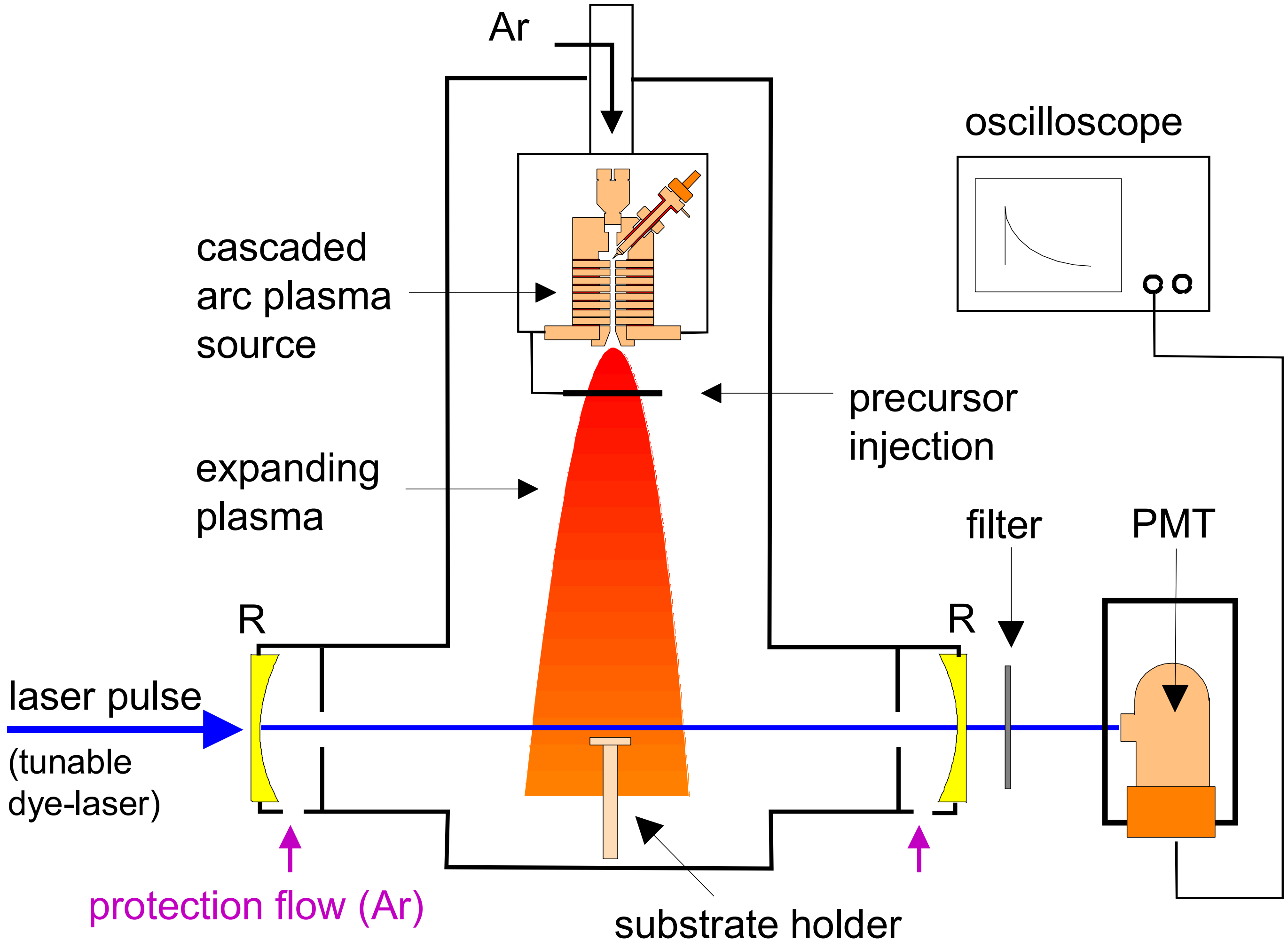
Plasma created at high pressure (~400 mbar) in cascaded arc plasma source

Expansion into low-pressure chamber (0.2 mbar)

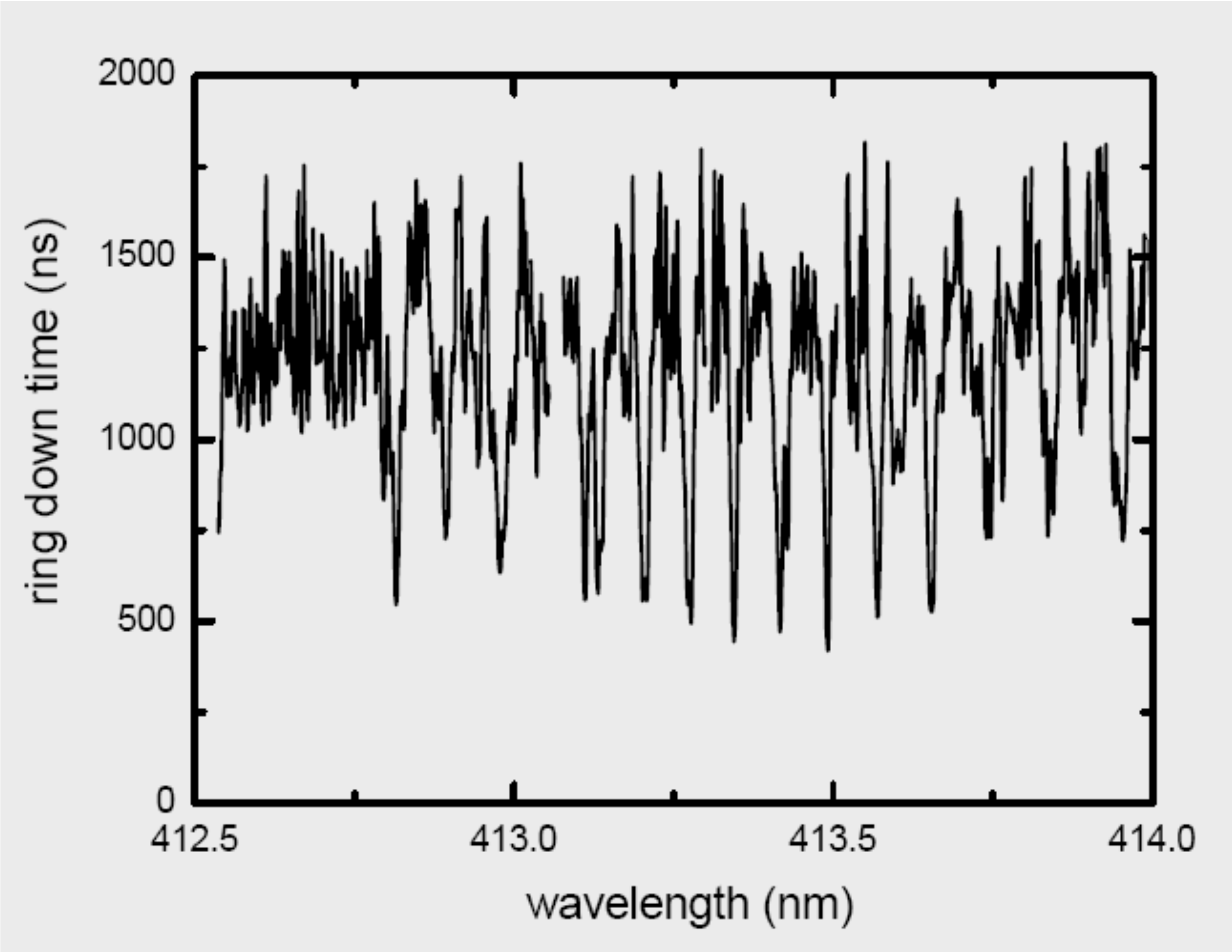
+ injection of e.g. SiH_4

Plasma in interaction with surface, leading to e.g. deposition or etching

CRD for the detection of SiH during a:Si-H deposition



CRD spectrum of SiH measured during a:Si-H deposition



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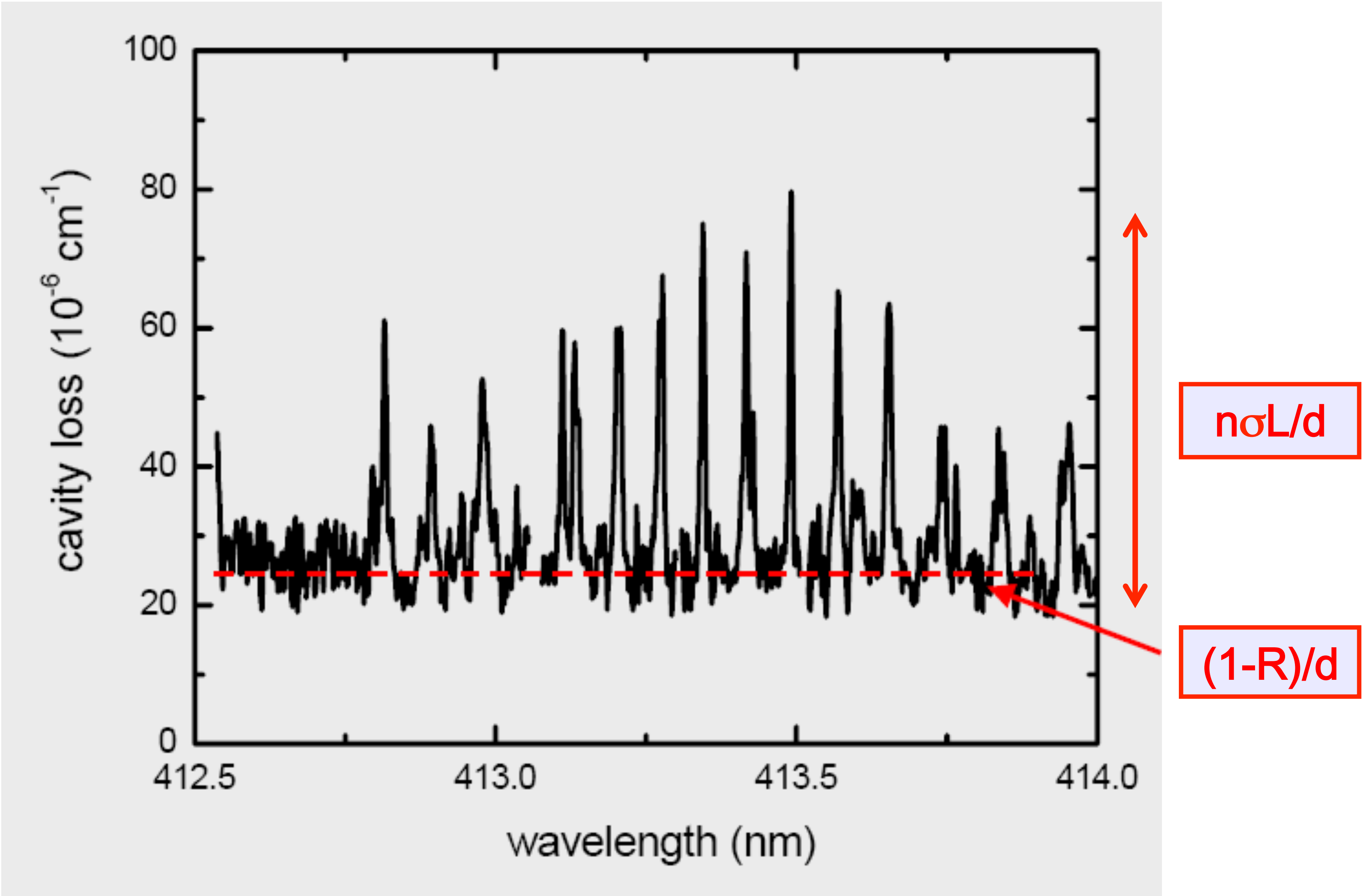


SiH detection: A $^2\Delta \rightarrow X\ ^2\Pi$, 405 – 430 nm

line width

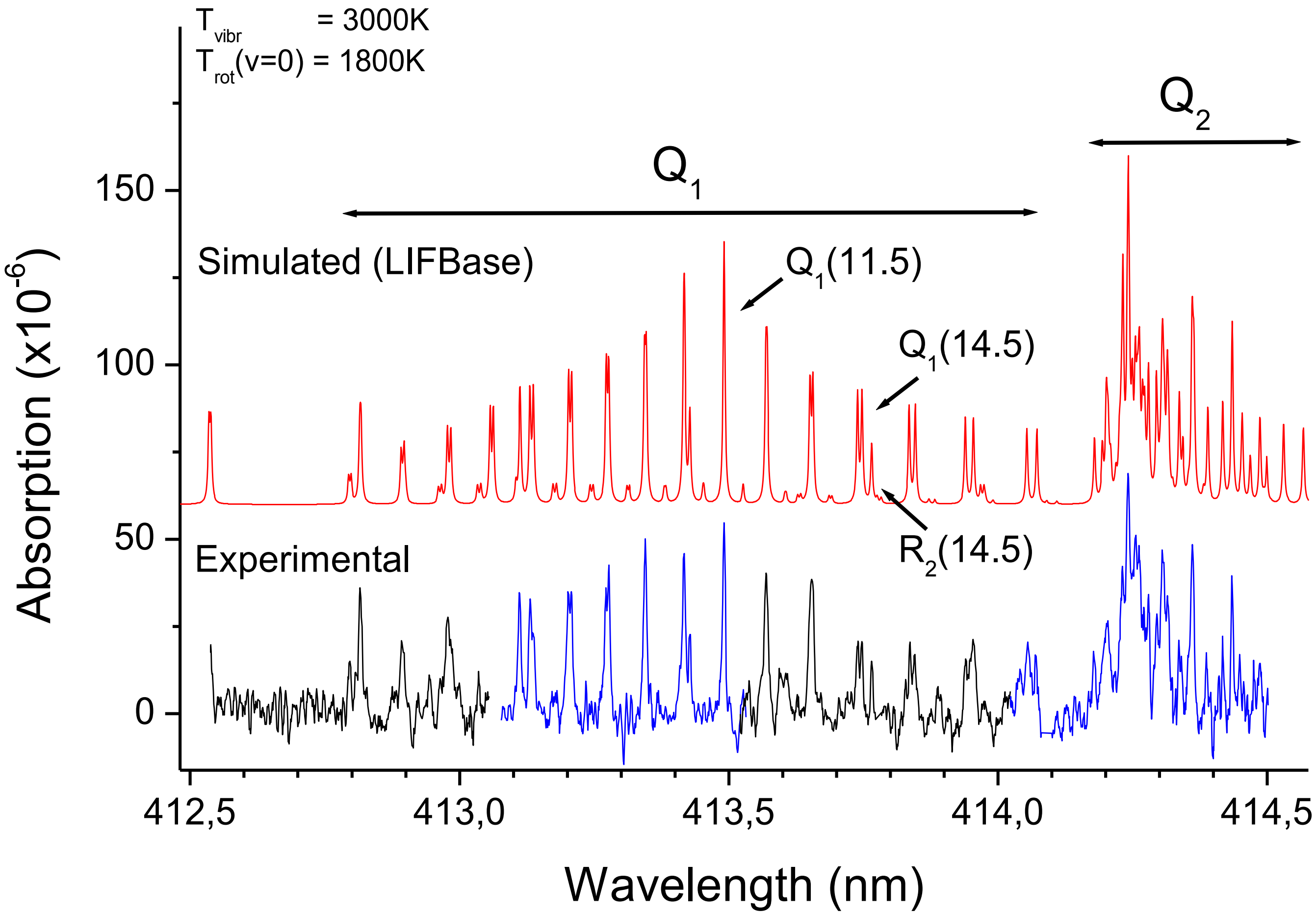
⇩

temperature

absorption
+
cross-section

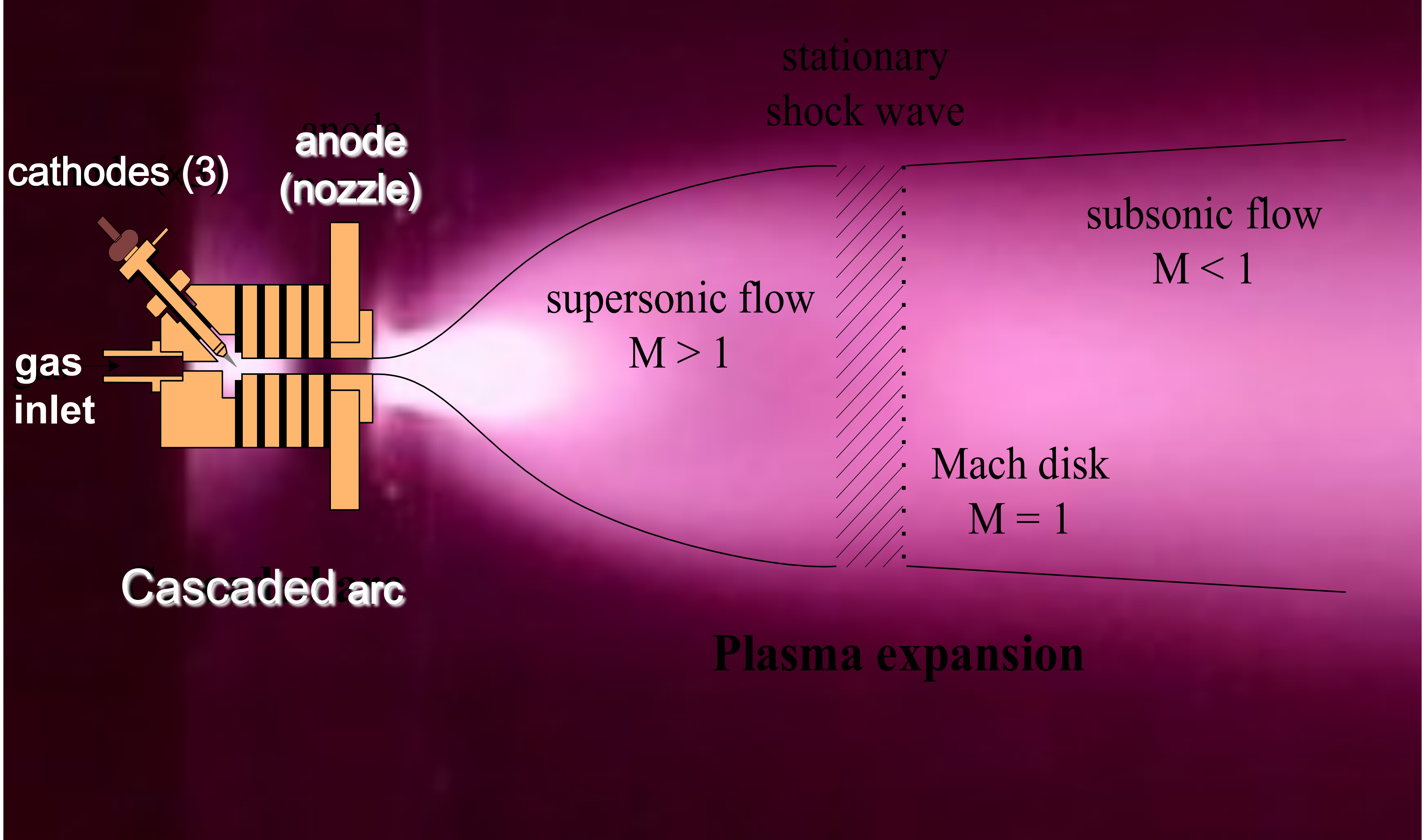
⇩

density

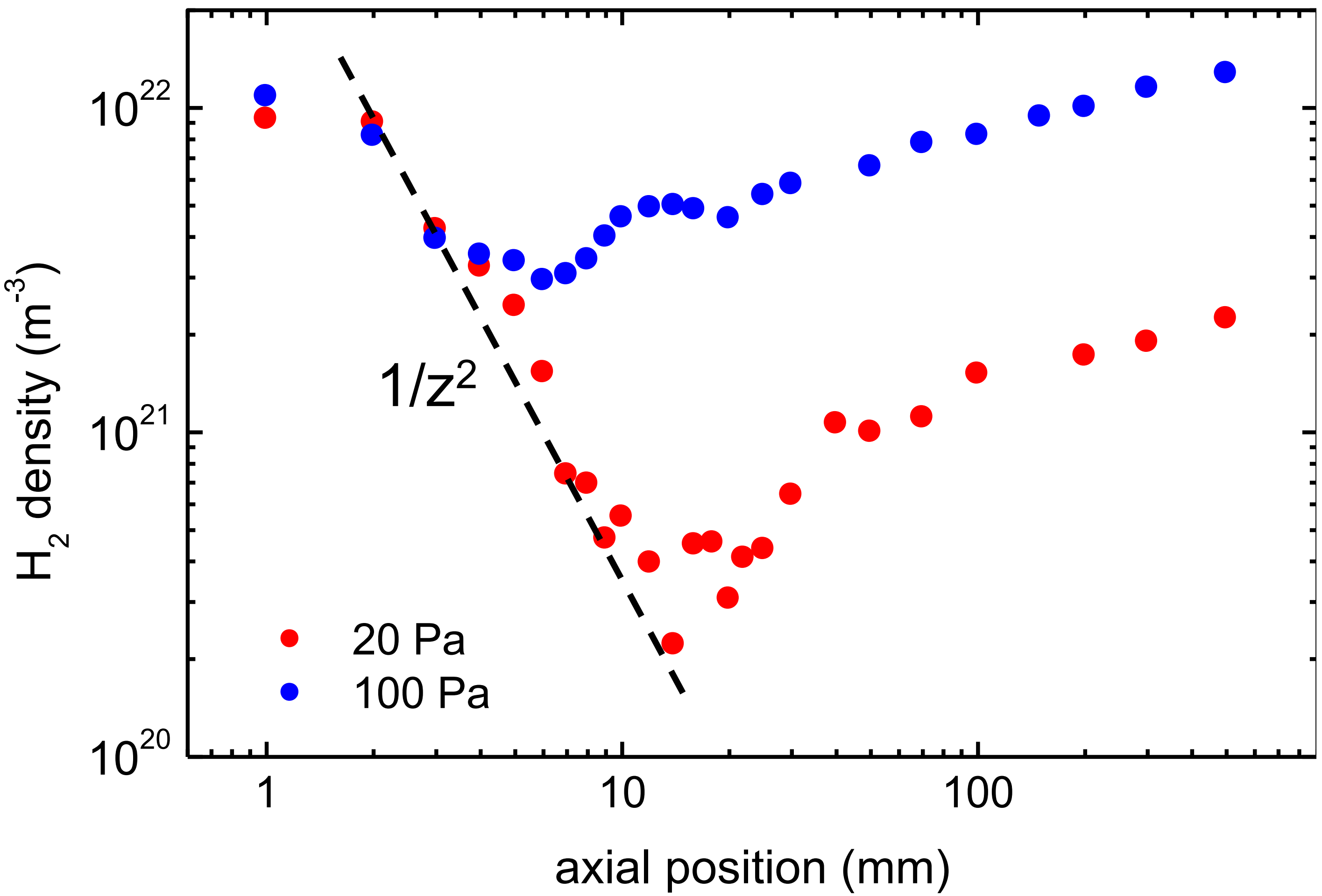


TALIF spectroscopy
on
H atoms

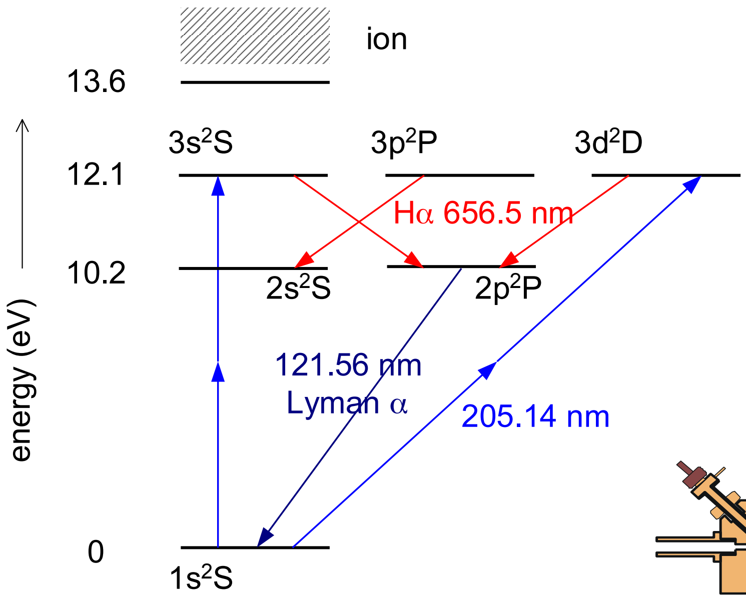
Ar/H_2 plasma expansion



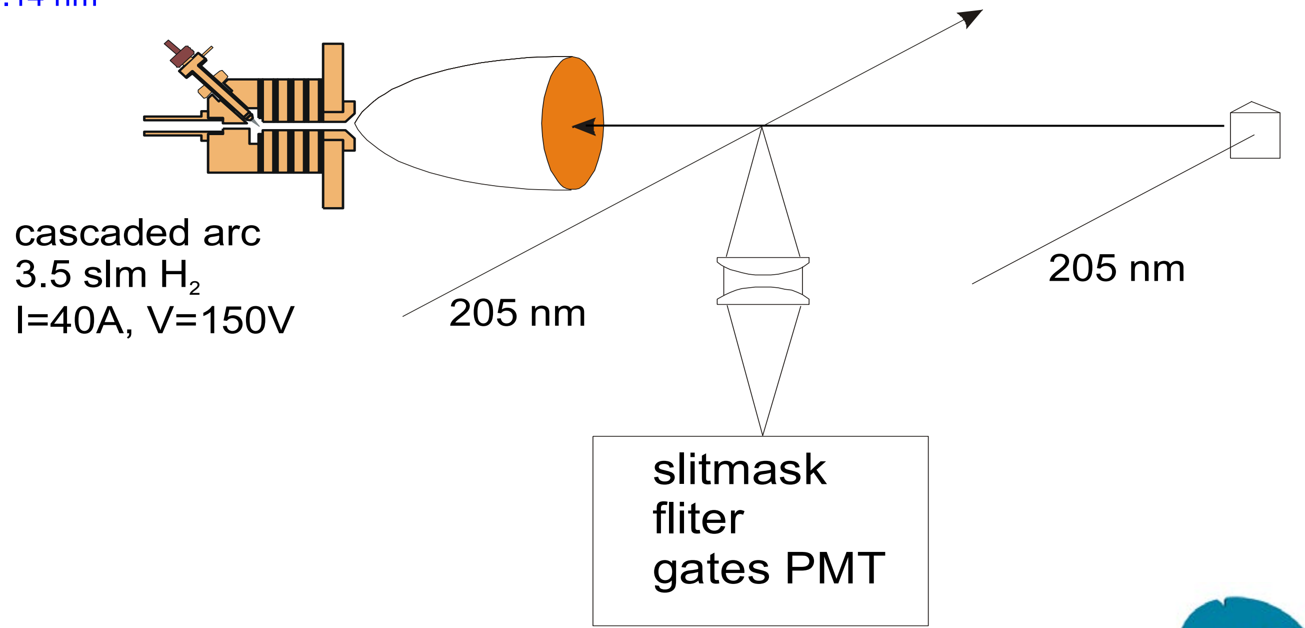
Rayleigh scattering on H/H_2 plasma expansion



