Quantitative Diagnostics of Inductively-Coupled Plasmas in O_2 : Densities and energy distributions

Laboratoire de Physique des Plasmas

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