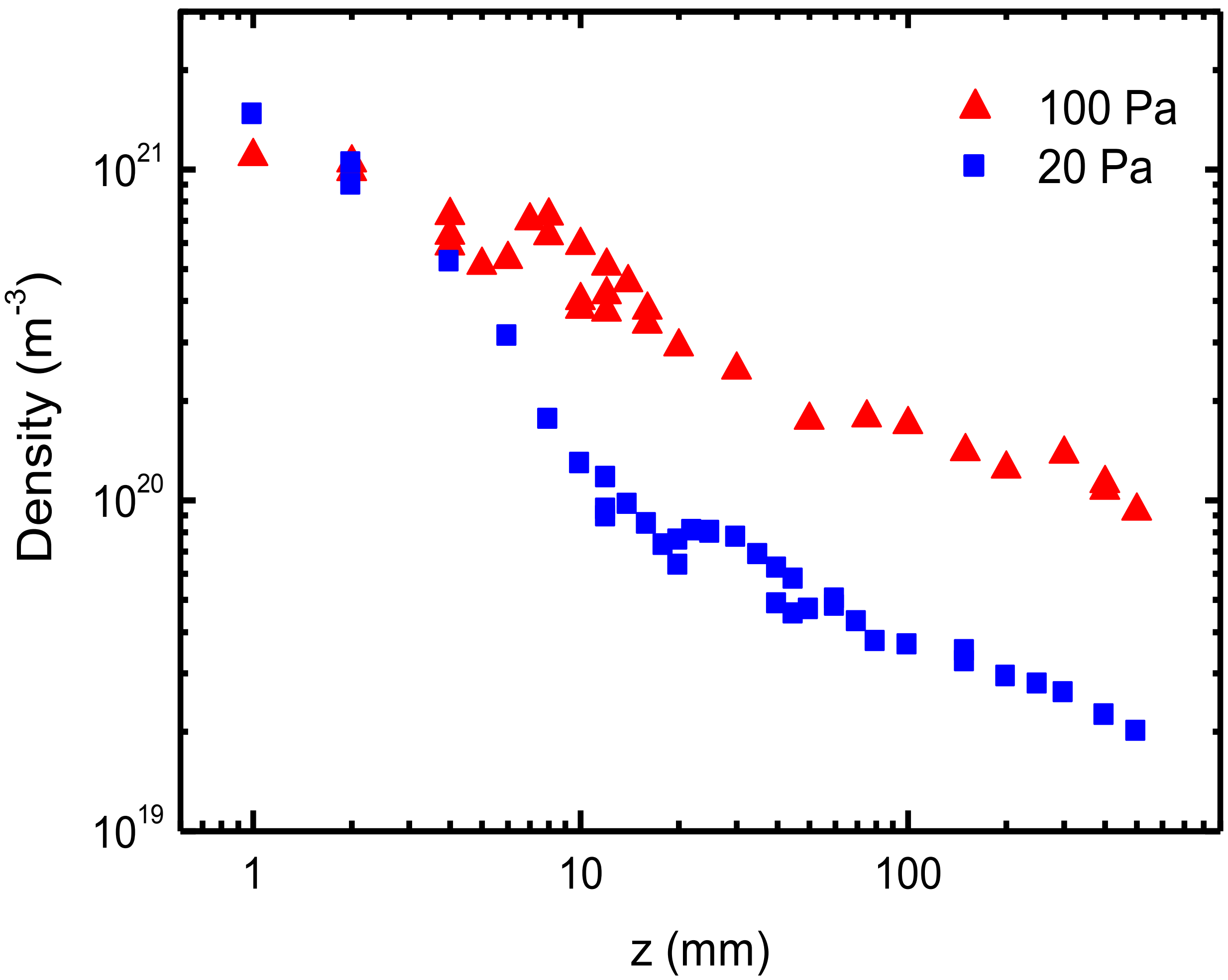
TALIF detection of H atoms



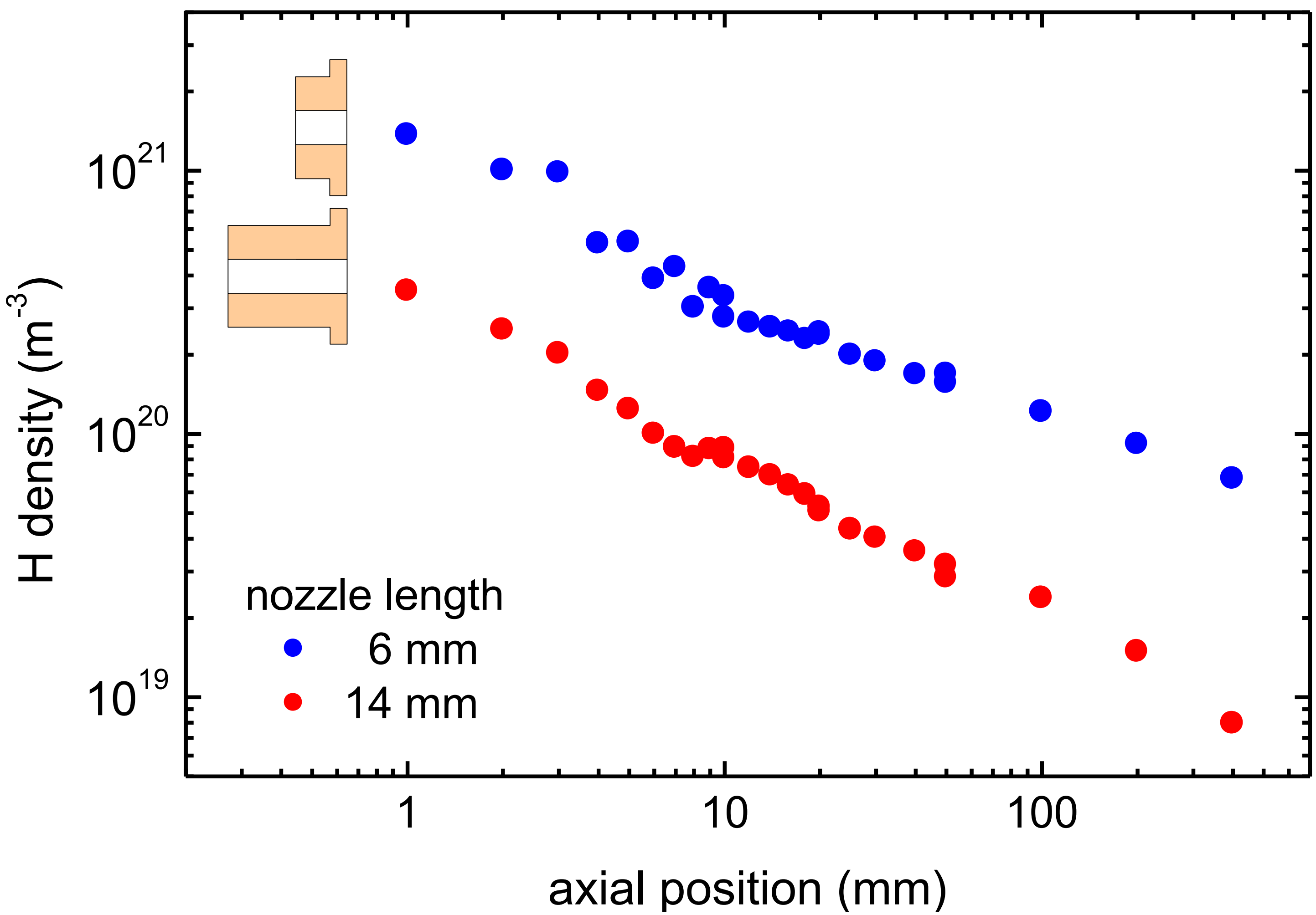
- produce 205 nm via THG of a Nd:YAG pumped dye laser
- from spectral scans data on: n,T,v,f(v)



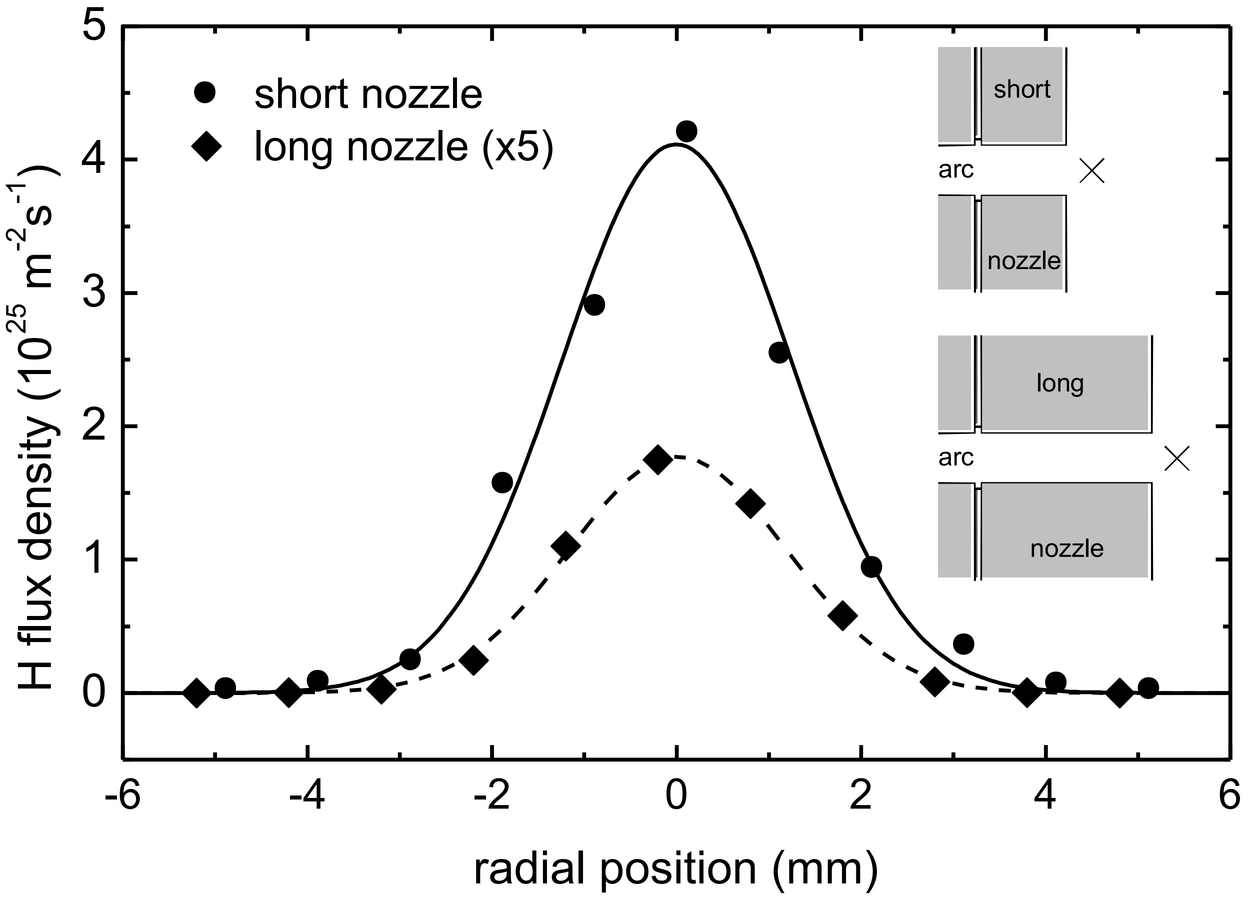
H atom density along the jet axis
(TALIF)



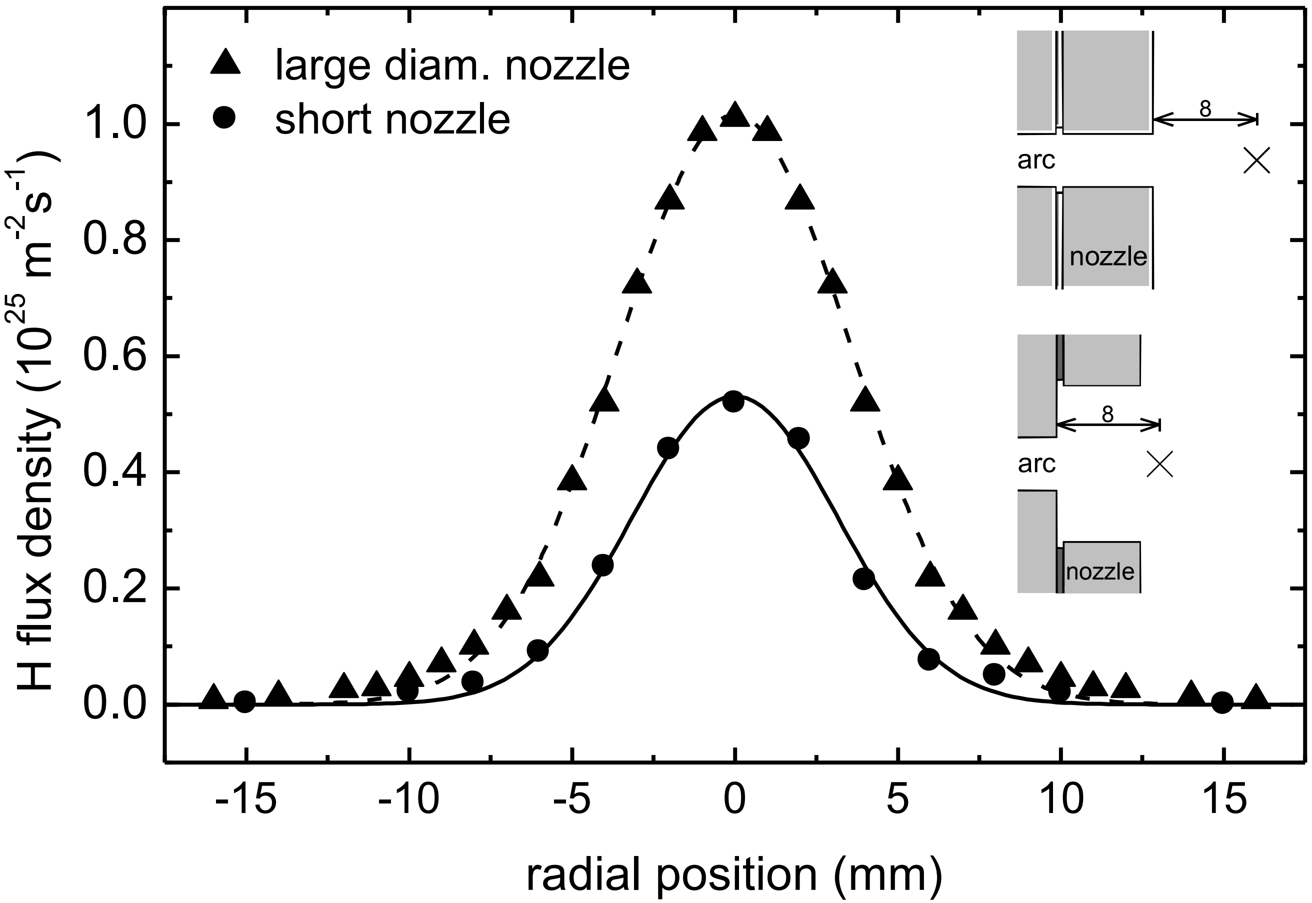
Effect of nozzle-length on H density



Effect of nozzle-length on H flux



Effect of nozzle-width on H flux



Conclusions

1. Large influence of nozzle geometry on H flux

2. Loss of H atoms due to surface association (volume association far too slow)

loss of *H* atoms = production of *H_2^{rv} at the surface*

H flux: Φ_H > 10^{21} s^{-1}

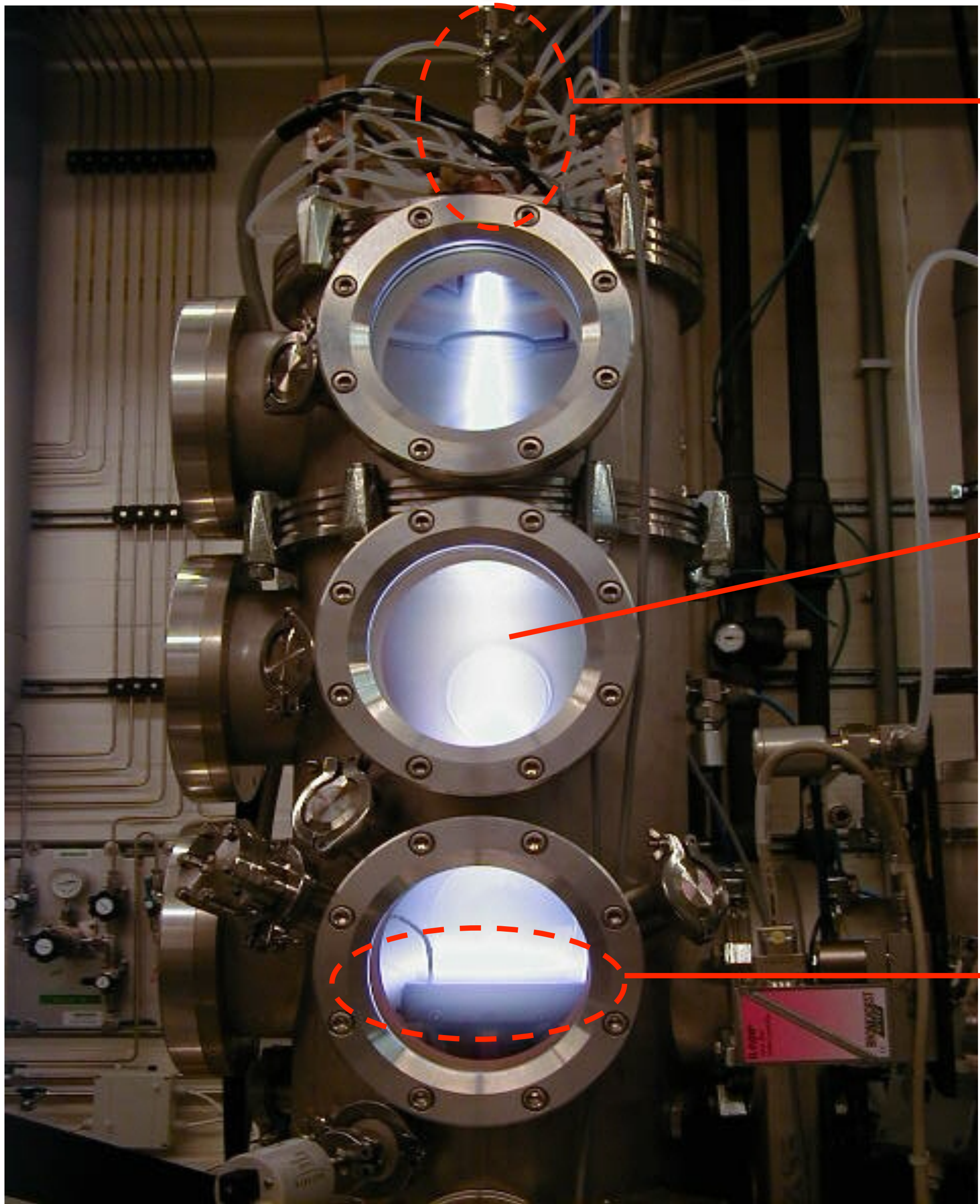
Dissociation degree = *0.4*

P. Vankan et al., *Appl. Phys. Lett.* **86** (2004) 101501

S. Mazouffre et al., *Phys Rev. E* **64** (2001) 066405

Doppler-LIF spectroscopy
on
Ar atoms

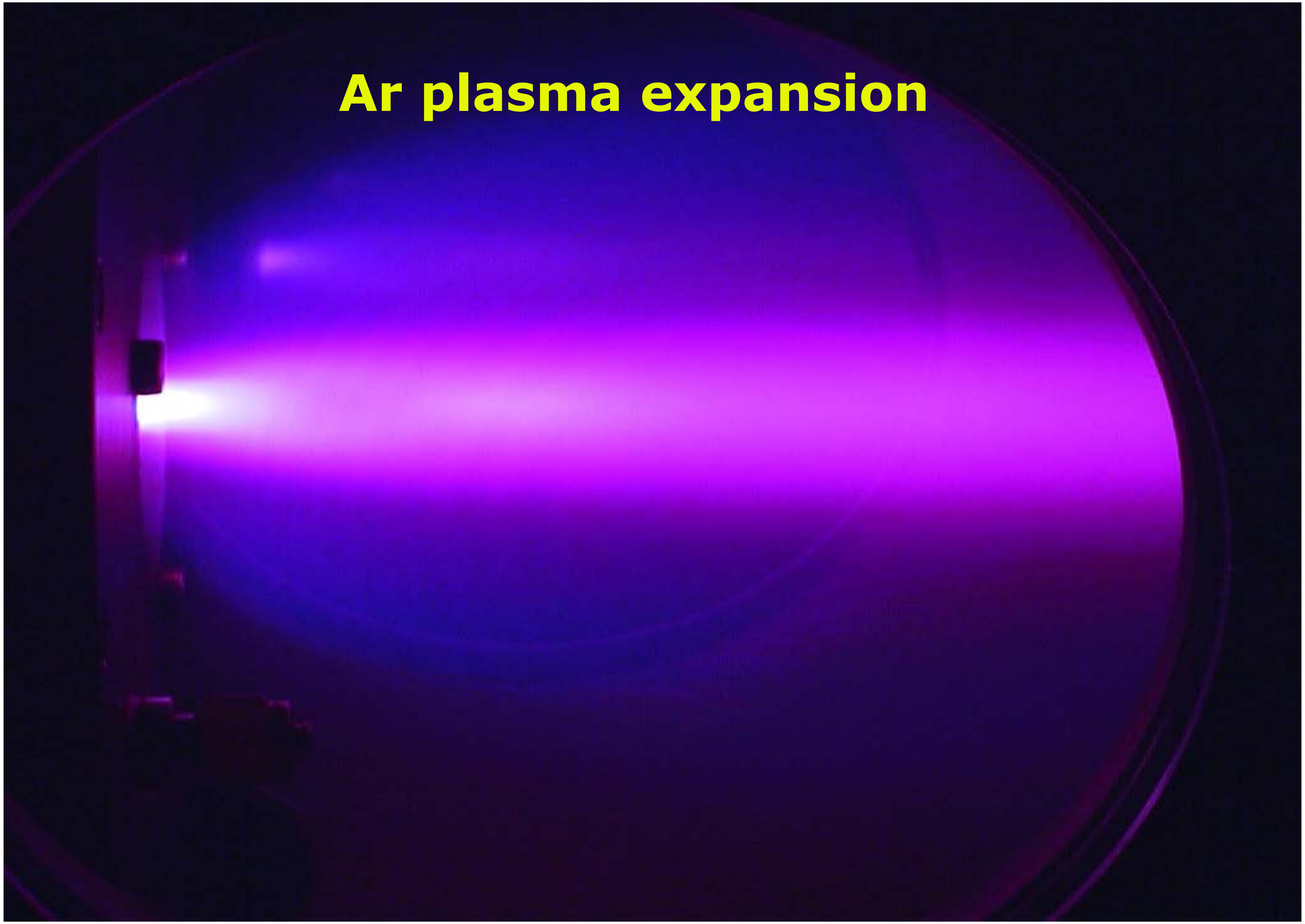
Expanding Thermal Plasma (ETP)



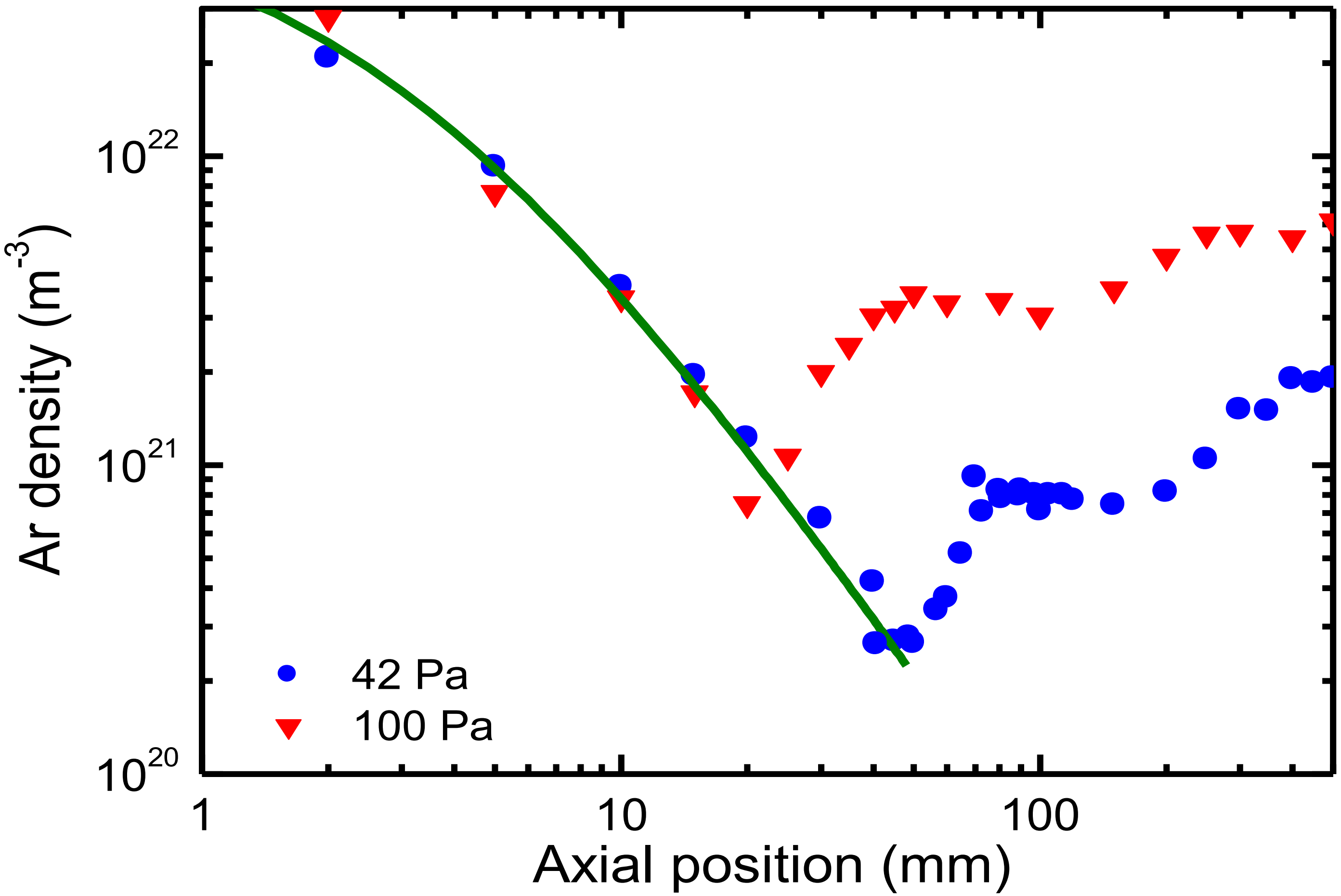
Plasma creation

Plasma chemistry

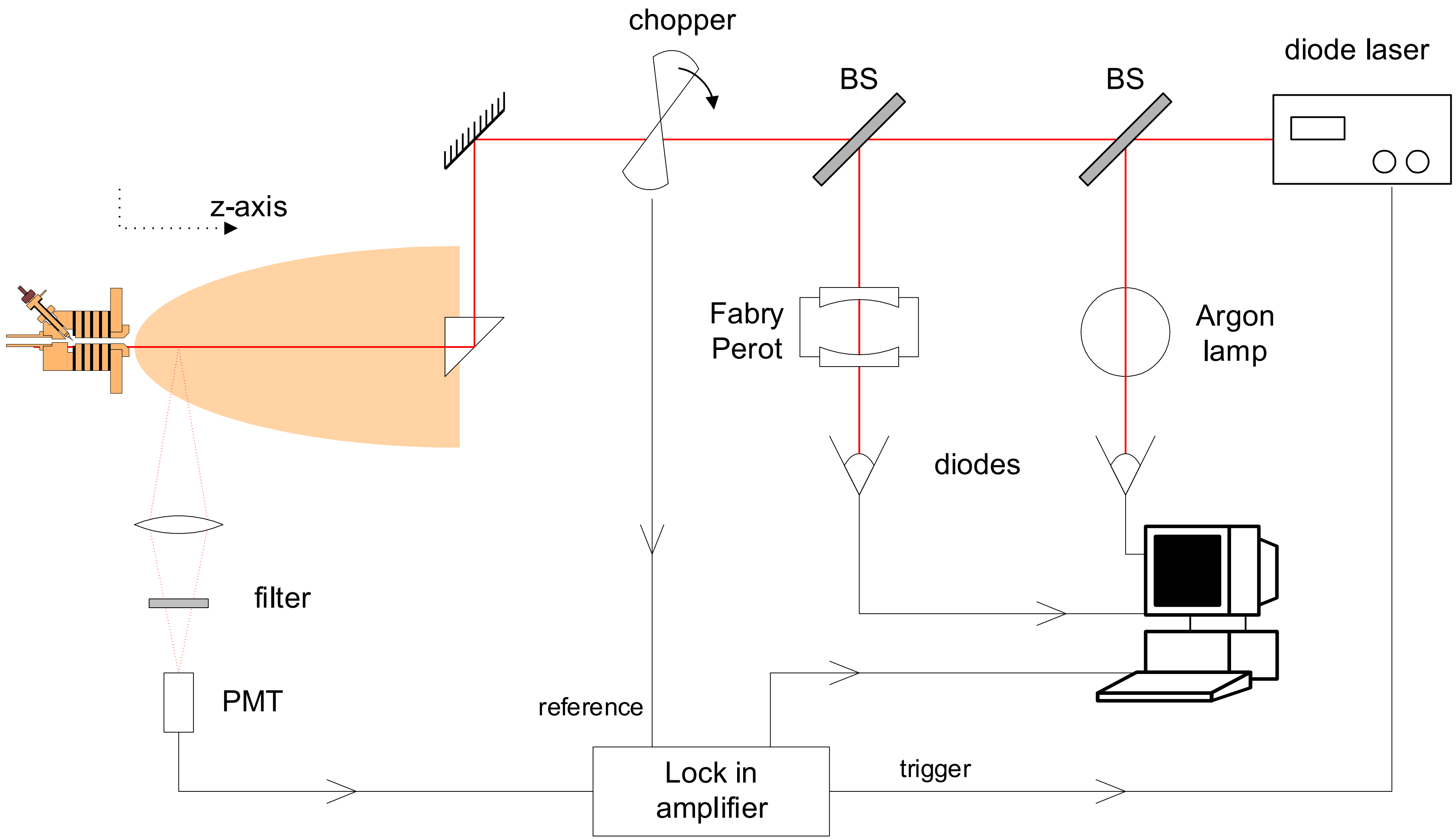
Material processing


Ar plasma expansion

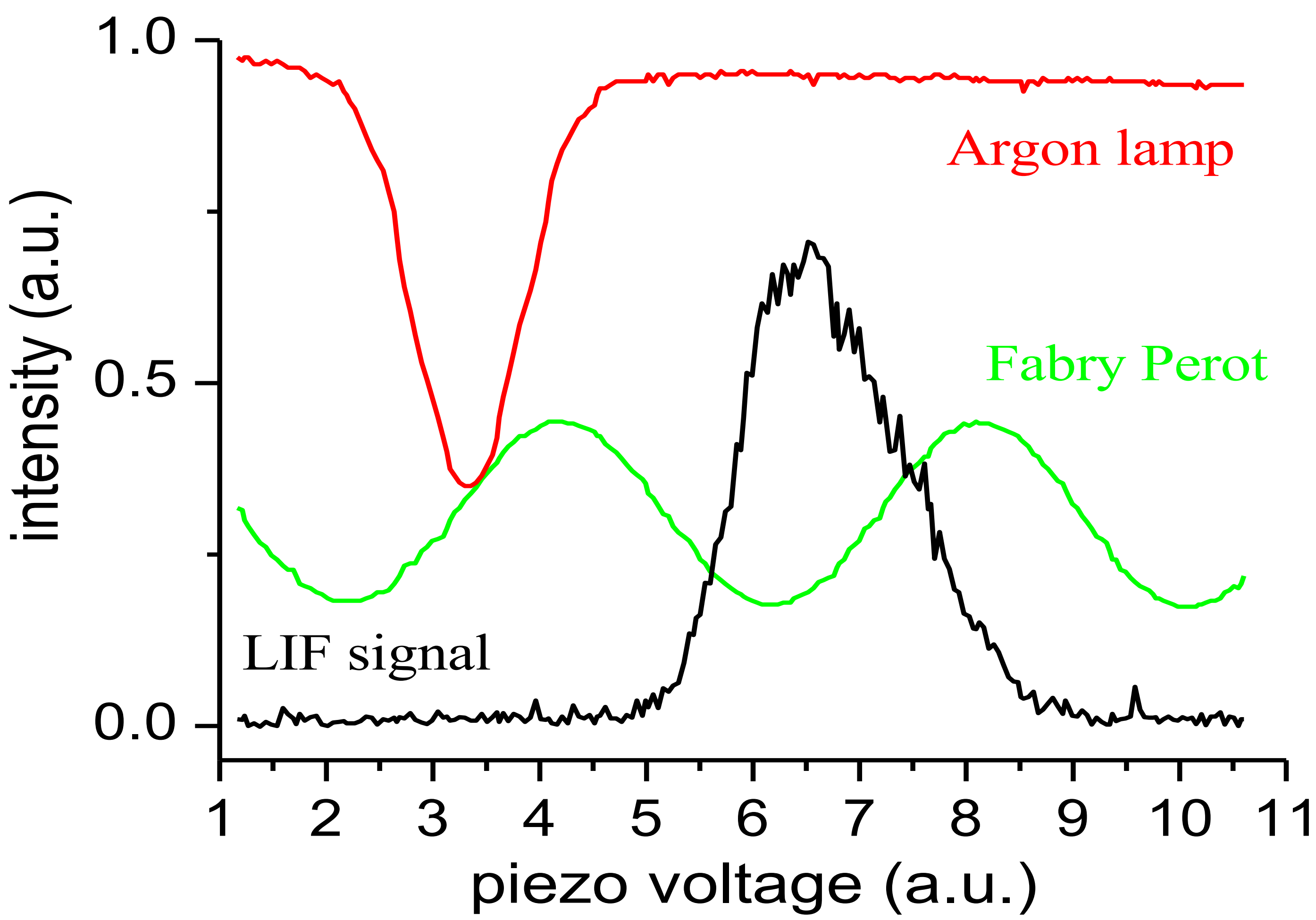
Ar density as function of distance from the exit of the source



Doppler LIF experimental setup

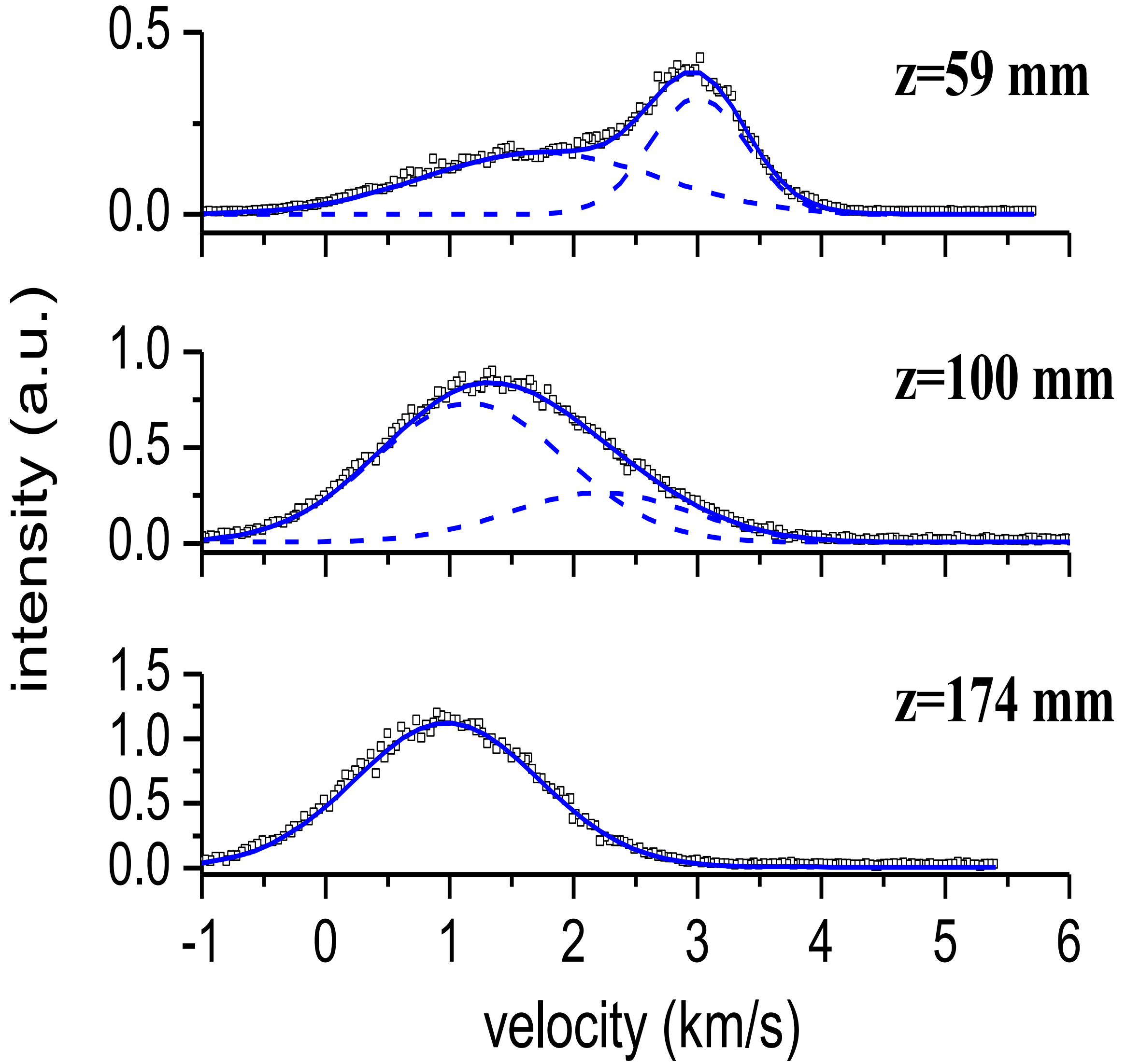


Typical result of a Doppler LIF measurement

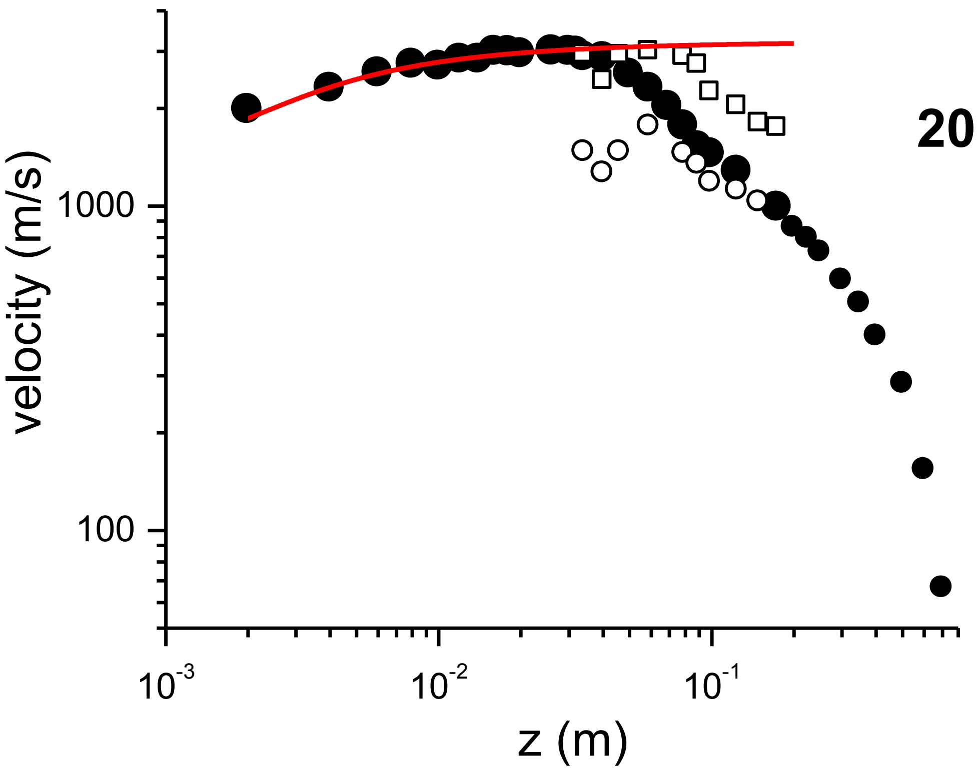


Doppler LIF

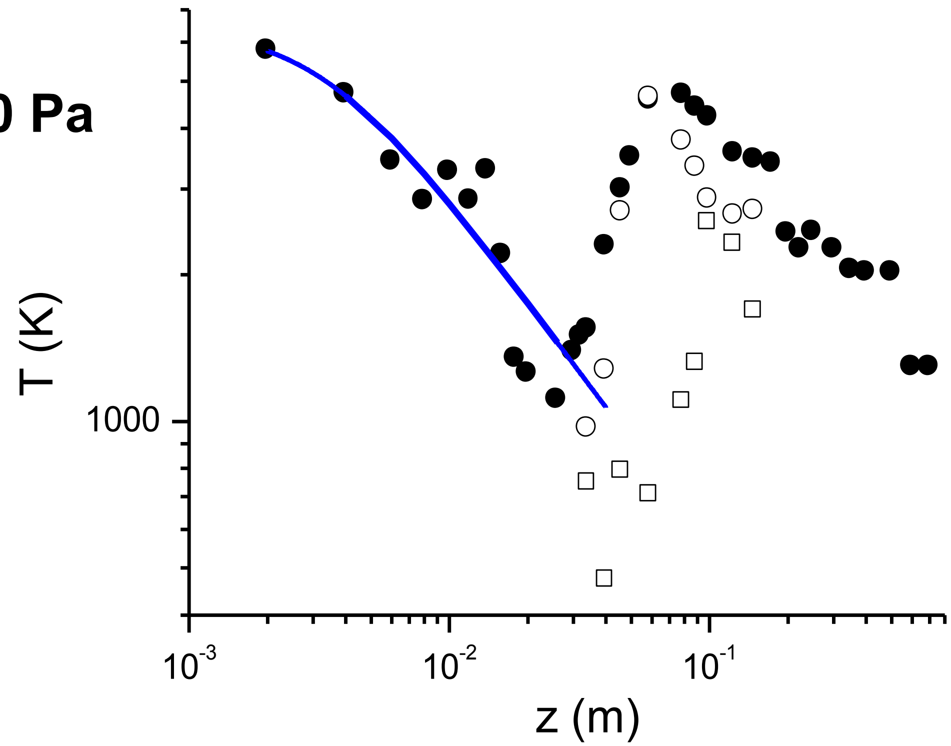
Ar velocity distribution functions



Ar atom velocity



Ar atom temperature



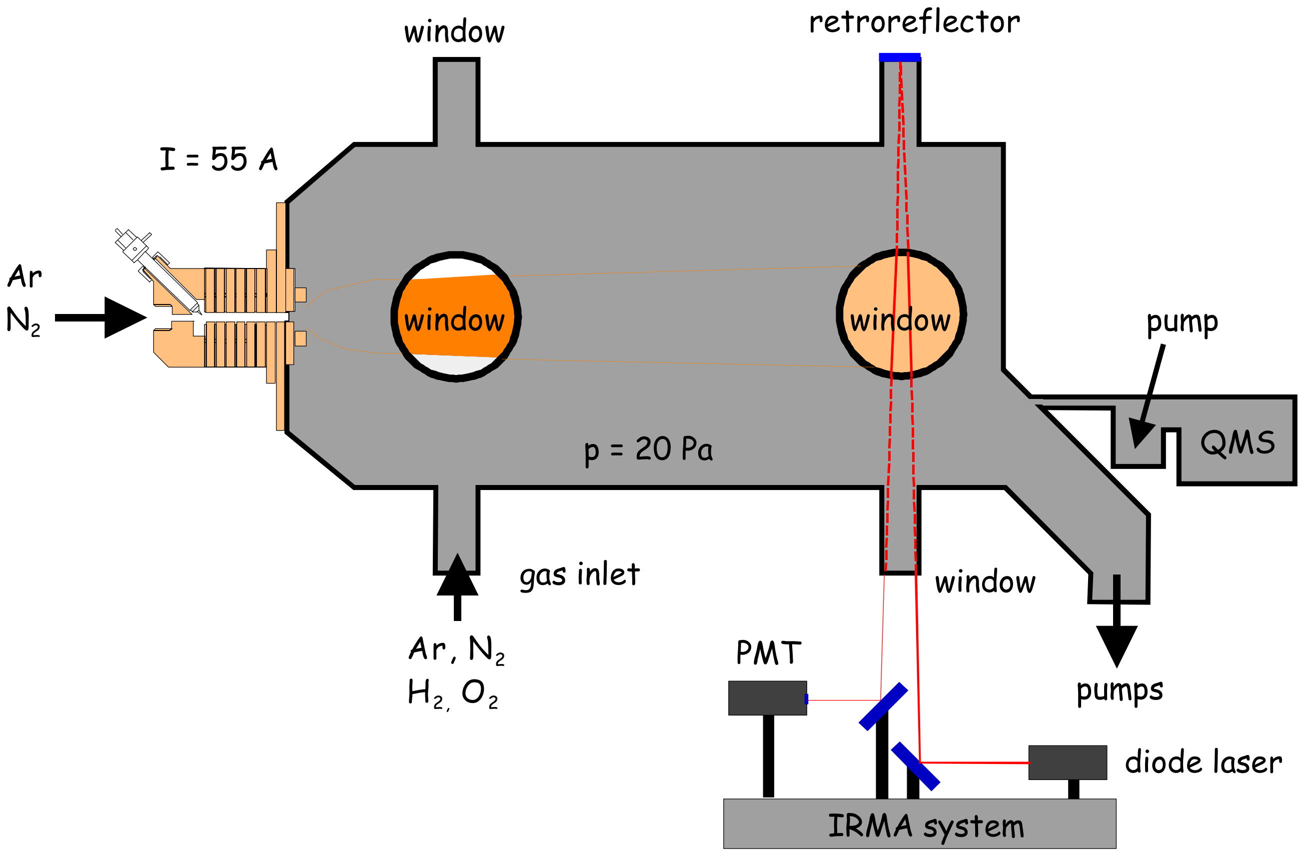
calculated with: $\gamma = 1.4$ *(theoretically: 5/3 for mono-atomic gas)*

$z_{ref} = 0.0025$ m

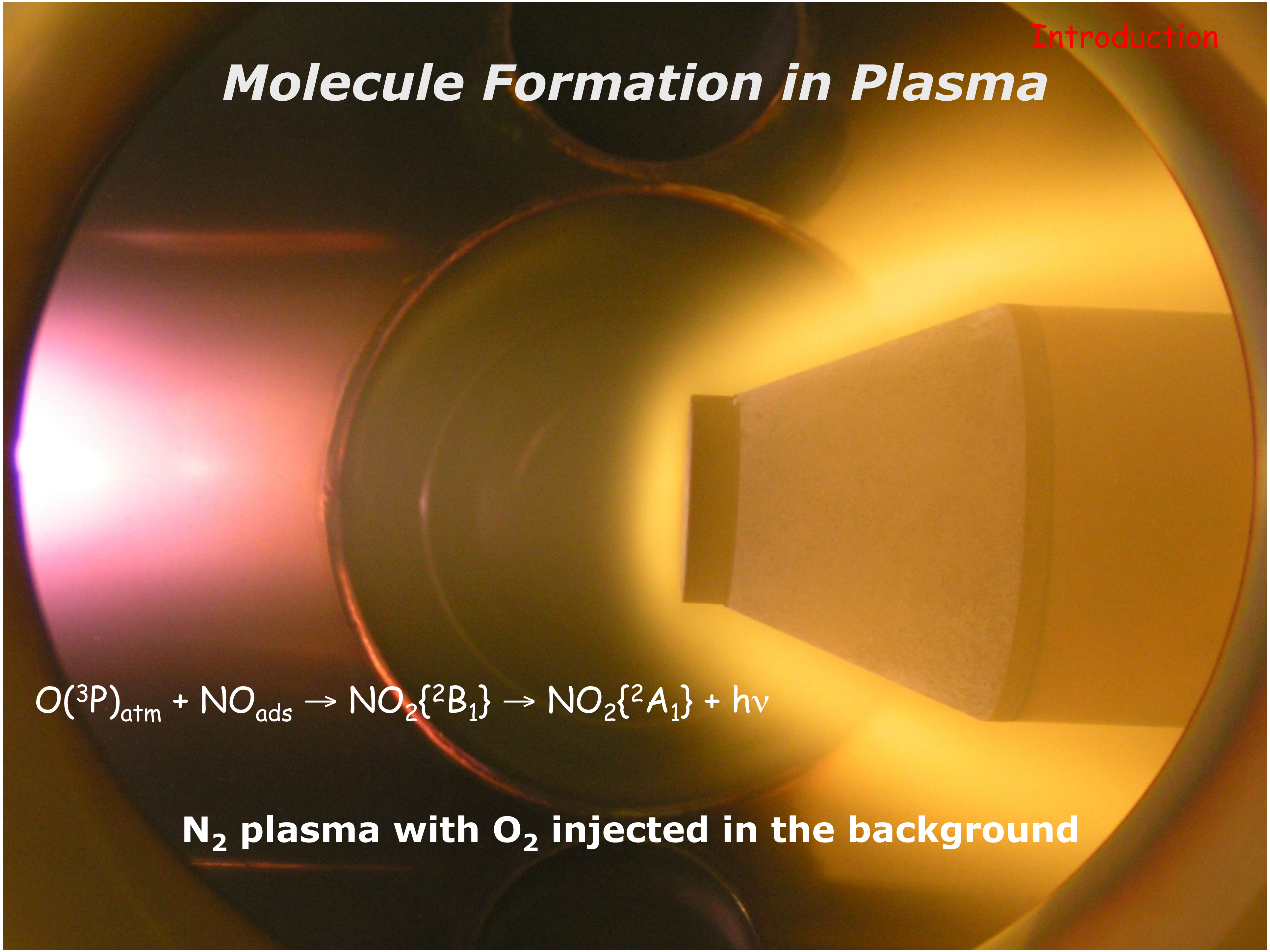
$T_0 = 6000$ K

IR absorption spectroscopy
on
N_2/O_2 plasma

N_2/O_2 plasma setup
(IR diode laser absorption spectroscopy)

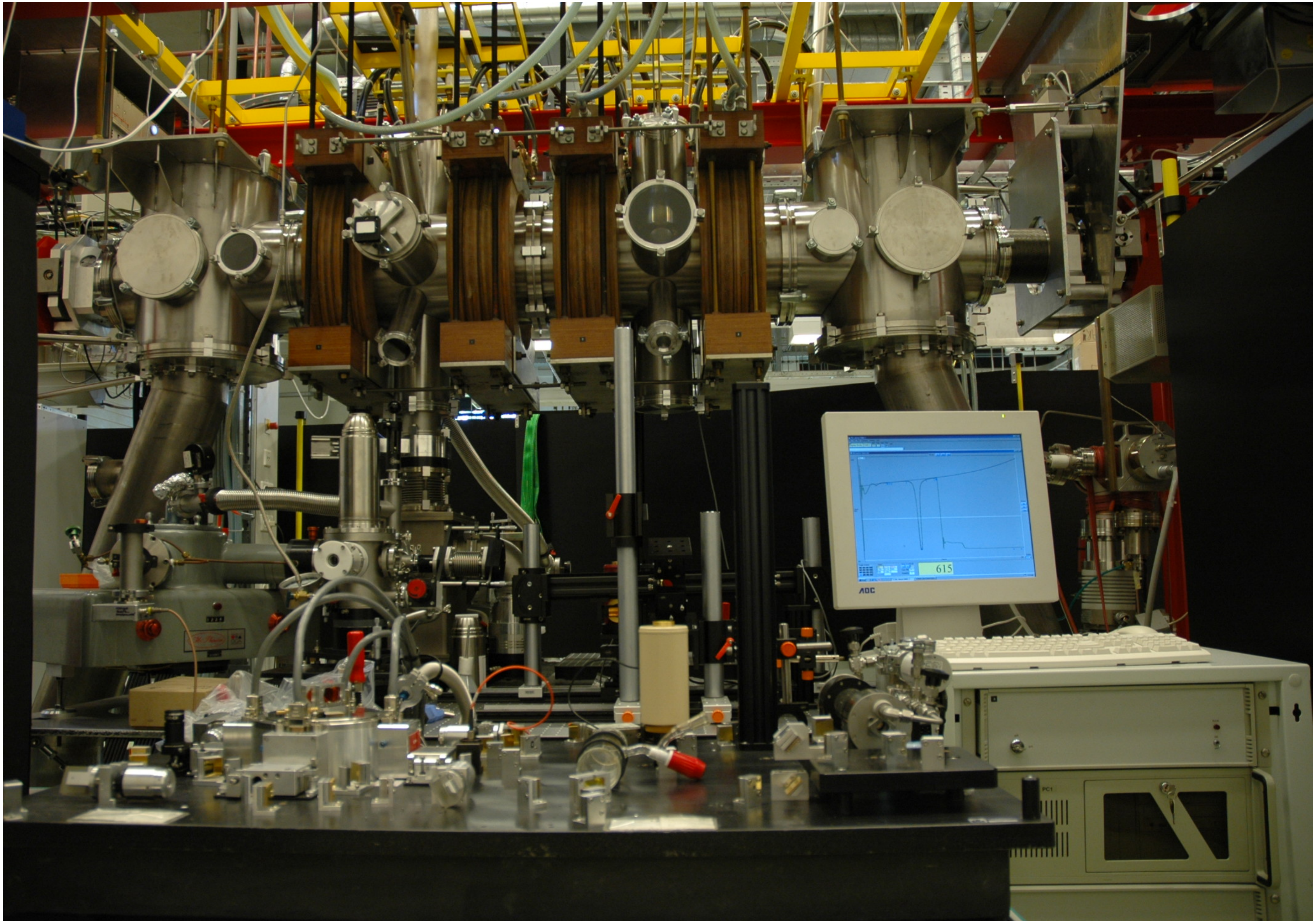


Molecule Formation in Plasma

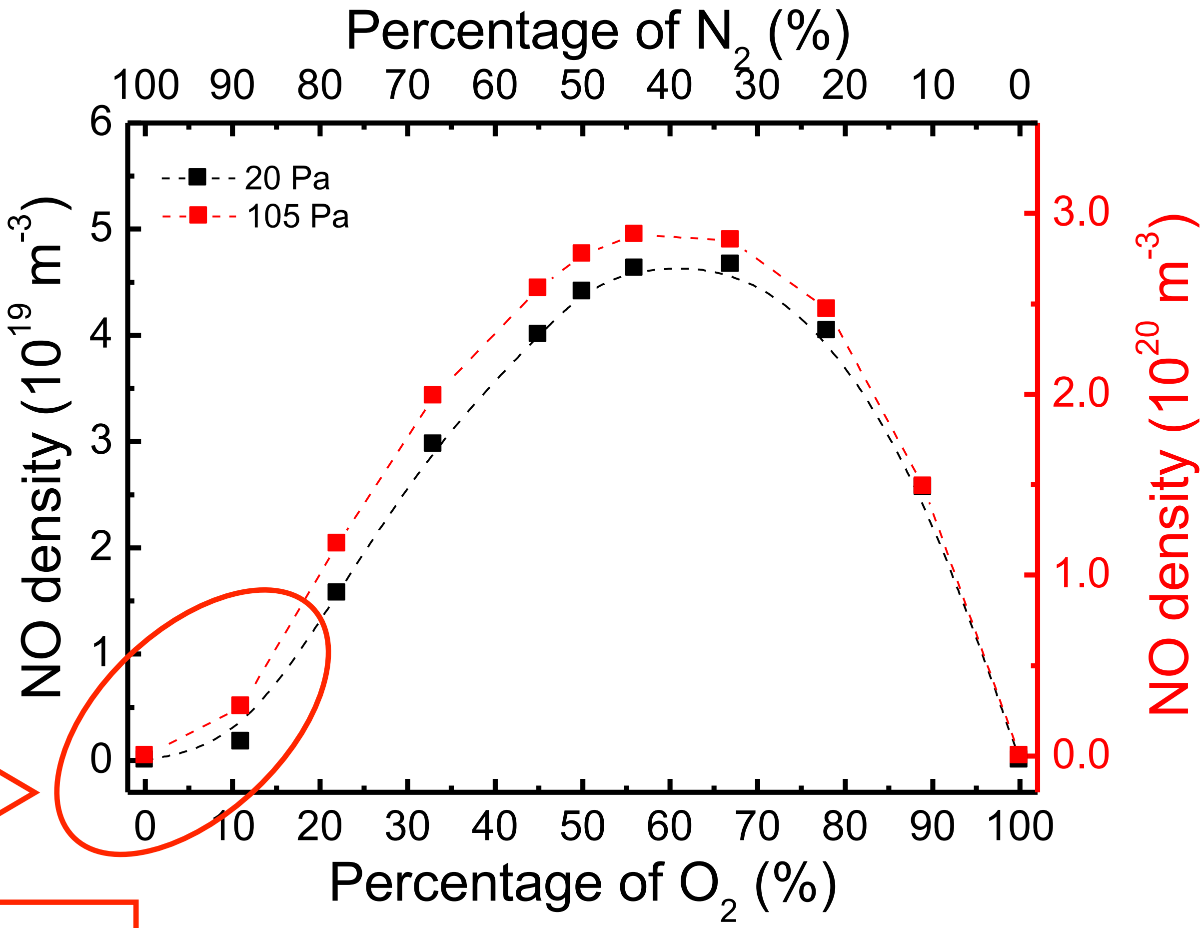


$O(^3P)_{atm} + NO_{ads} \rightarrow NO_2\{^2B_1\} \rightarrow NO_2\{^2A_1\} + h\nu$

N_2 plasma with O_2 injected in the background


615
AOC

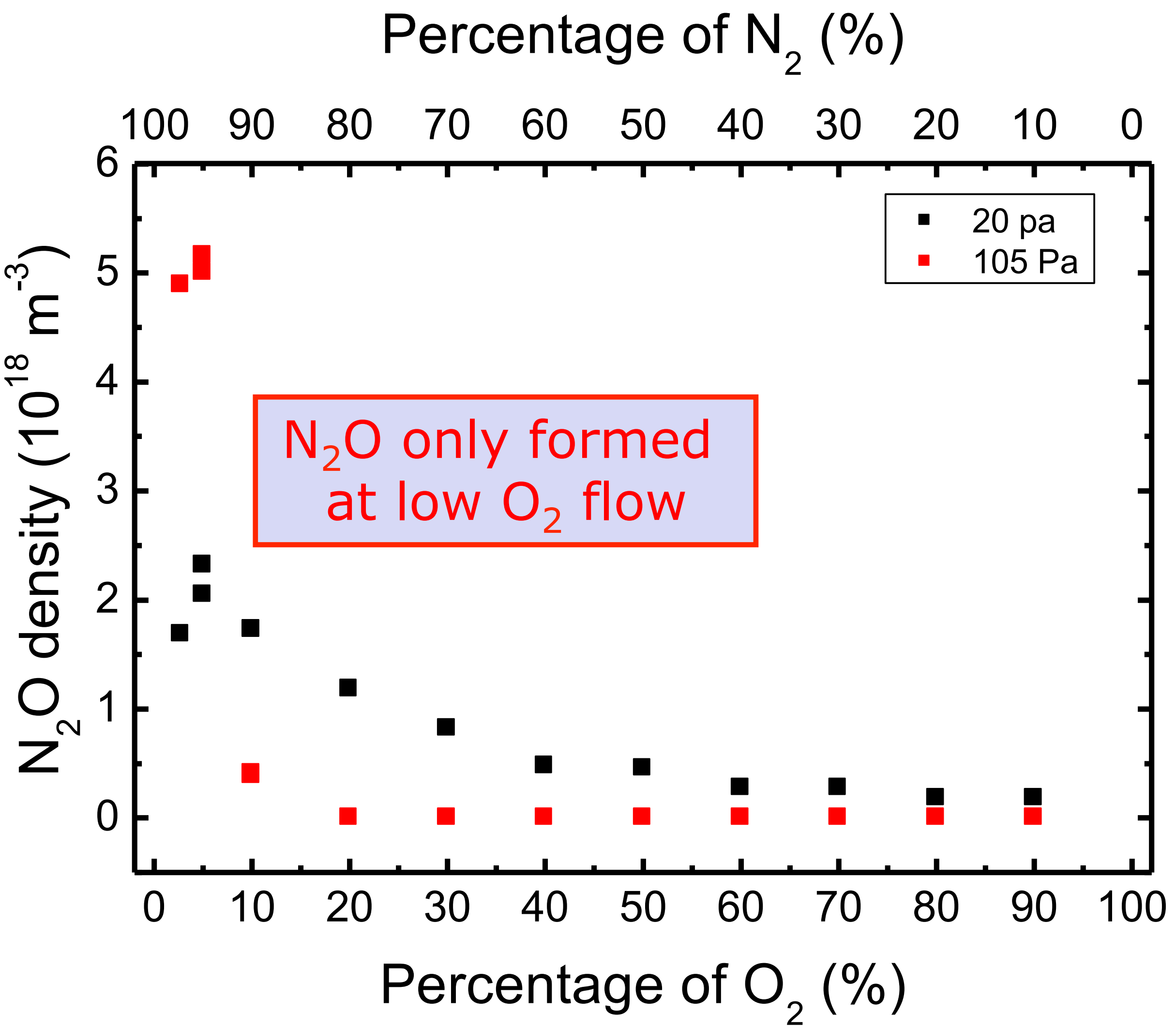
NO formation in an Ar-N_2-O_2 plasma



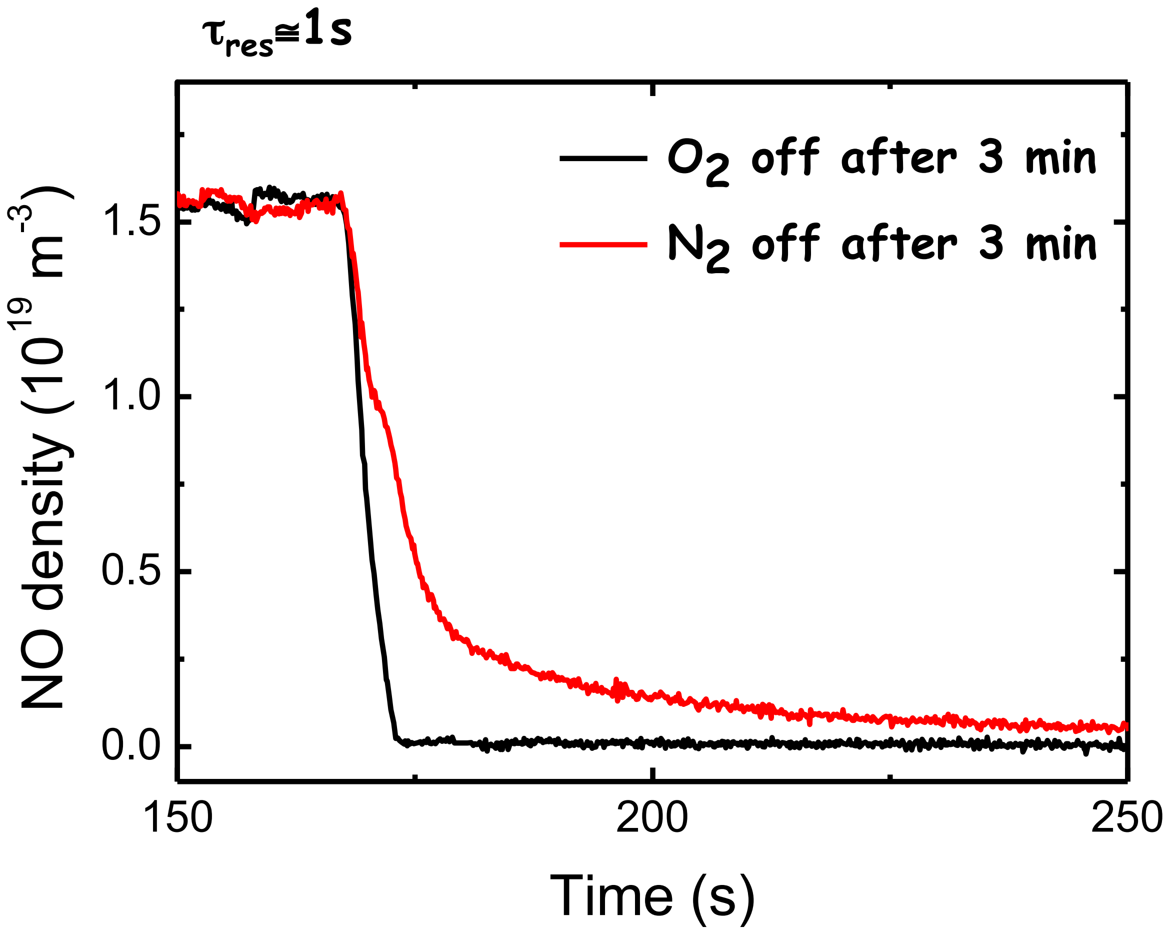
$N + NO \rightarrow N_2 + O$

$N + NO_{ads} \rightarrow N_2O$

N_2O formation in an Ar-N_2-O_2 plasma



Time behavior of NO formation in Ar-N_2-O_2 plasma



no O_2 flow

⇓

no NO formation

no N_2 flow

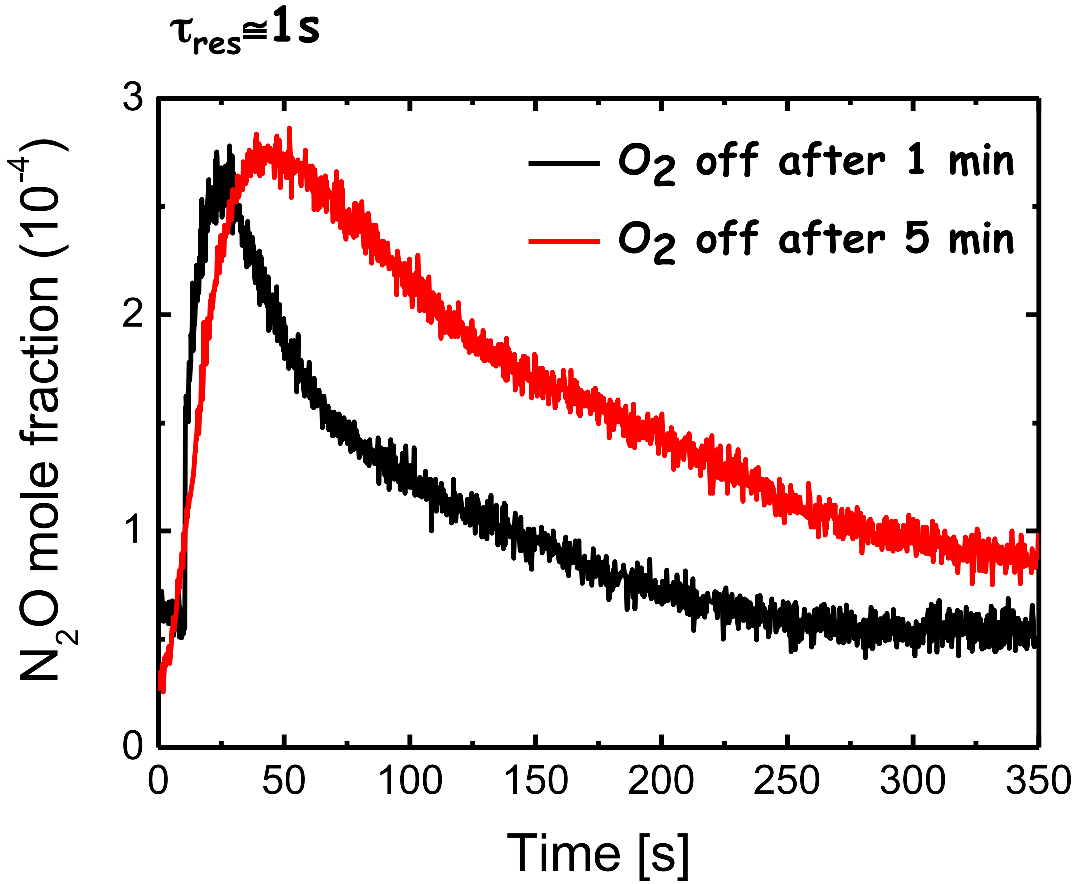
⇓

NO formation >> τ_{res}

N on/in the surface

(no O storage)

Time behavior of N_2O formation in an N_2-O_2 plasma



no O_2 flow

⇓

N_2O formation >> τ_{res}

NO on/in the surface

(depends upon O_2 conditioning)

Conclusions

1. Input gas mixture, N_2 and O_2, changes into a mixture of N_2, O_2 and NO, N_2O and NO_2.
2. Time-resolved measurements show that surfaces become saturated with N atoms and NO radicals.
3. *In Ar-NO plasmas, up to 90% conversion of NO into N_2 and O_2*

VUV-LIF spectroscopy
on
$H_2^{r,v}$ molecules in plasma

Why study hydrogen plasma expansions?
(produced from a cascaded arc)

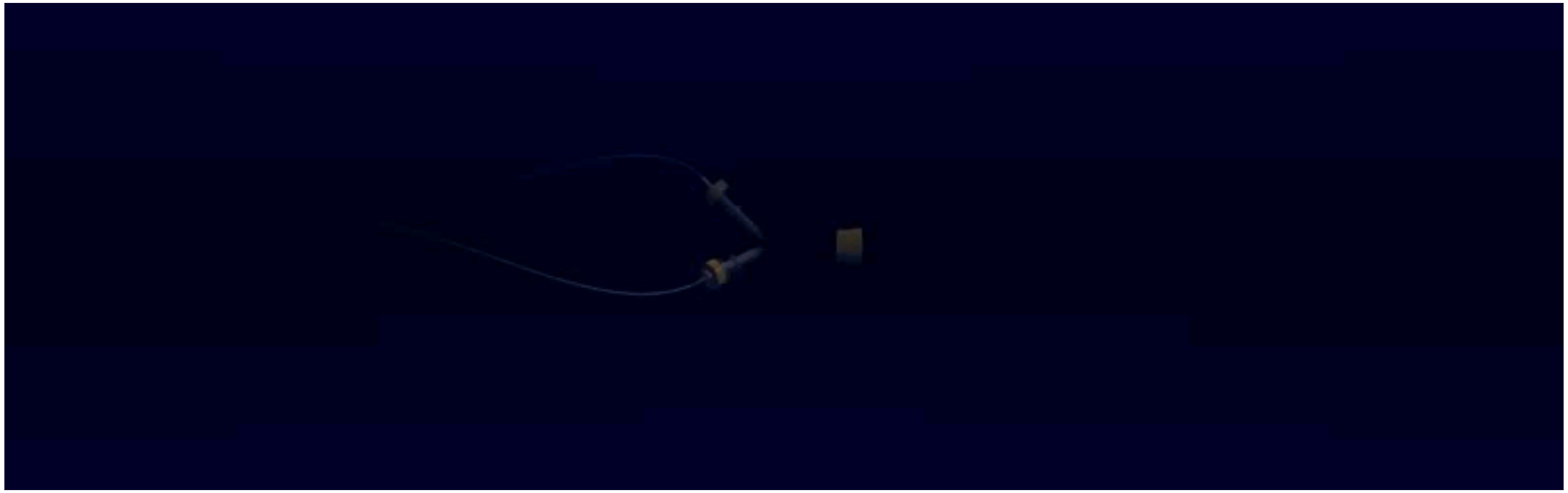
1. Use of H_2 gas in processing plasma application
- etching and cleaning
- passivation during deposition

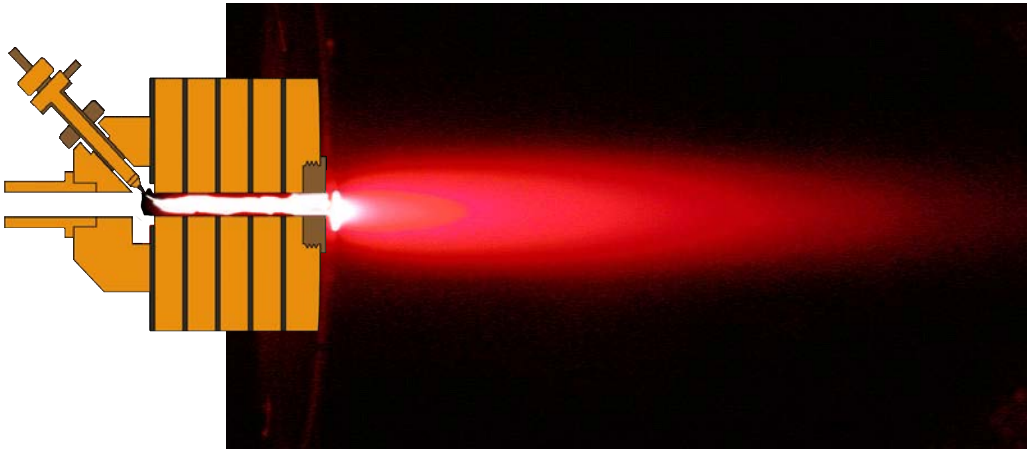
2. Astrophysical interest
- 'hot' H_2, formed at grains through surface association, and acts as precursor in astro-chemistry

3. Fundamental study of H_2/HD/D_2 Lyman transitions
- extension of database

4. The cascaded arc might be used as H^- ion source, because of high fluxes of $H_2^{r,v}$ at low T_e (around 1 eV)

Plasma source and expansion

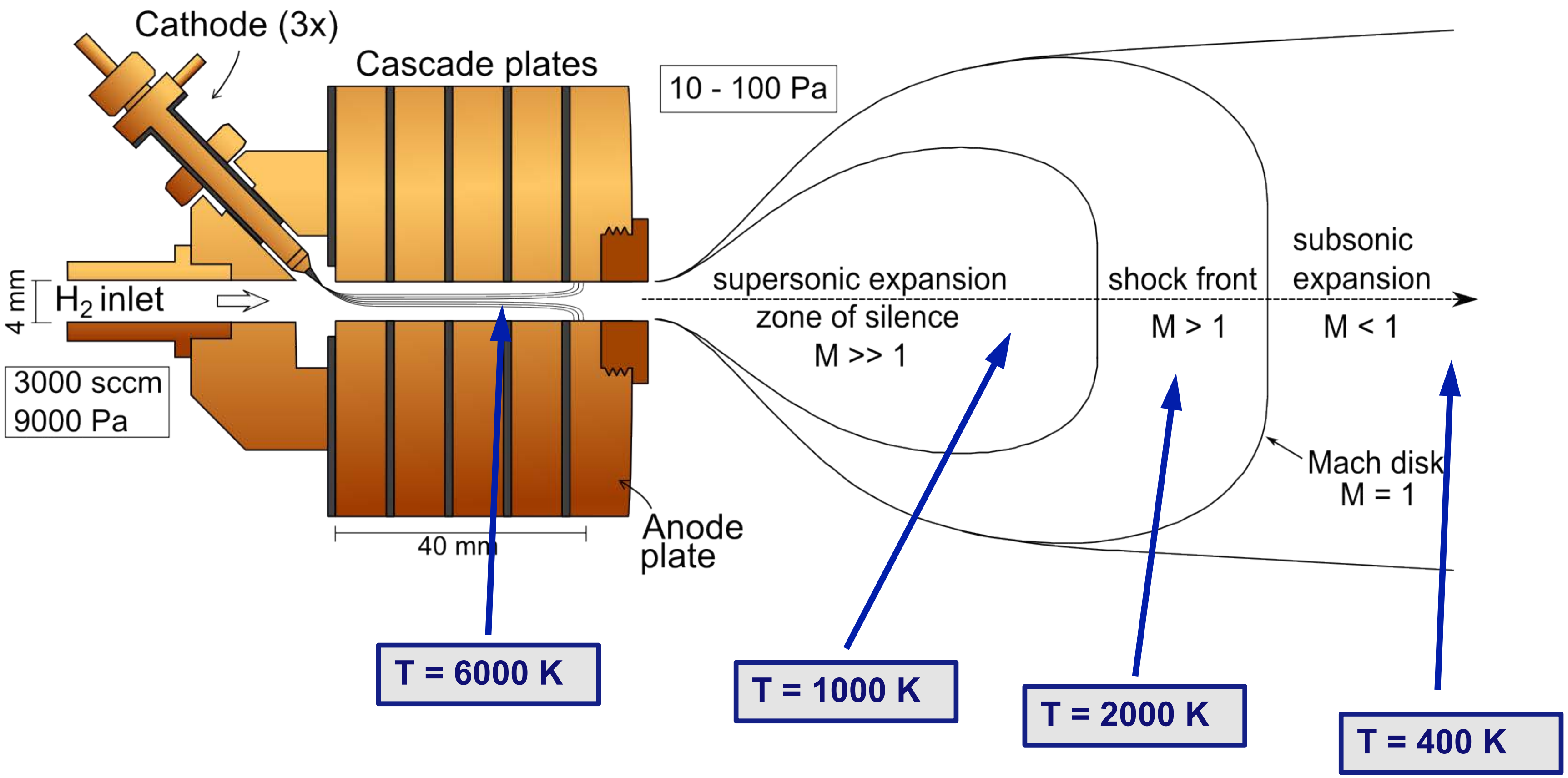




I	= 40 – 60 A
P	= 5 – 10 kW
Φ_{arc}	= 3 slm

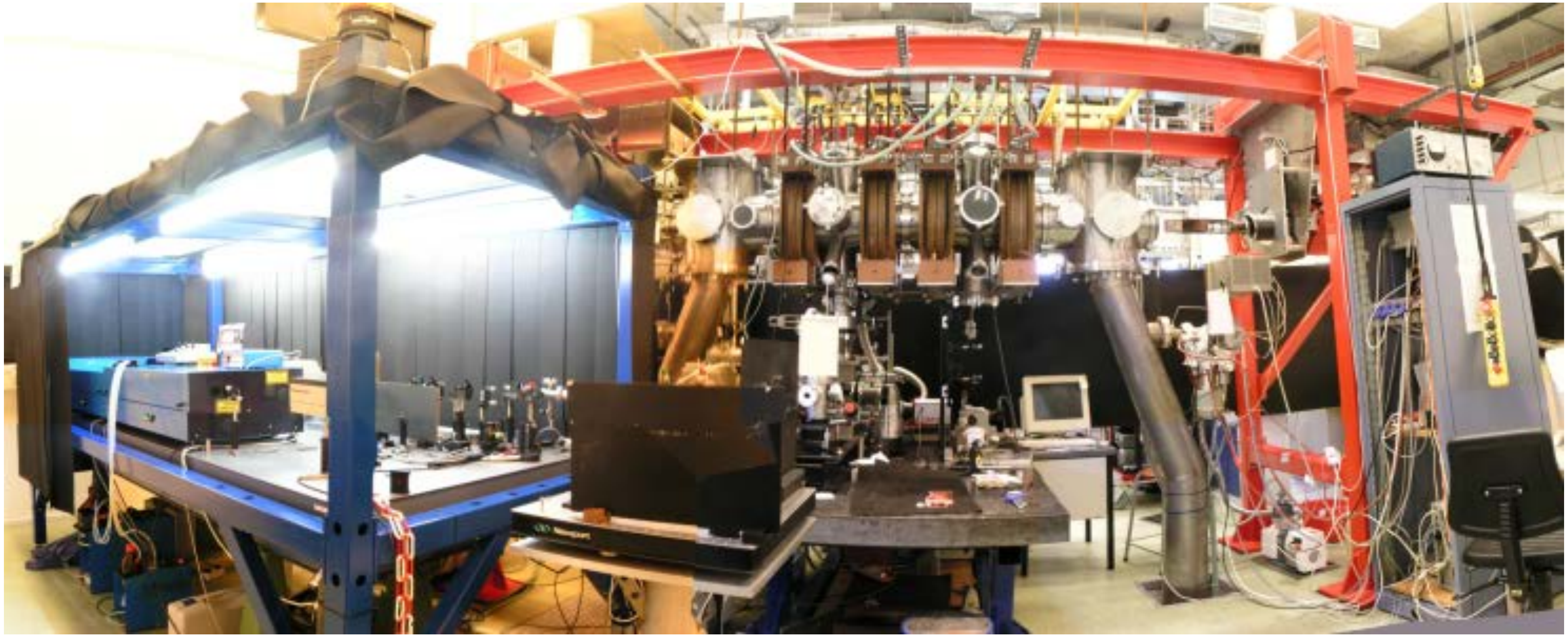
p_{arc}	= 0.2×10^5 Pa
p_{bg}	= 100 Pa

Plasma expansion



PLEXIS setup

PLEXIS setup



Laser table
Nd:YAG
(450 mJ/shot @ 355 nm)
dye laser
(50 mJ/shot @ 460 nm)
(8 mJ/shot @ 230 nm)

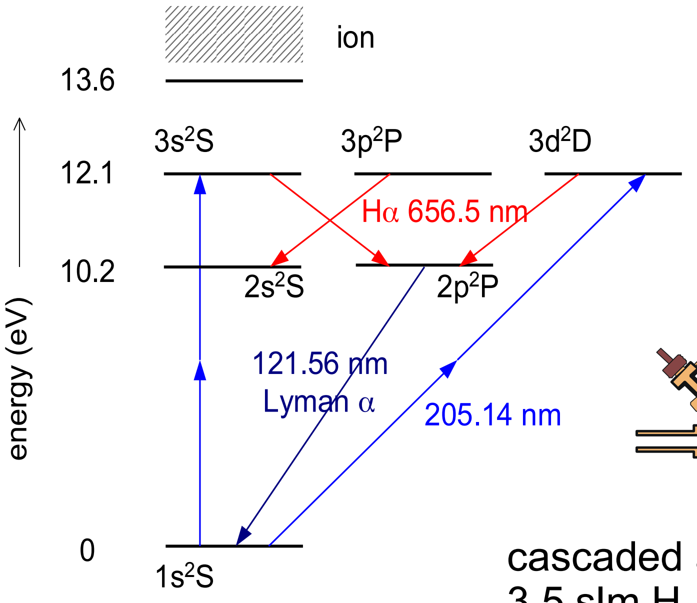
Vacuum chamber
cylindrical (2m x 0.3m)
9 Pa / 3000 sccm H_2

- Movable plasma source and substrate

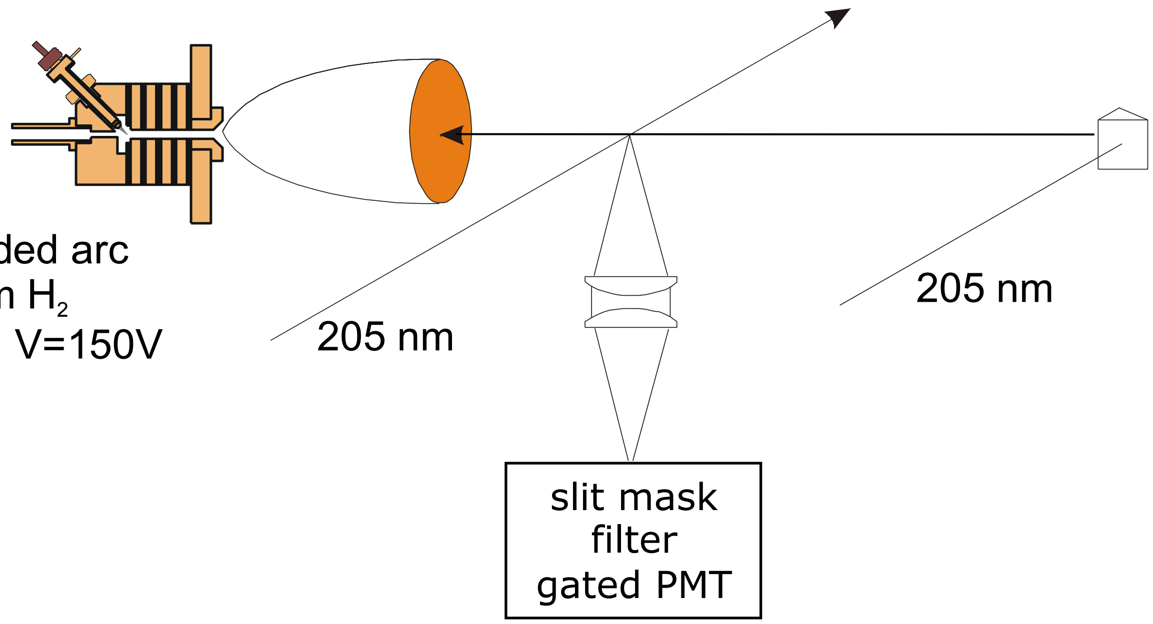
- Axial magnetic field B_{max} = 0.2 T

Ar/H_2 plasma expansion

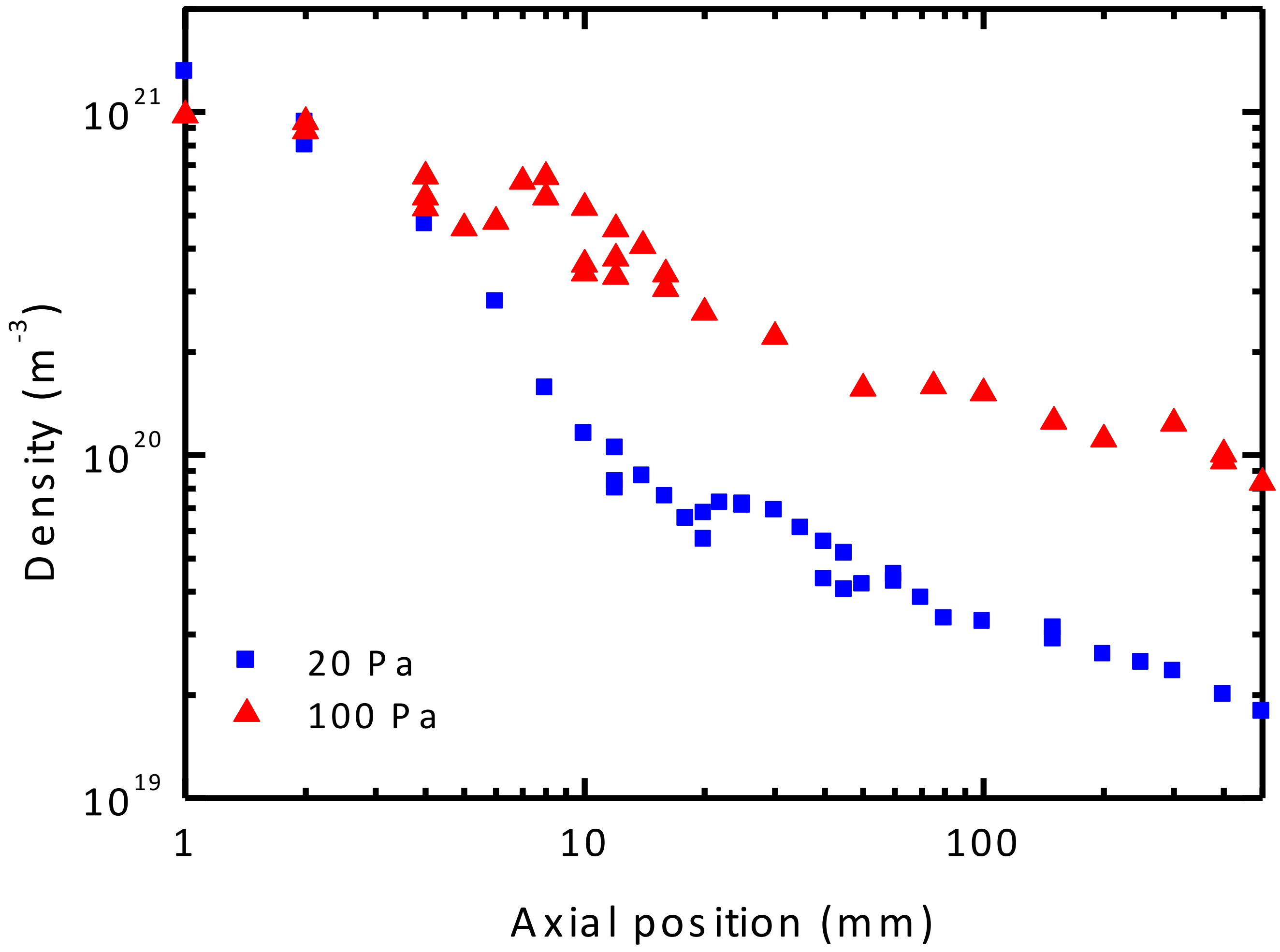
Two photon Absorption LIF (TALIF) on atomic hydrogen



- Produce 205 nm via THG of a Nd:YAG pumped dye laser
- From spectral scans data on: n,T,v,f(v)



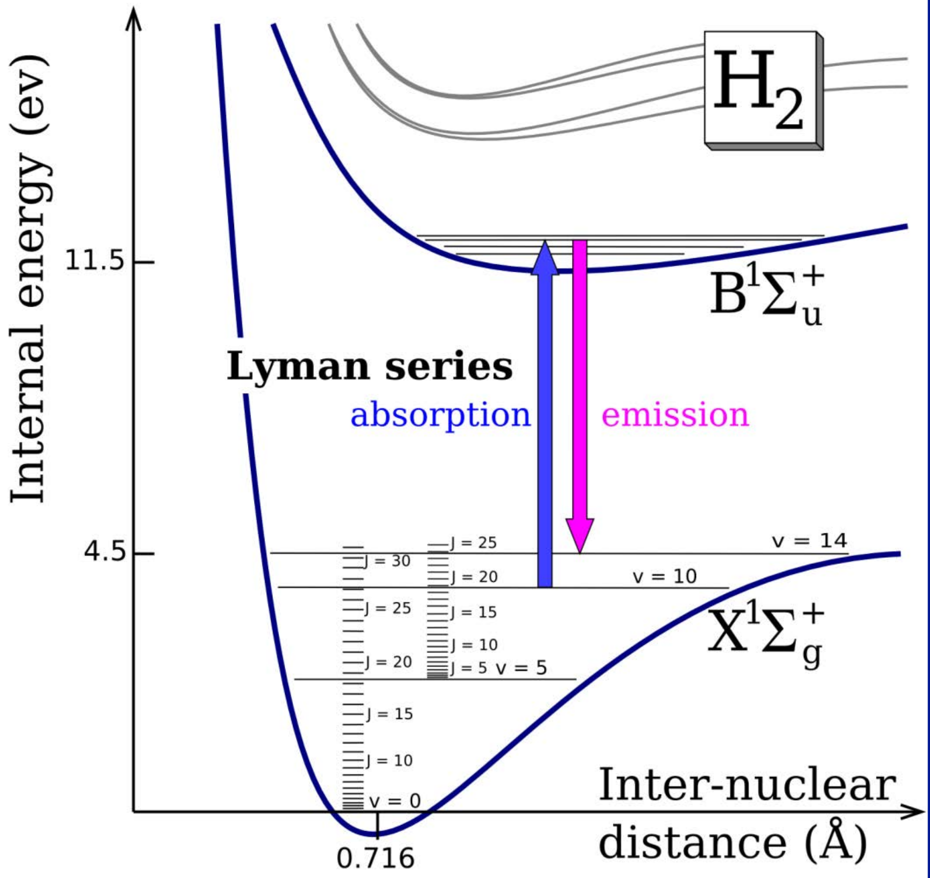
H atom density in H_2 plasma expansion (TALIF)



Mazouffre et al. *Phys. Rev.* **E 64**, 016411 (2001)

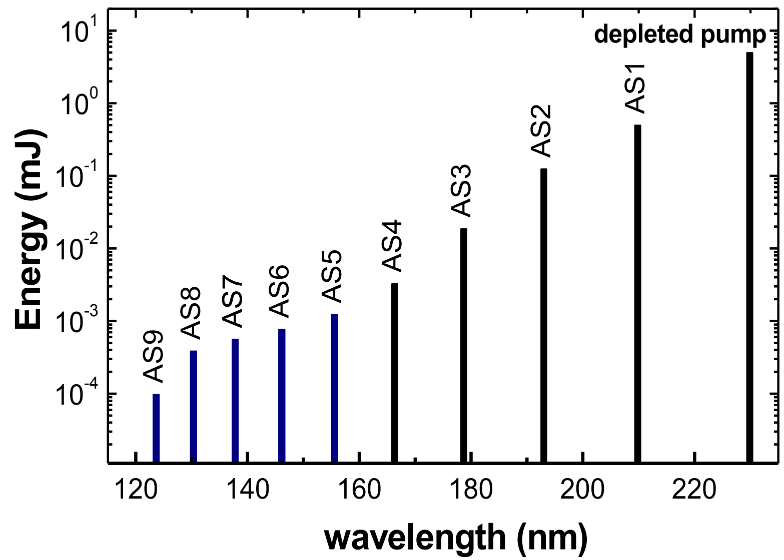
VUV-LIF detection of $H_2^{r,v}$

H_2 energy scheme

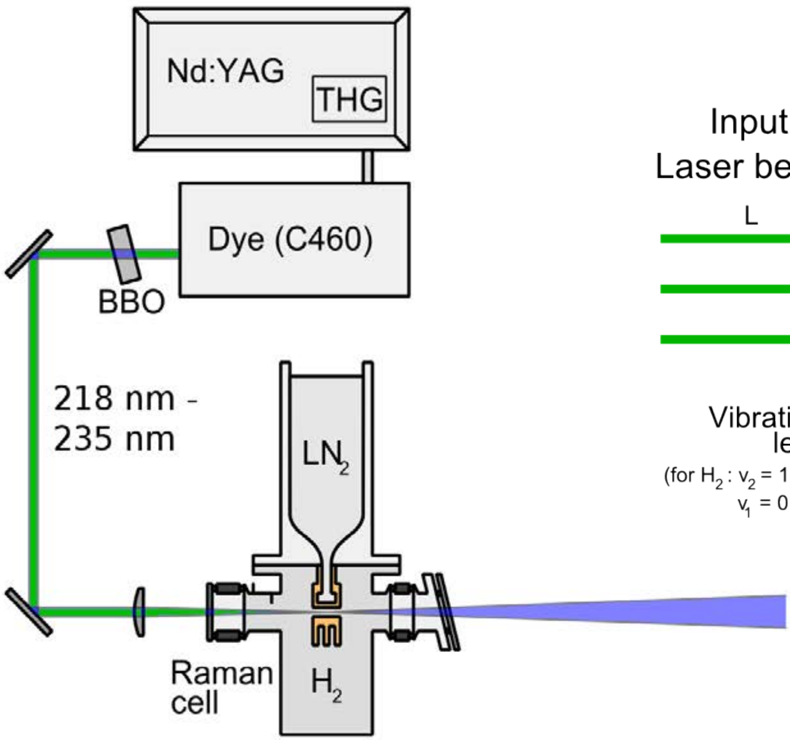


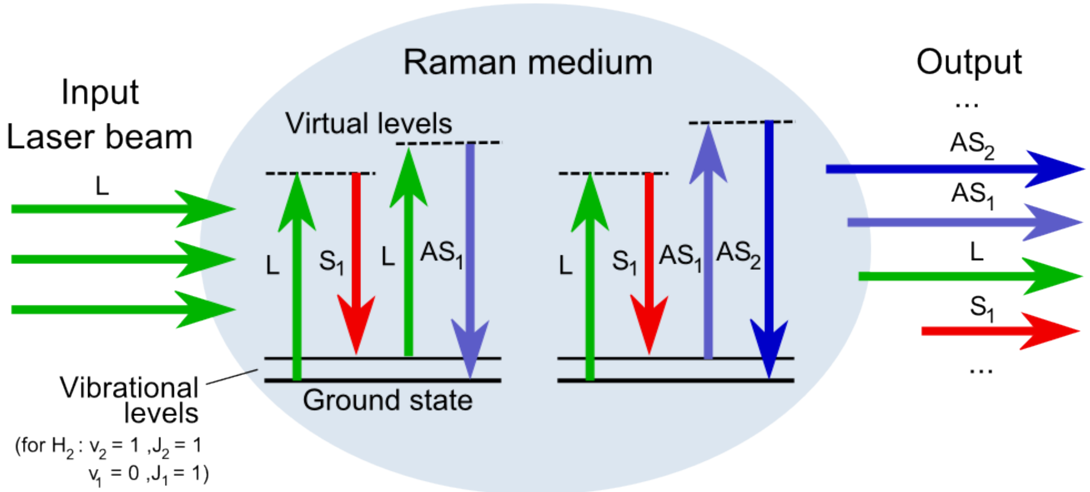
Excitation and detection

- X → B transition in H_2 (~11 eV)
- Detection of fluorescence in the VUV range
- Excitation with 120 – 165 nm photons, produced via SARS



SARS technique



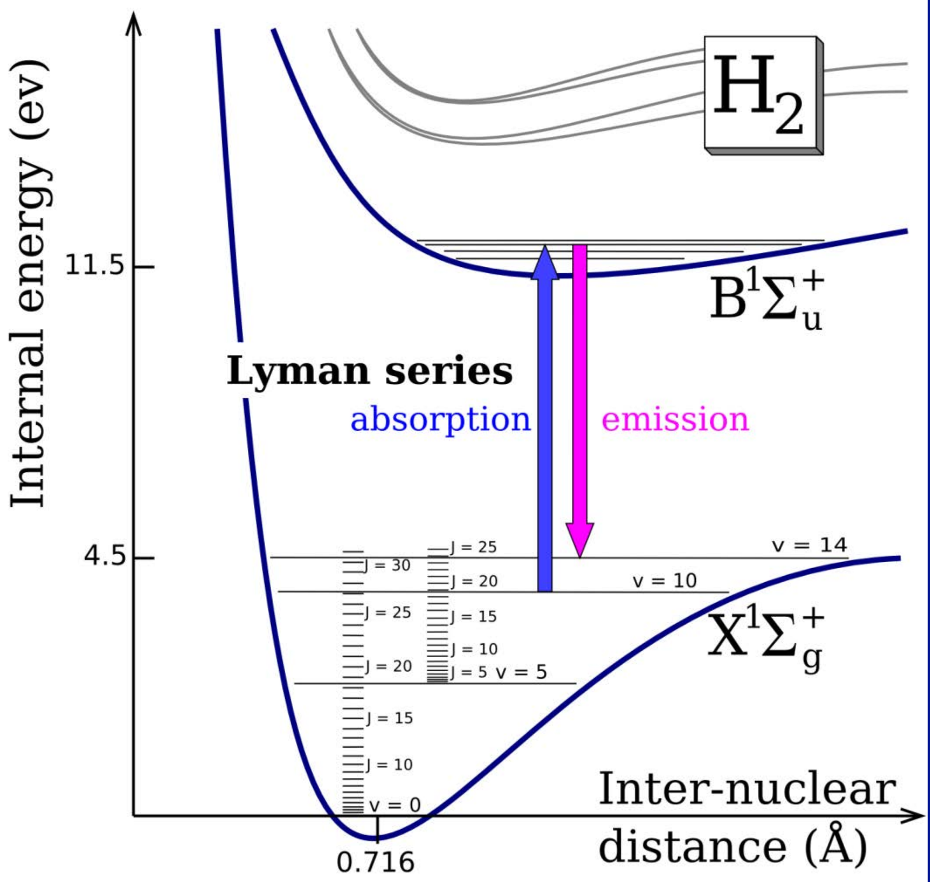


Four-wave mixing process

M. Spaan, A. Goehlich, V. Schultz-von der Gathen, H. F. Döbele, *Applied Optics* **33** (1994) 3865
T. Mosbach, H. M. Katsch, H. F. Döbele, *Rev. Sci. Instrum*. **85** (2000) 3420
P. Vankan, S.B.S. Heil, S. Mazouffre, R. Engeln and D.C. Schram, H. F. Döbele, *Rev. Sci. Instrum*. **75** (2004) 996

VUV-LIF detection of $H_2^{r,v}$

H_2 energy scheme



Excitation and detection

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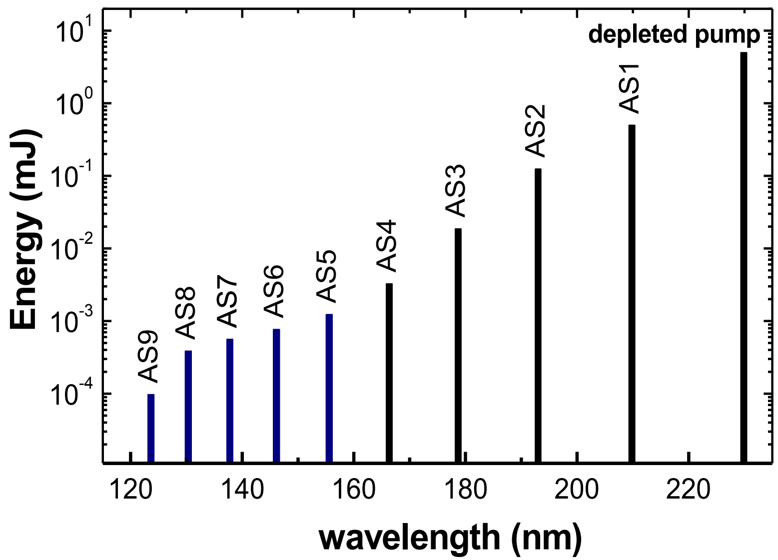
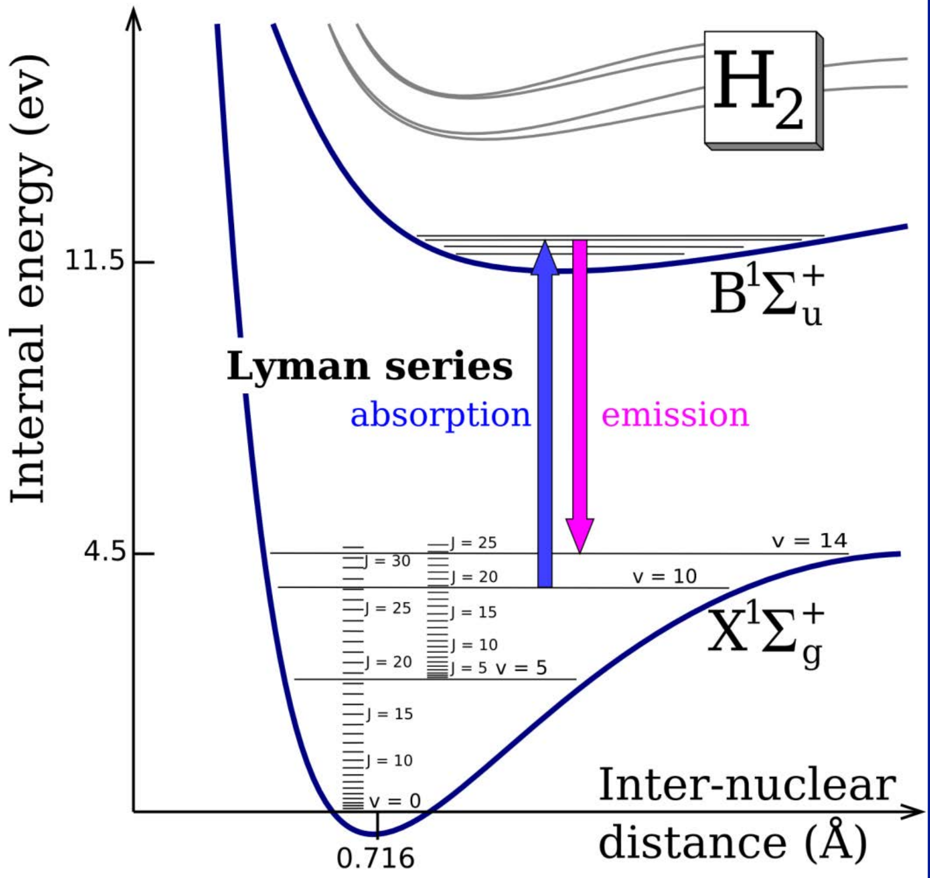
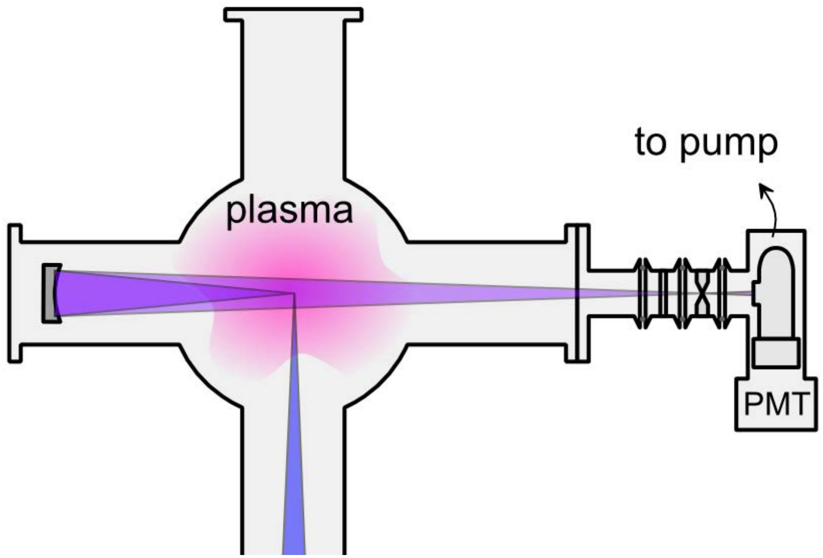


VUV-LIF detection of $H_2^{r,v}$

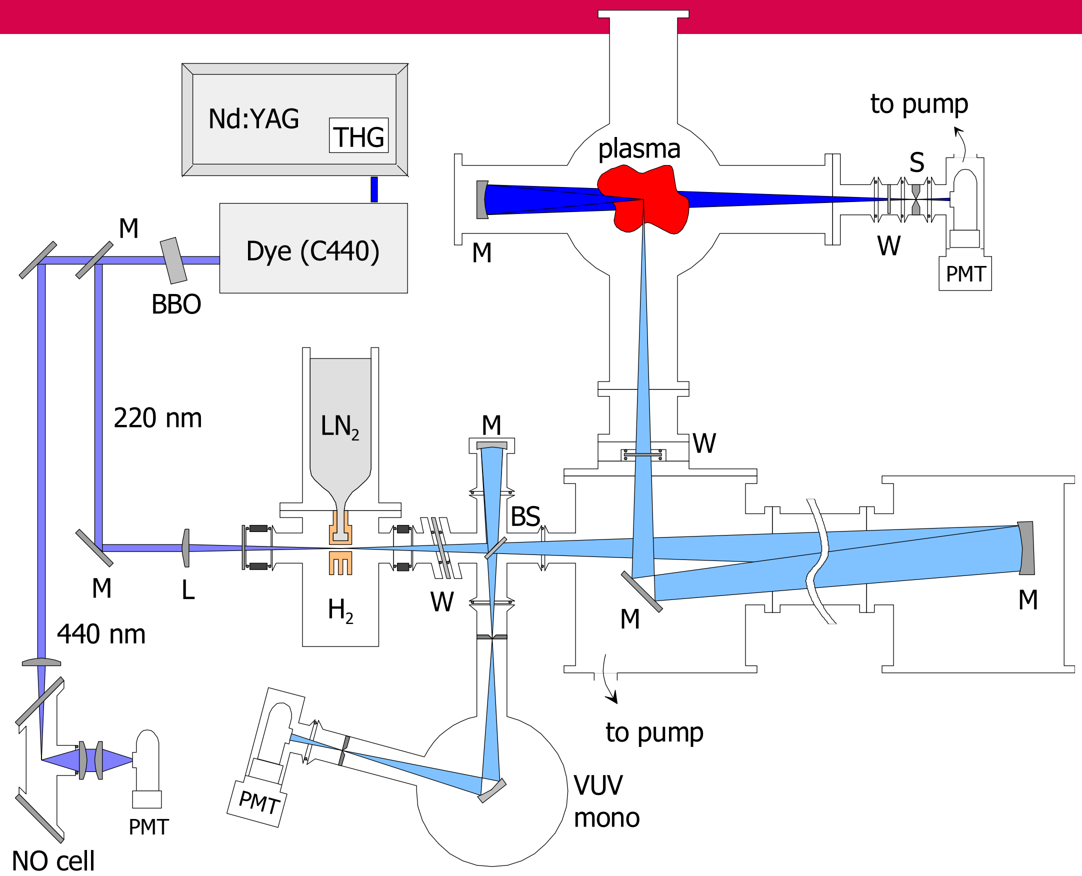
H_2 energy scheme



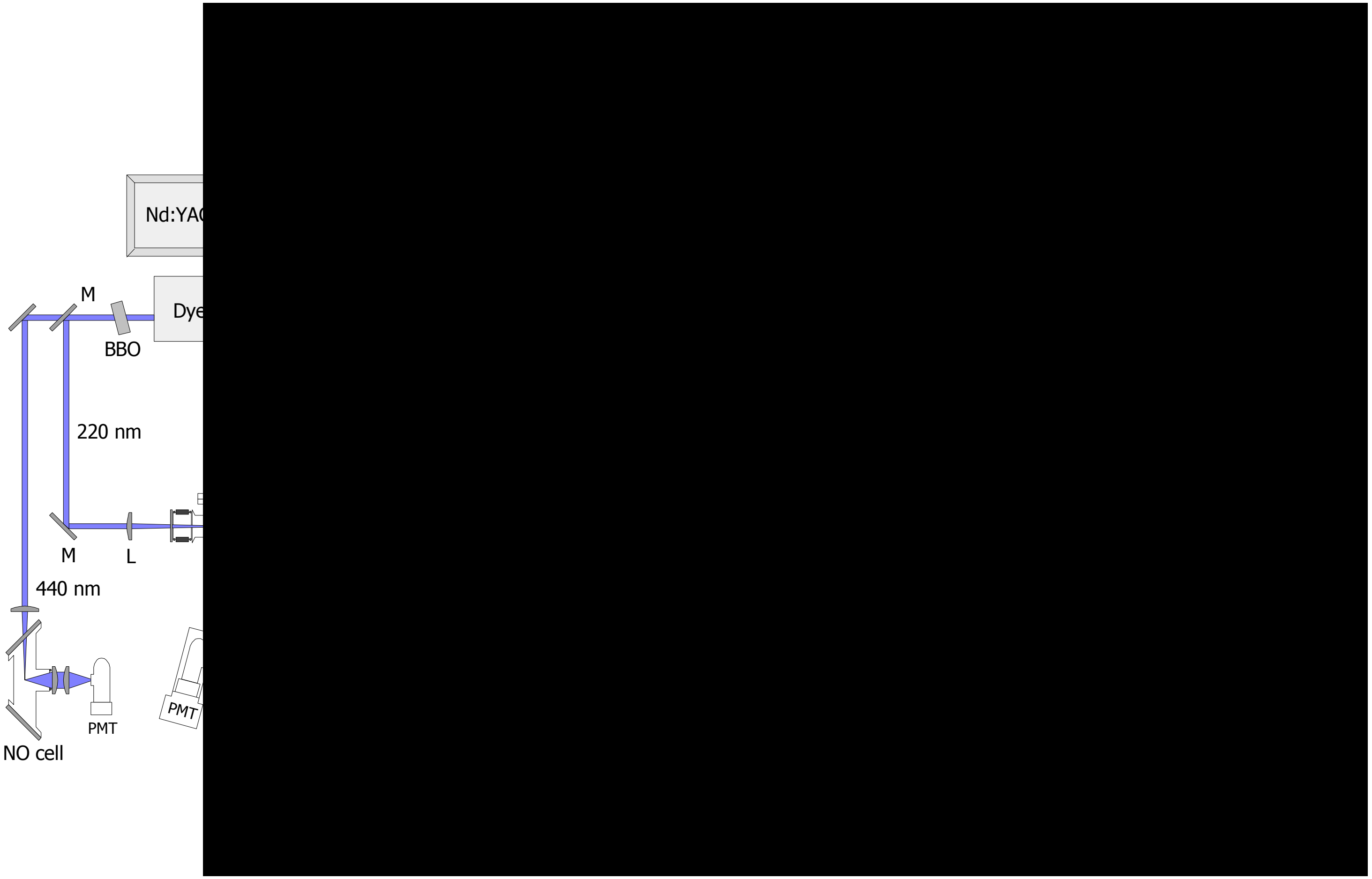
VUV-LIF detection scheme



VUV-LIF setup

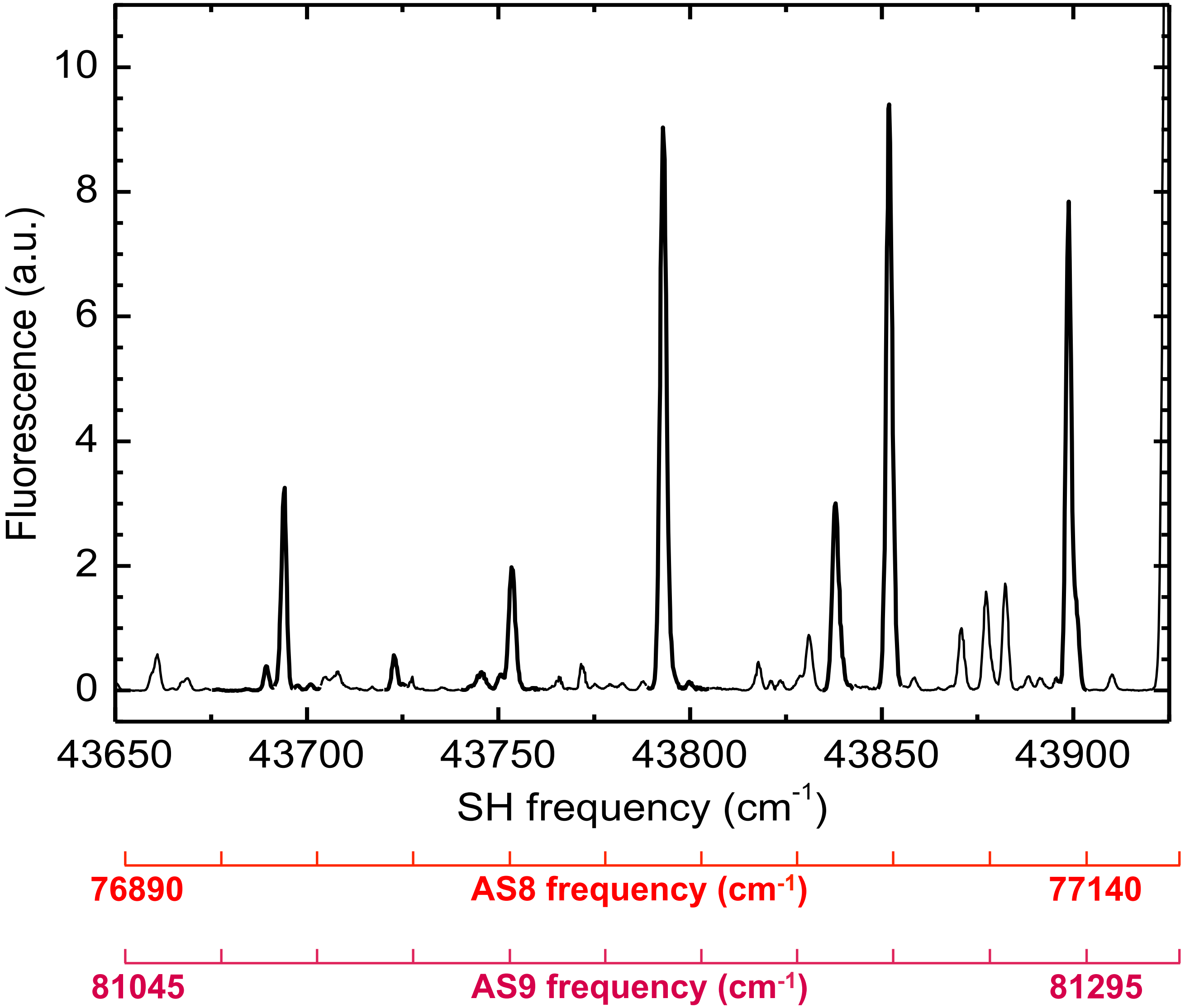


VUV-LIF setup

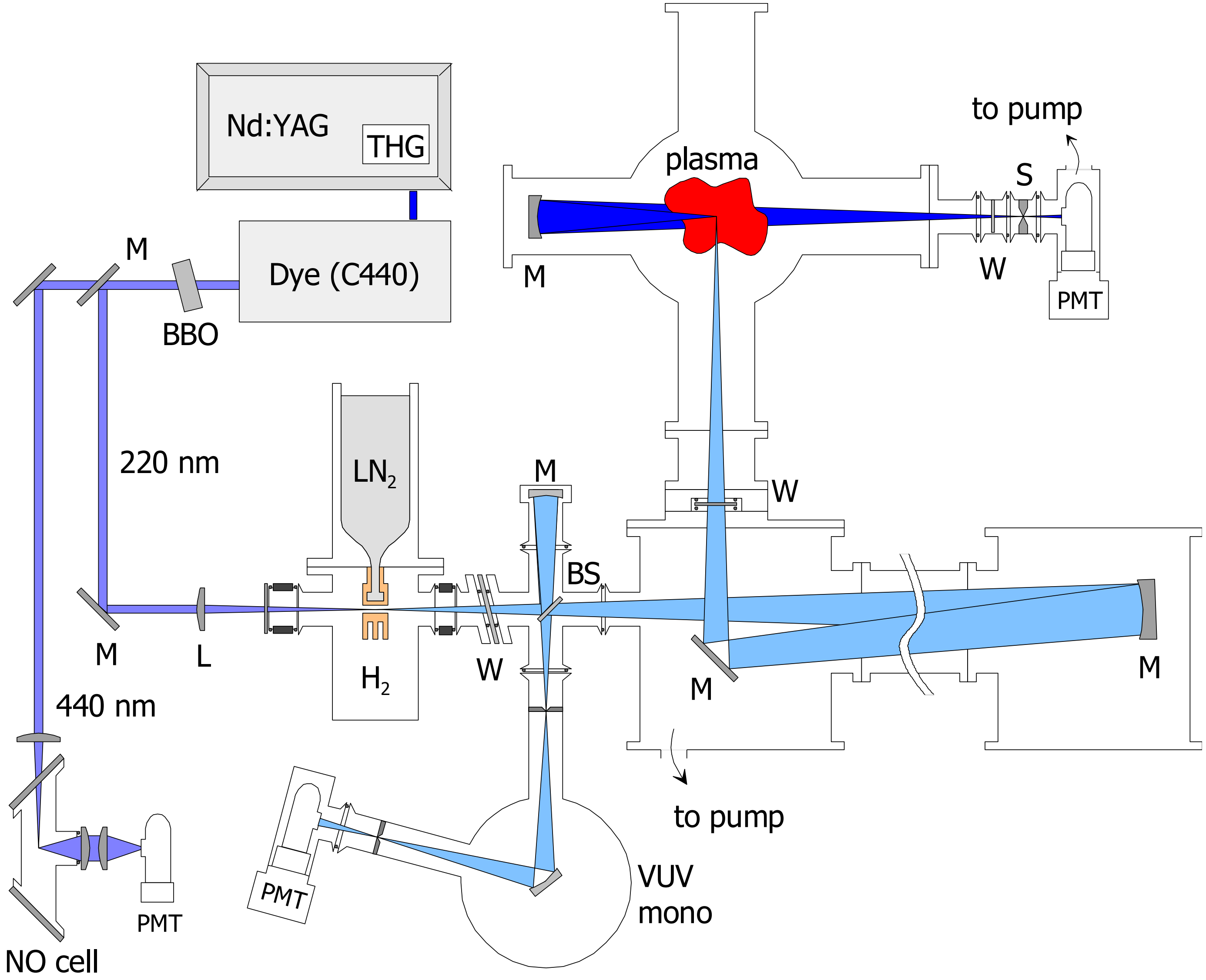


[redacted]

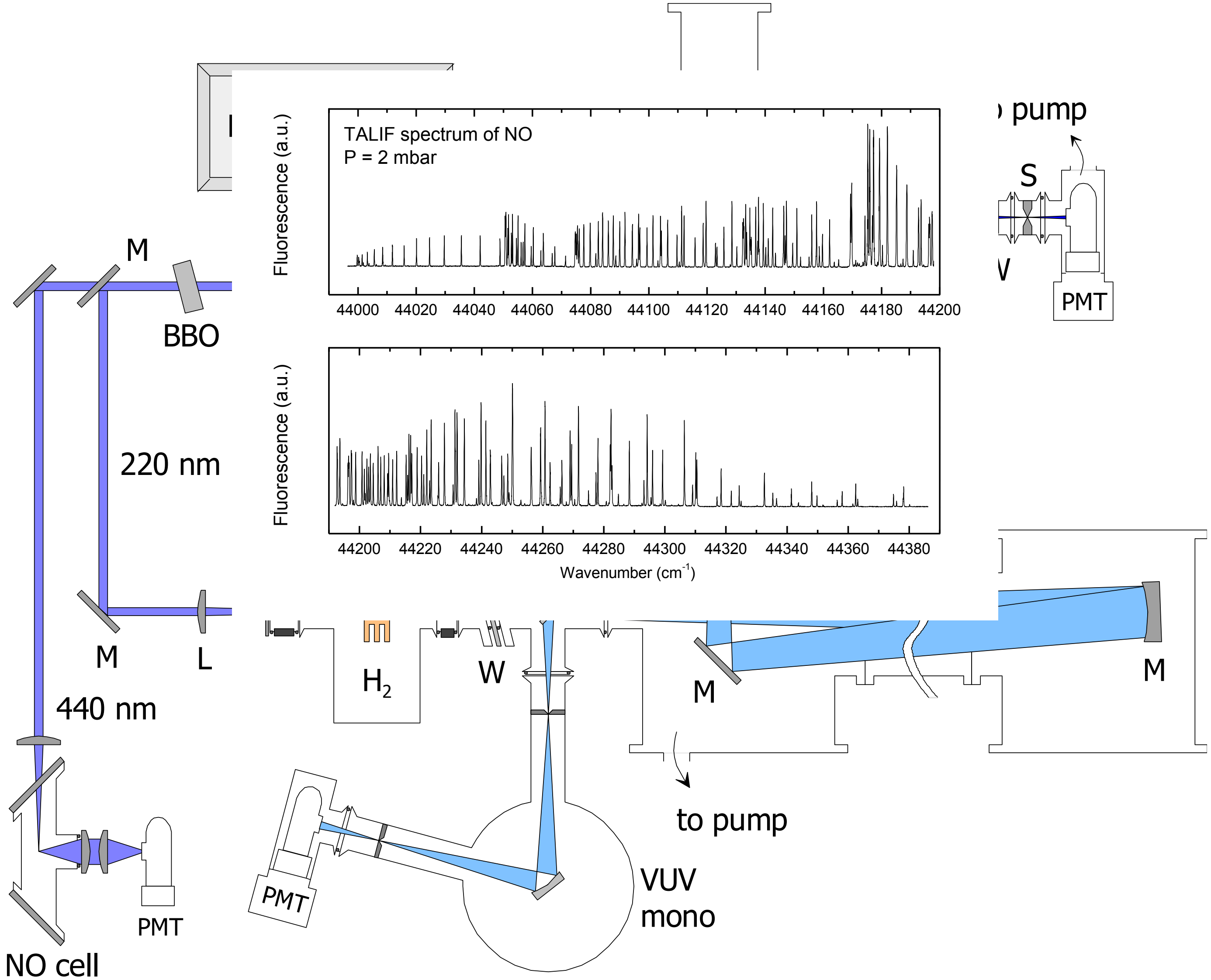
Measured H_2 Lyman spectrum



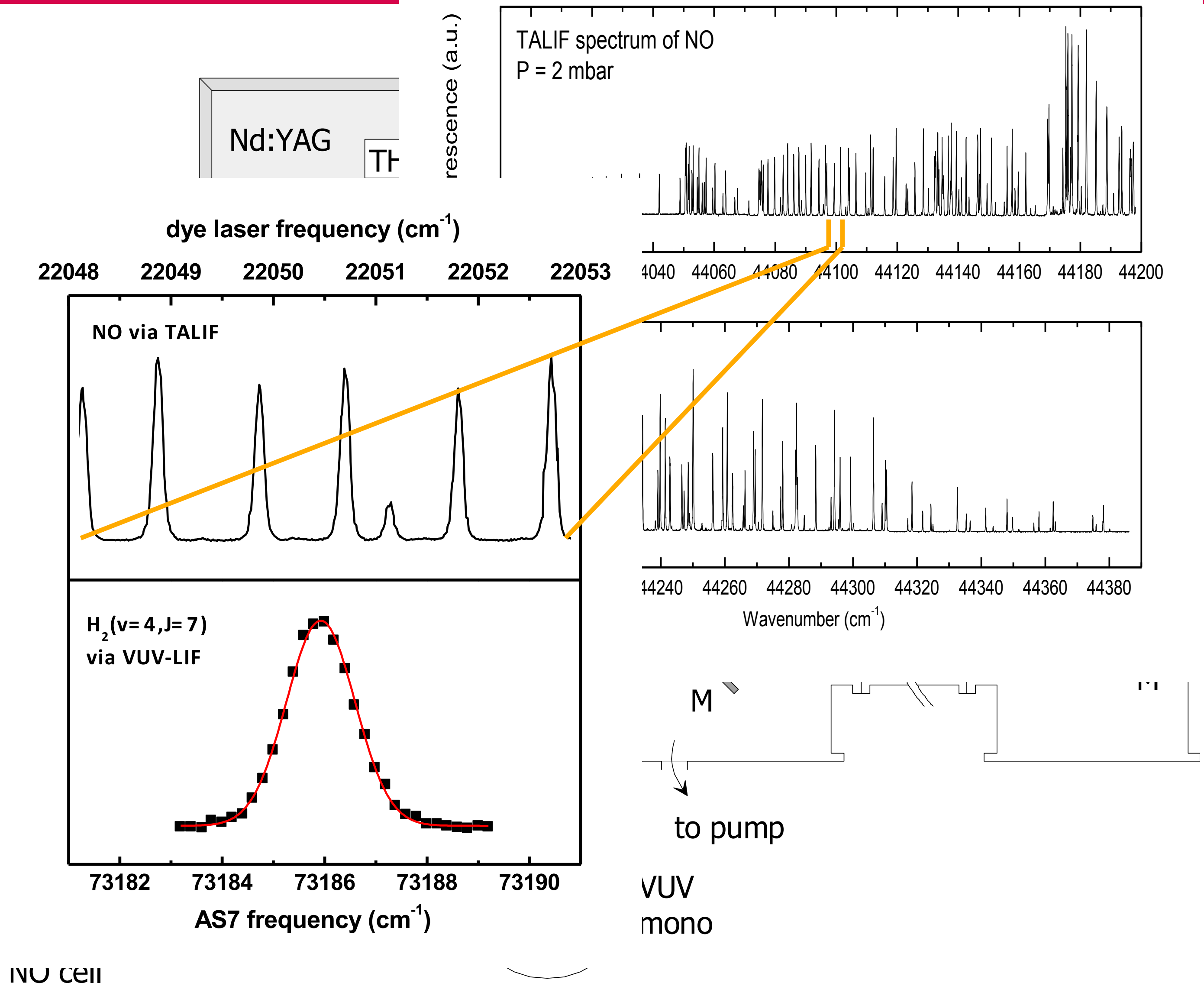
VUV-LIF setup



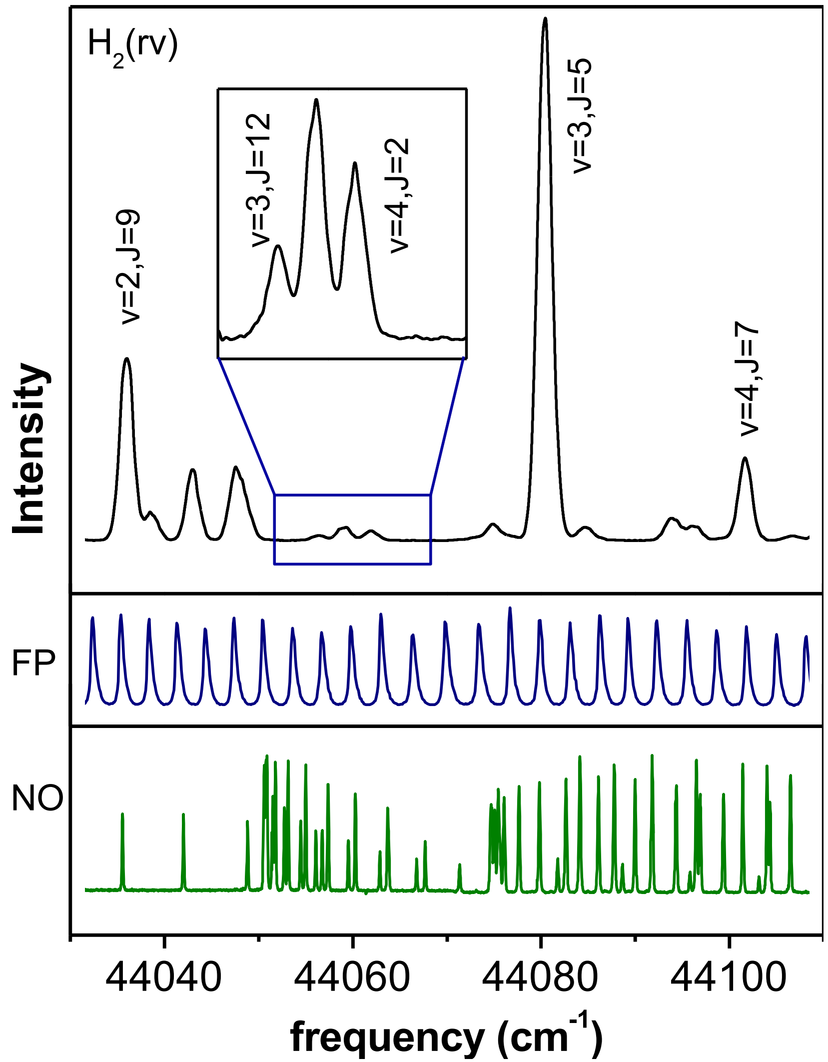
VUV-LIF setup



VUV-LIF spectroscopy



Measured H_2 Lyman spectrum



state-selective

spatially resolved

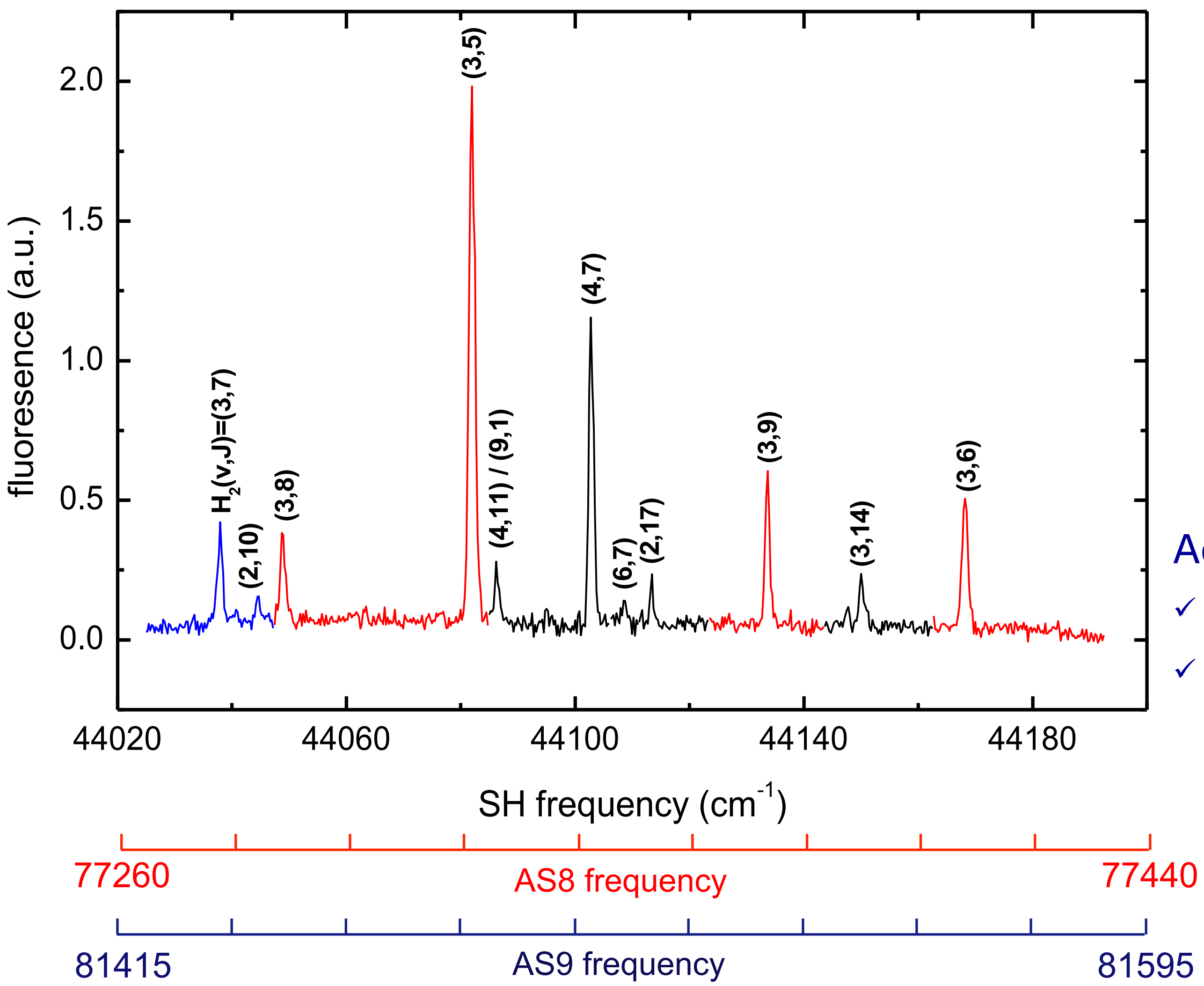
non-intrusive

dynamic range > 4 orders

detection limit ~ 10^{13} m^{-3}

P. Vankan et al., *Rev. Sci. Instrum.* **75** (2004) 996

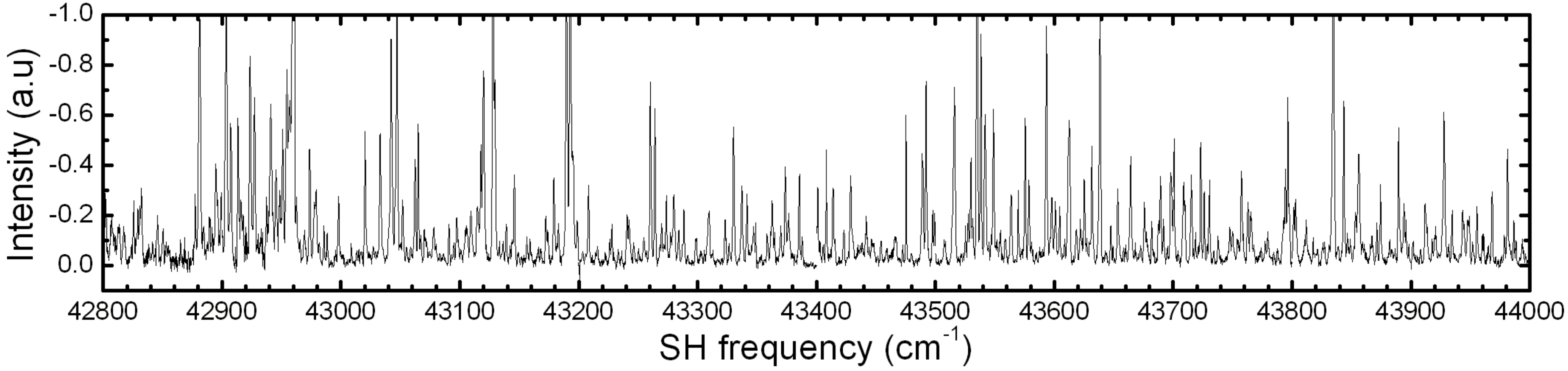
Measured H_2 Lyman spectrum

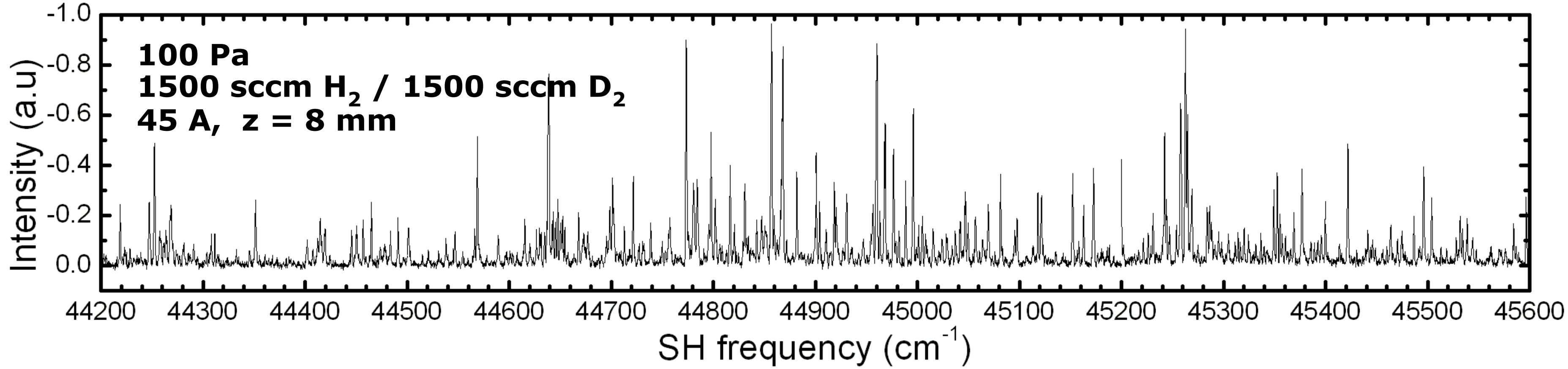


Advantages multiplexing:

- ✓ **spectrum more dense**
- ✓ **efficient measurement**

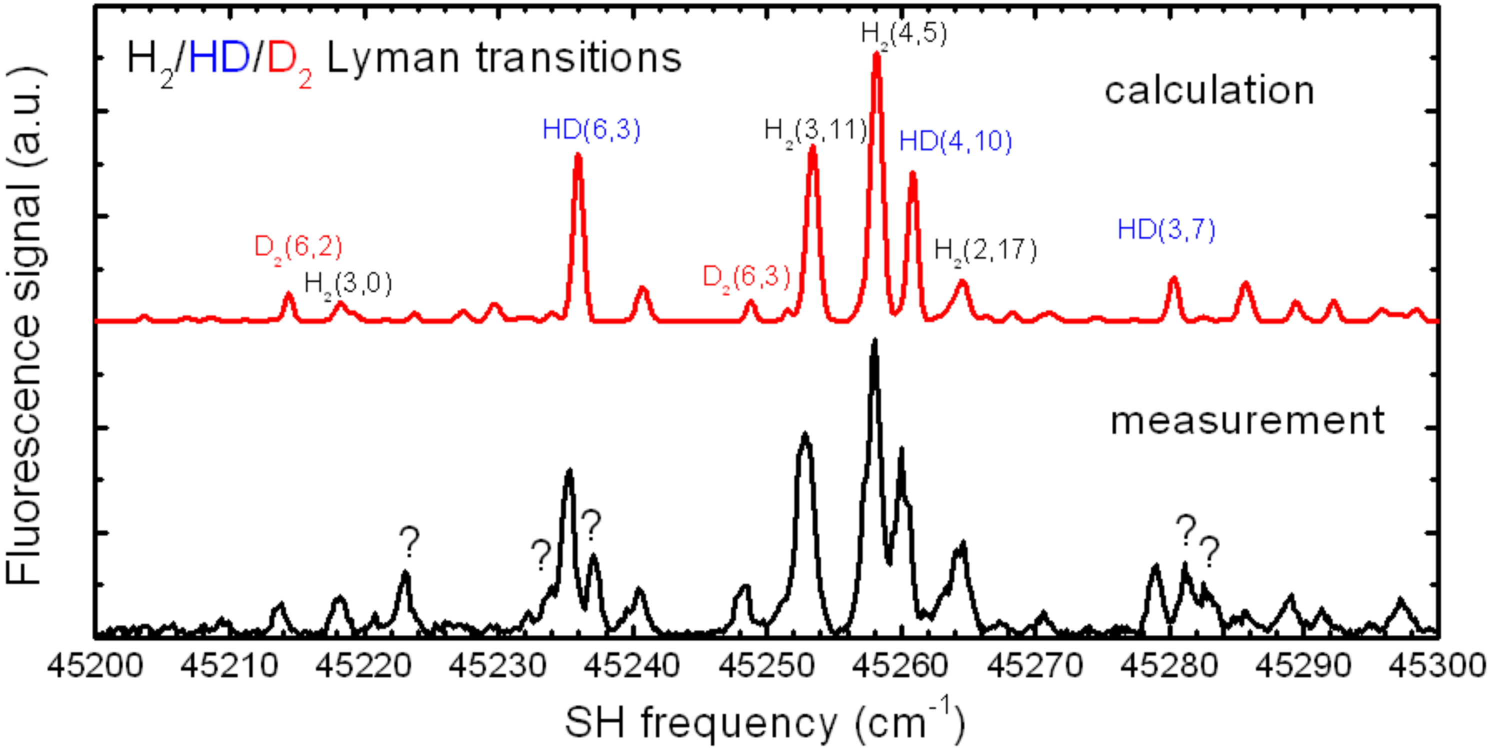
Measured H_2/HD/D_2 Lyman spectra





O. Gabriel et al. *Chemical Physics Letters* 451 (2008) 204

Measured and calculated H_2/HD/D_2 Lyman spectrum



Spectroscopic data for H_2

H. Abgrall et al. *Astron. Astrophys. Suppl. Ser.* 101 (1993) 273

All H_2 Lyman transitions

Spectroscopic data for HD

H. Abgrall, E. Roueff, *Astron. Astrophys.* 445 (2006) 361

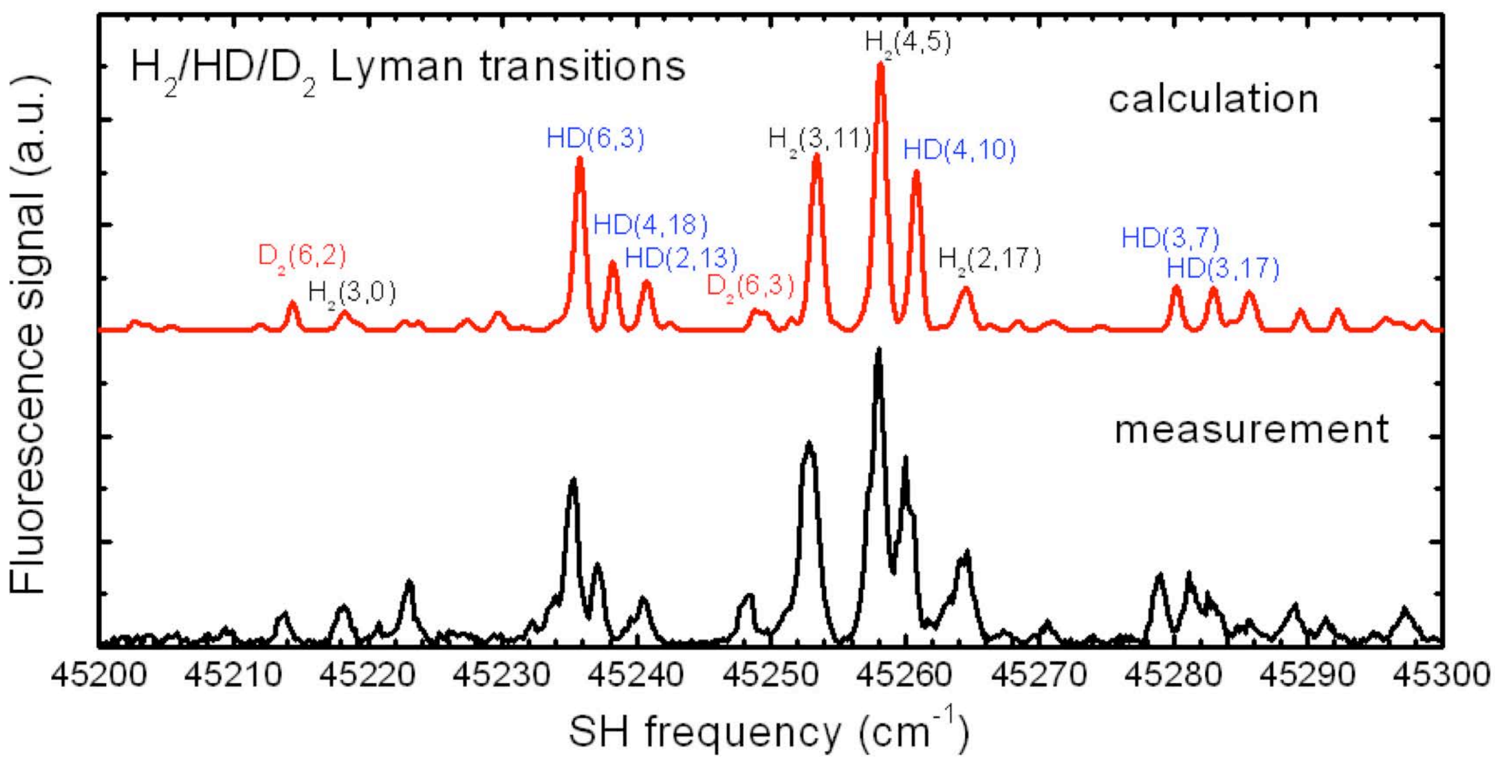
HD Lyman transitions J < 11

Spectroscopic data for D_2

H. Abgrall et al. *J. Phys. B: At., Mol. Opt. Phys.* 32 (1999) 3813

D_2 Lyman transitions J < 12

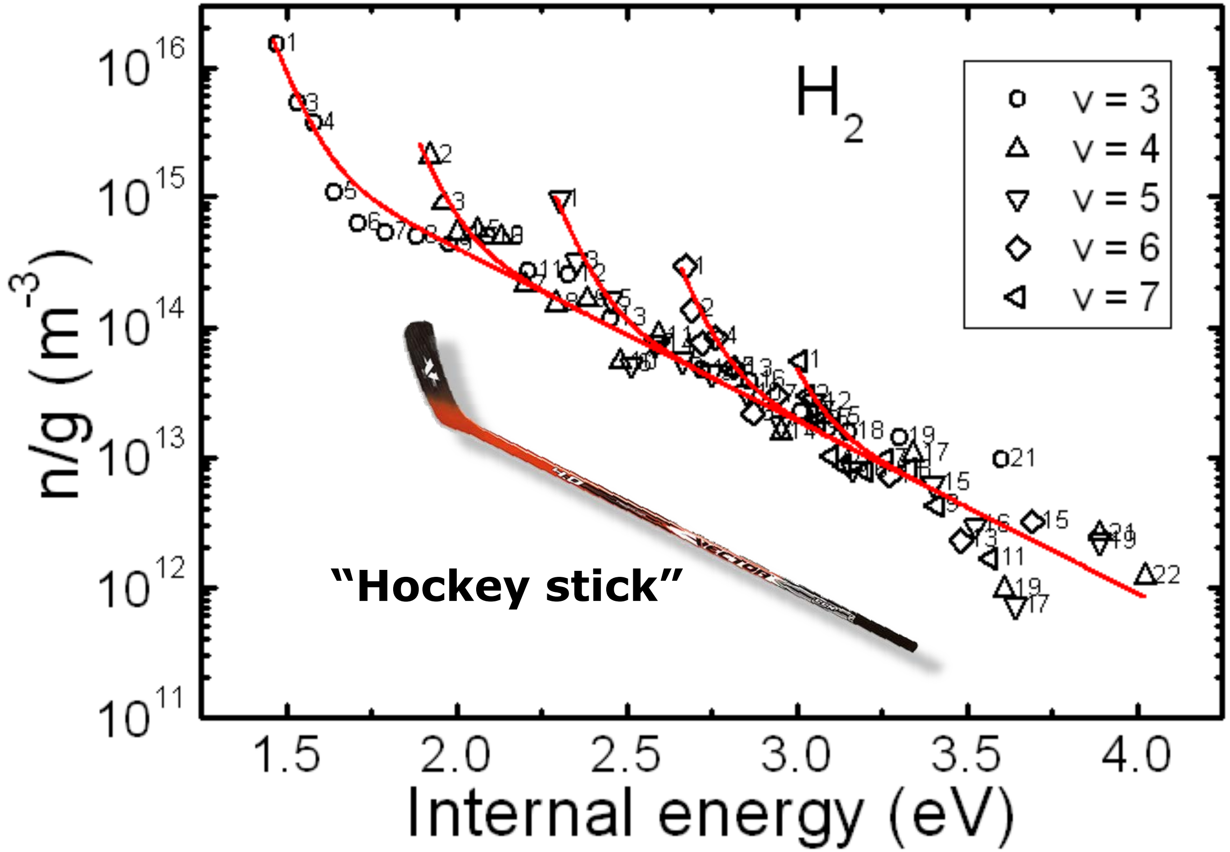
Measured and calculated H_2/HD/D_2 Lyman spectrum



New calculated Lyman transitions including higher rotational states (J > 10), incollaboration with Abgrall and Roueff

O. Gabriel et al. *J. Mol. Spectrosc* ***253*** *(2009) 64*

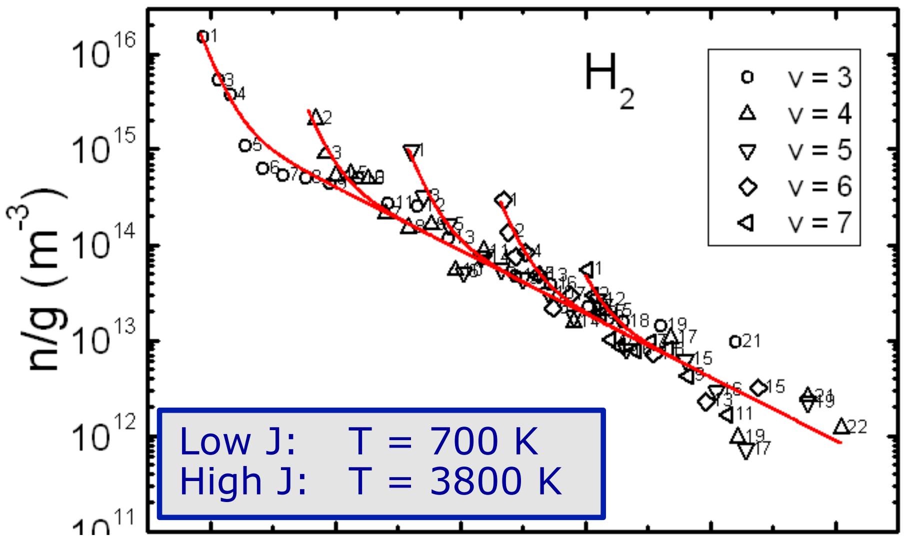
Non-Boltzmann distribution for H_2

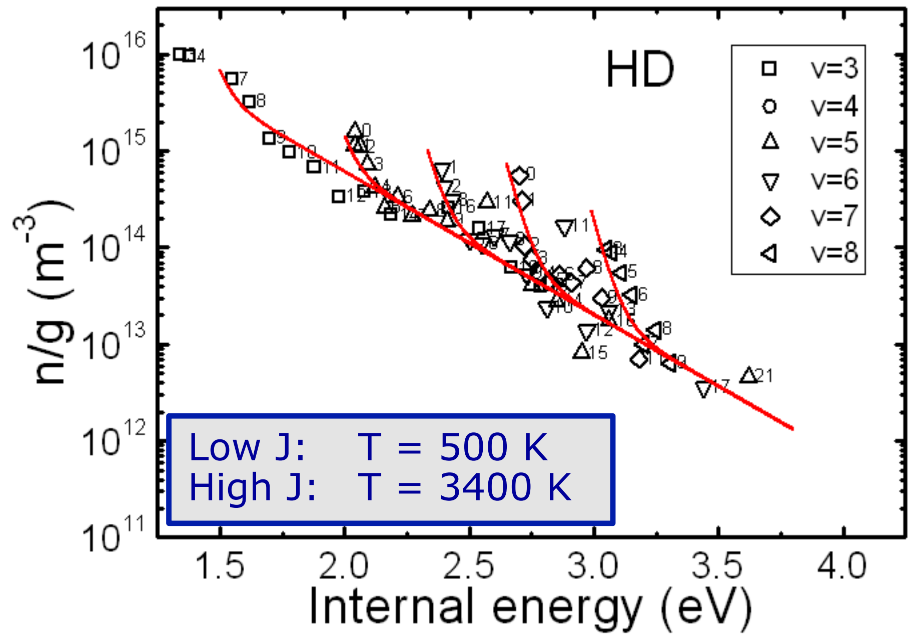


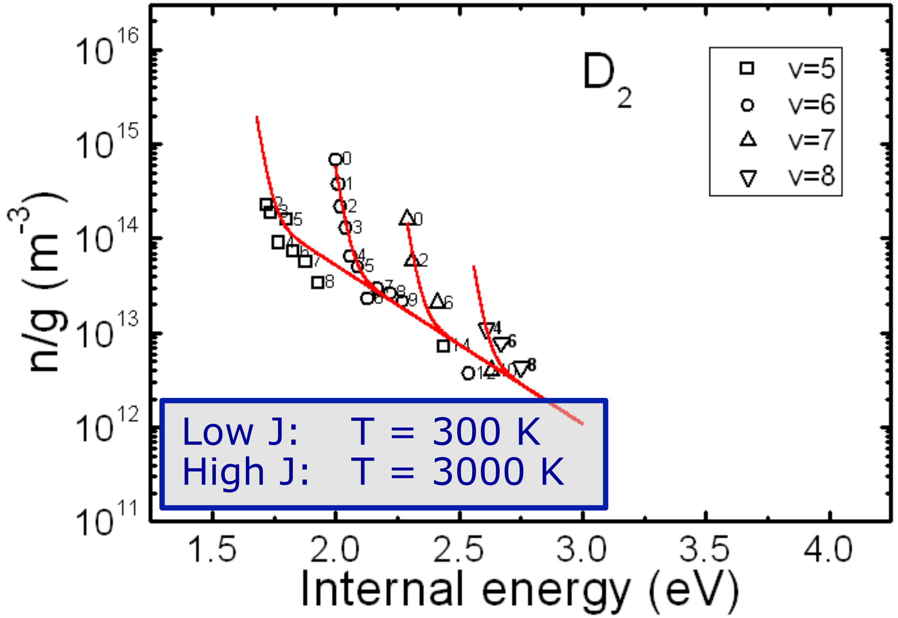
700 K for low J

3800 K for high J

Non-Boltzmann distributions in H_2/D_2 jet

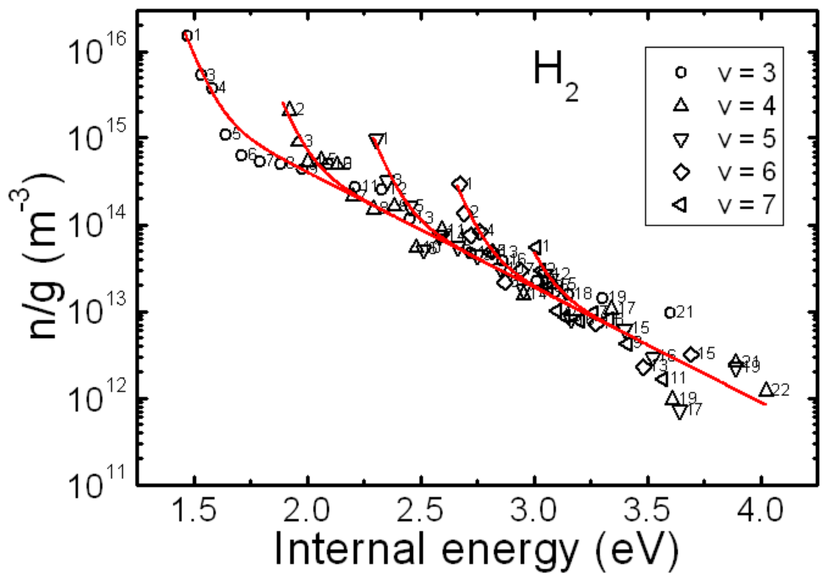


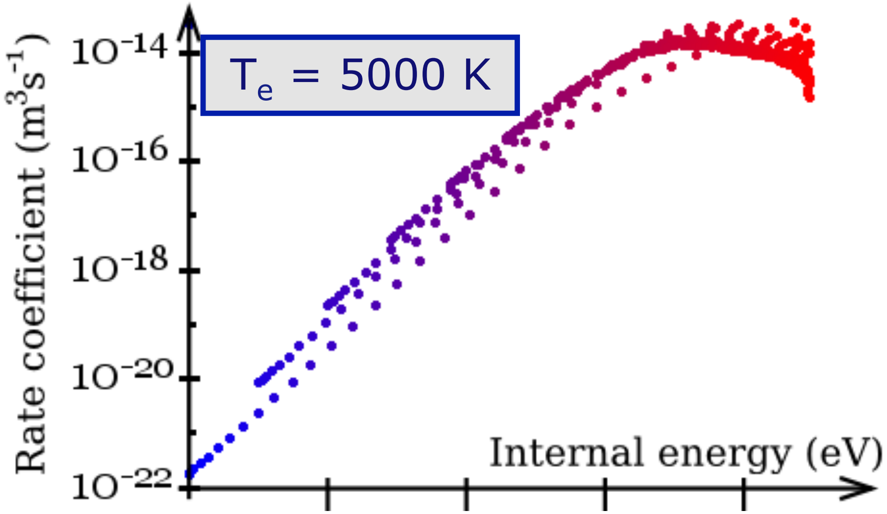


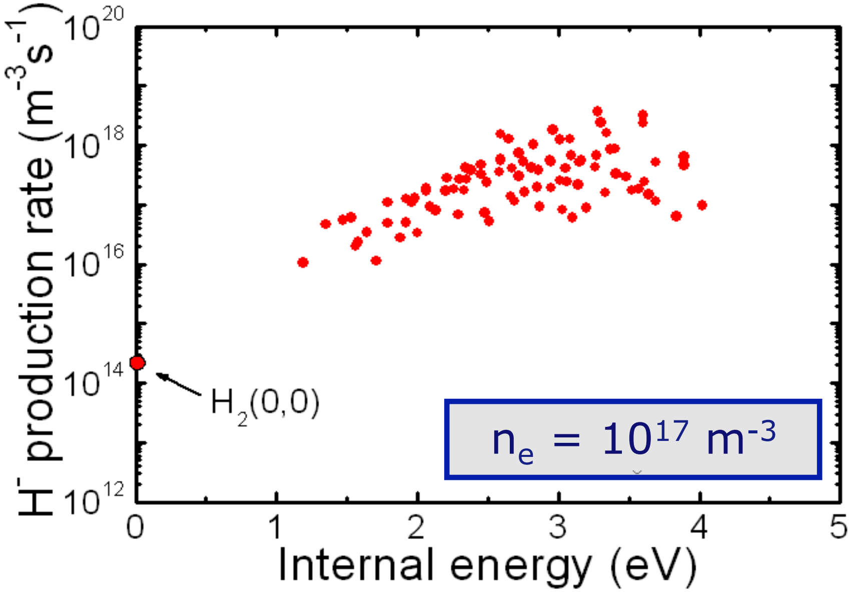


O. Gabriel et al, *J. Chem. Phys.* 132 (2010) 104305

Results on H^- production through DA process





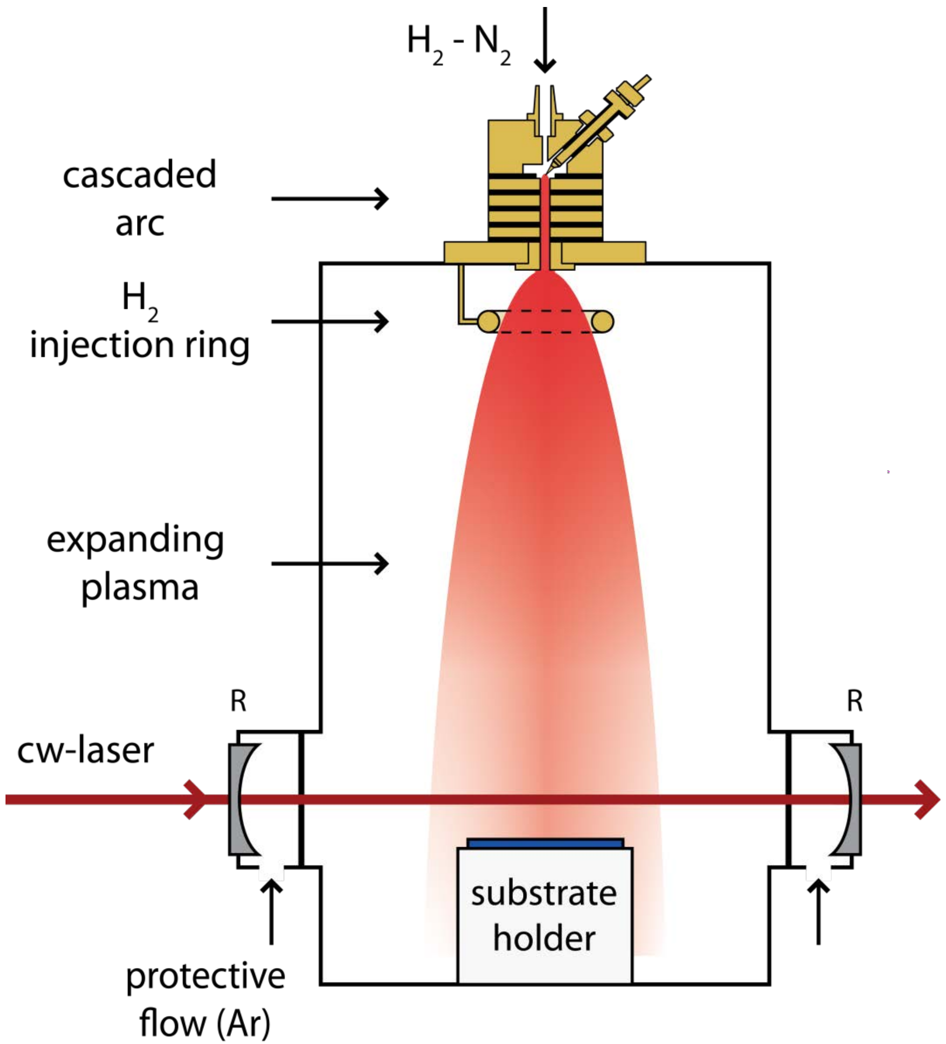


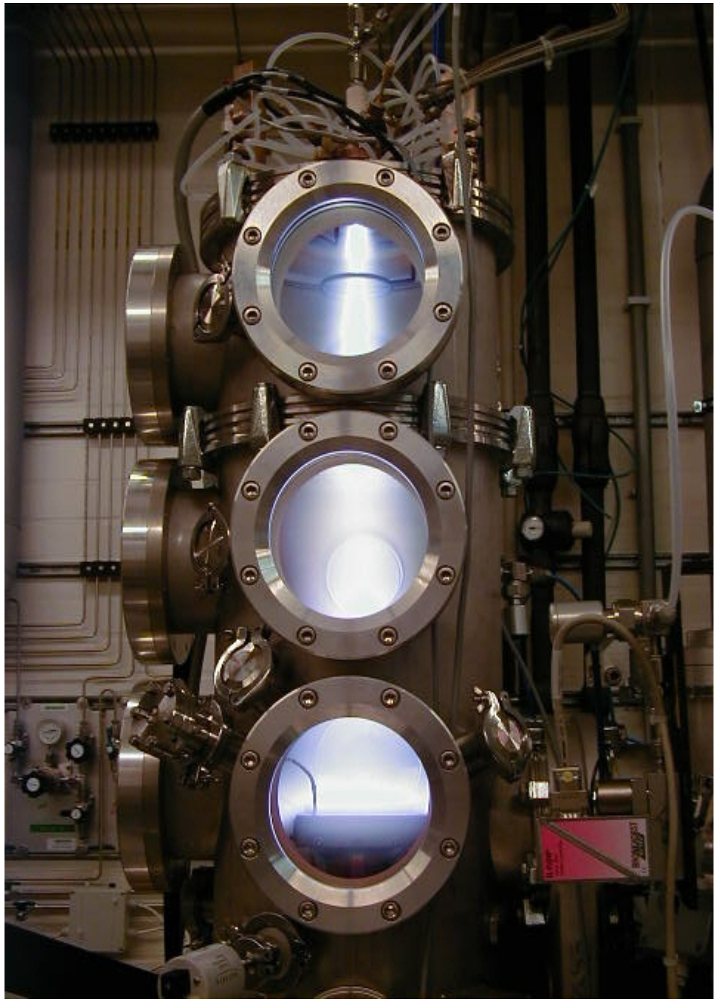
Production rate of H^- ions by dissociative attachment

O. Gabriel et al, *J. Chem. Phys*. 132 (2010) 104305

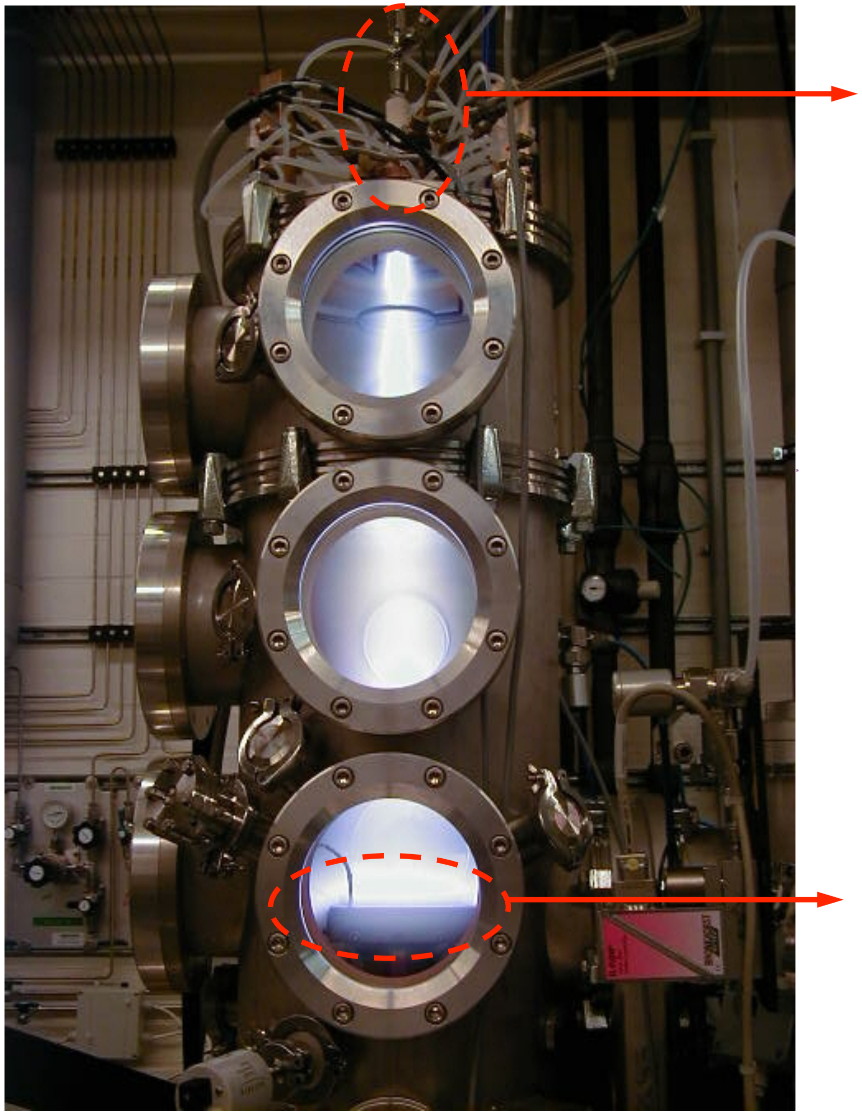
CRD spectroscopy
on
N_2/H_2 plasma

NH_3 production in N_2/H_2 plasma





NH_3 production in N_2/H_2 plasma



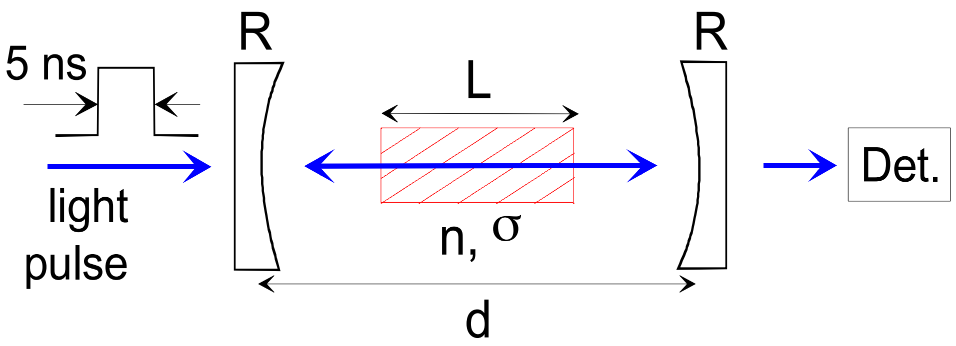
N_2/H_2 plasma creation

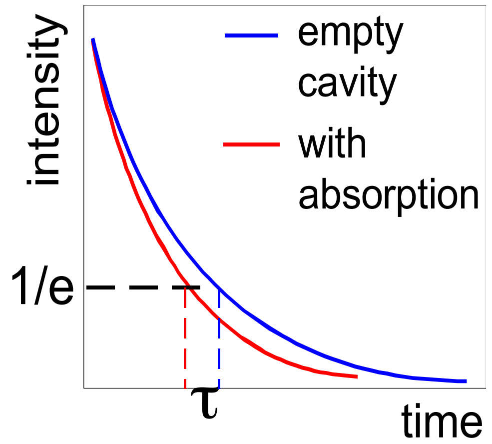
Plasma chemistry leading to e.g. NH_x

NH_3 formation ?

Cavity Ring Down: principals and features

(O'Keefe and Deacon, Rev. Sci. Instrum. **59** (1988) 2544)



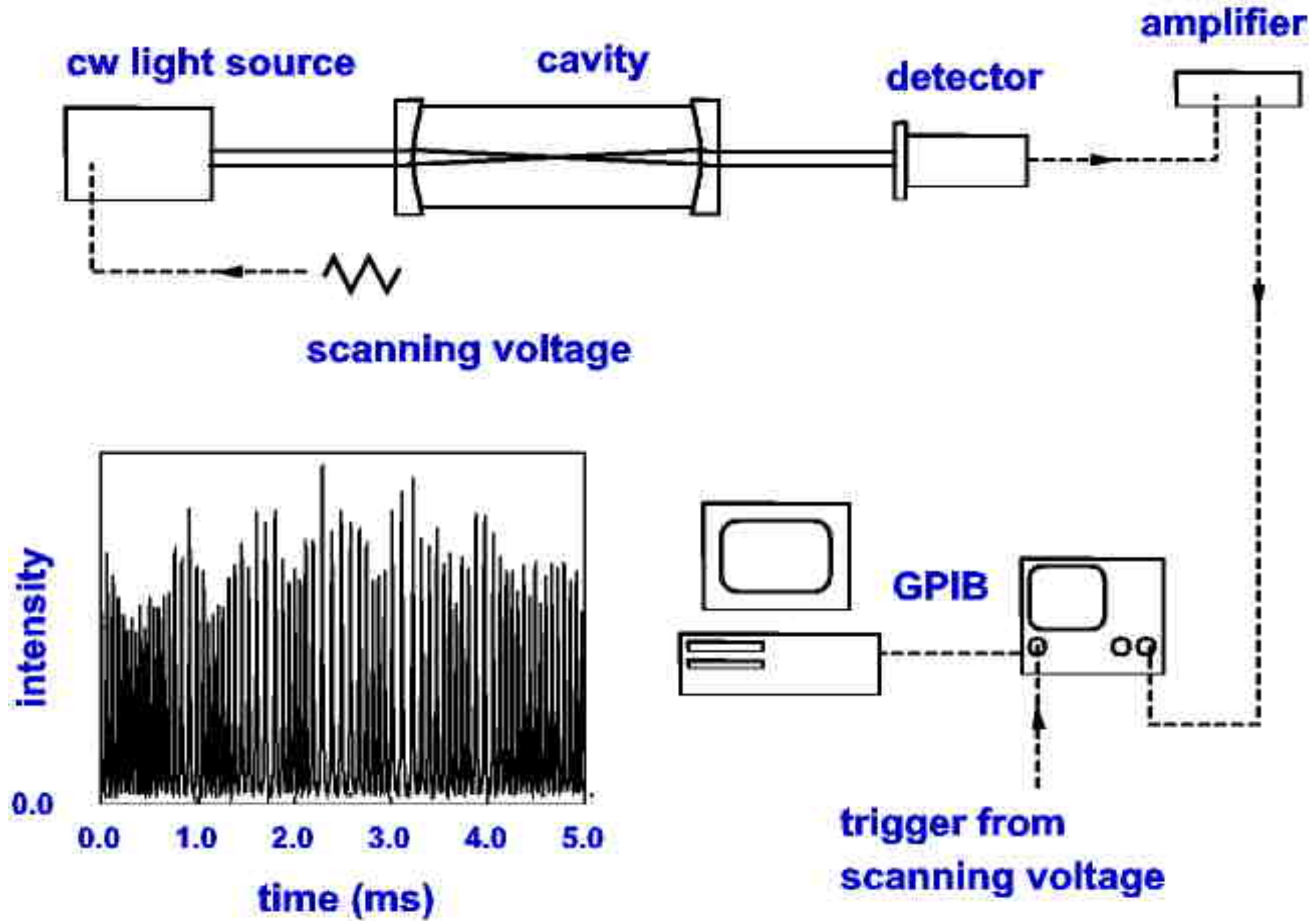


- absorption per unit of pathlength (cavity loss):

$$1/c\tau = (1 - R + n\sigma L)/d$$

- non-intrusive
- high sensitivity due to effective multipassing
- direct absorption –> line of sight measurement

Cavity Enhanced Absorption detection scheme



Rev. Sci. Instrum. 69, 3763 (1998)

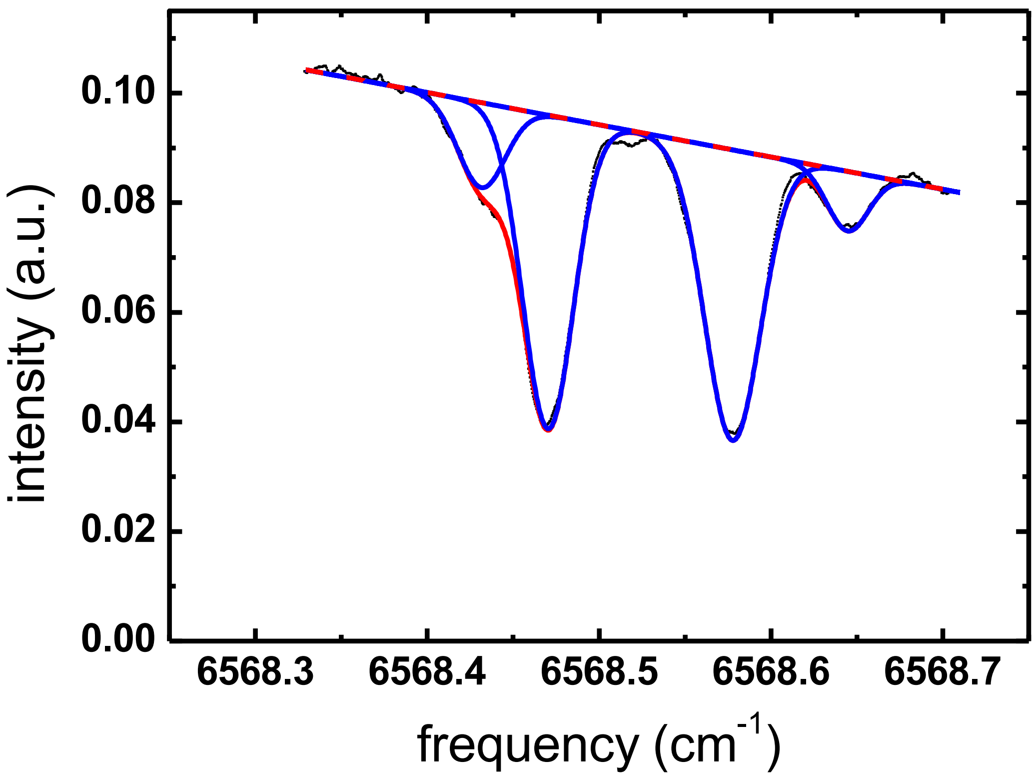
NH_3 production in N_2/H_2 plasma

CEA measurement recorded in a vessel in which N_2/H_2-plasma expands

Scanning frequency: 30 Hz
Frequency range: 15 GHz
Averages: 1000
Measurement time: 30 s

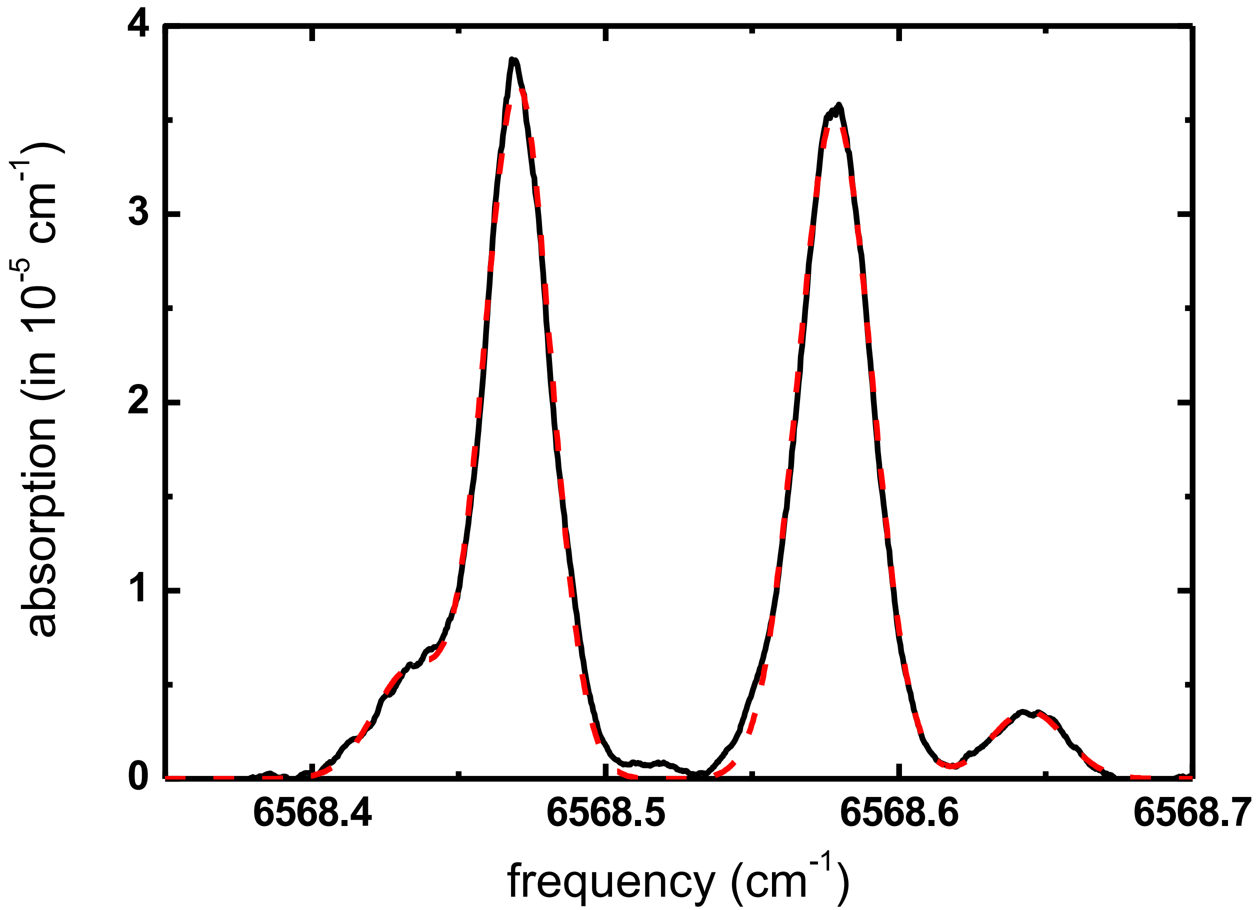
The absorption coefficient $\kappa(\nu)$ from intensity by:

$$\kappa(\nu) = \left(\frac{S_0(\nu)}{S(\nu)} - 1 \right) \times \left(\frac{1-R}{d} \right)$$



NH_3 production in N_2/H_2 plasma

Part of the absorption spectrum of NH_3 as measured in an expanding N_2/H_2 plasma



Line width

⇩

T_{tr} = 600 K

$\sigma \approx 10^{-22}$ m^2

⇩

$N \approx 10^{19}$ m^{-3}

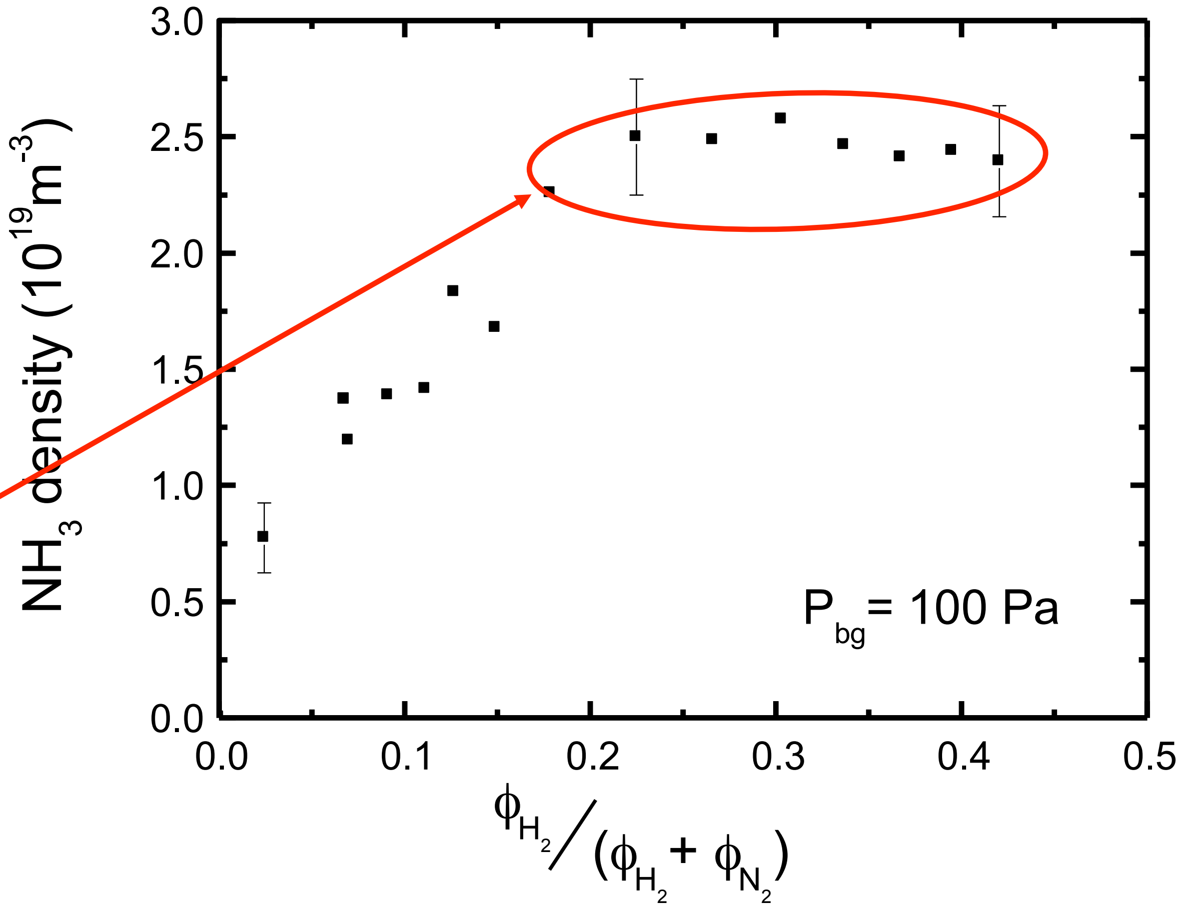
NH_3 production in N_2/H_2 plasma

Ammonia density produced in expanding N_2 plasma in which H_2 is injected in the background

Saturation behavior explained by rate determining steps:

$N^+ + H_2 \rightarrow NH^+ + H$
$NH^+ + e \rightarrow N + H$

Total N^+ flow is consumed



NH_3 production in N_2/H_2 plasma

Ammonia density as function of background pressure at *constant* gas flow (N_2-arc/H_2-background)

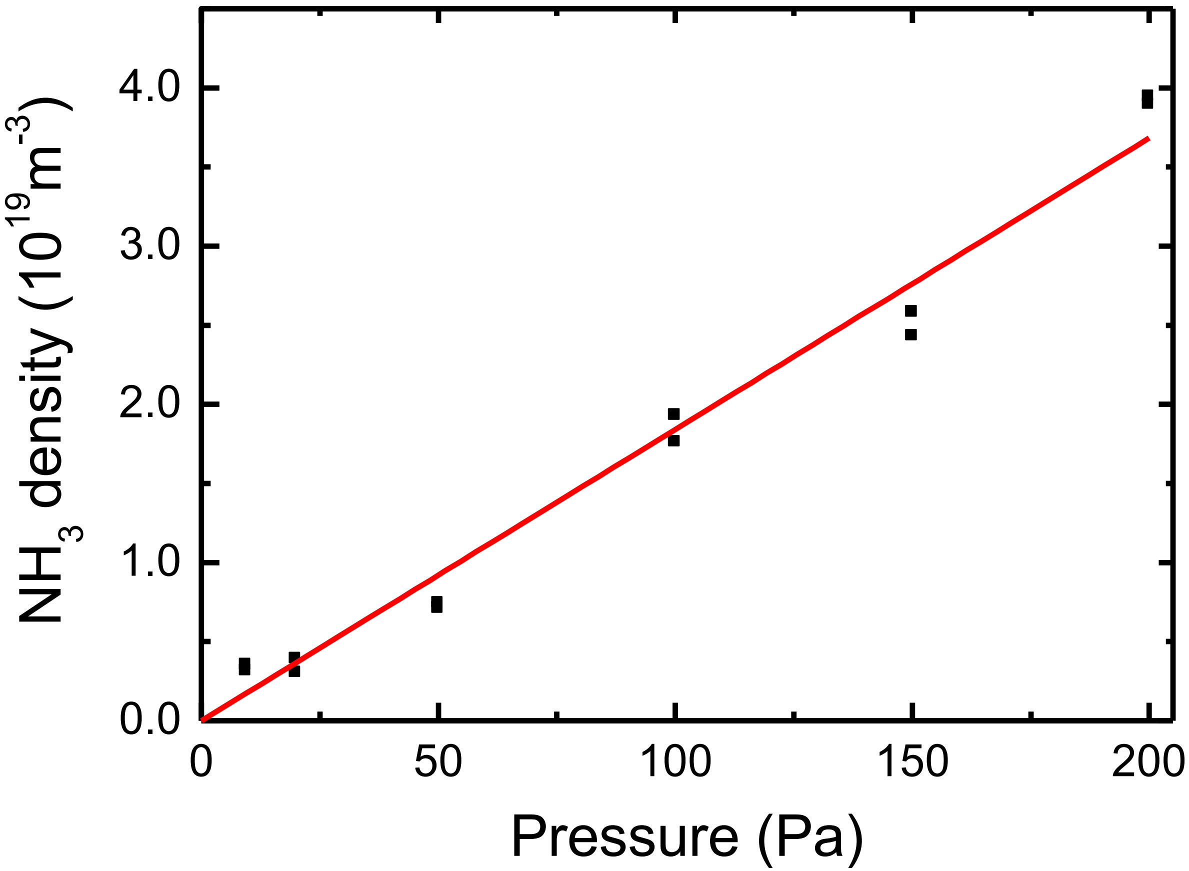
Linear with pressure
(dNH_3/dt constant)

⇩

~~3 particle reaction~~
~~stable intermediate~~

⇩

Wall production
(?)

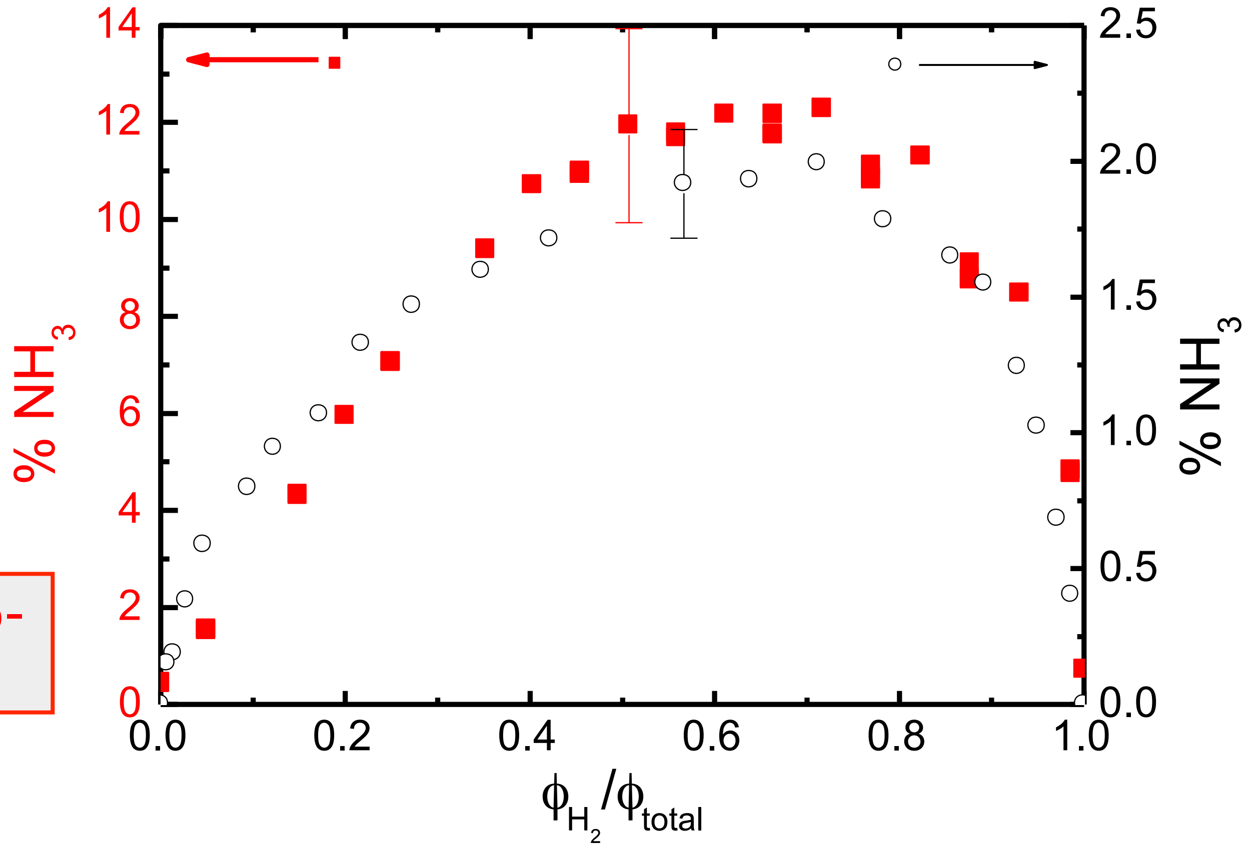


NH_3 production in N_2/H_2 plasma

NH_3 production in two different vessels

- Total gas flow of 2 slm through cascaded arc
- At maximum **12 %** of the background gas is NH_3

larger surface-to-volume ratio



Appl. Phys. Lett. 2002, **81**, 418

Conclusions

Input gas mixture, N_2/H_2, changes into $N_2/H_2/NH_3$ mixture (12 % of the background gas is NH_3).

NH_3 is formed at surfaces.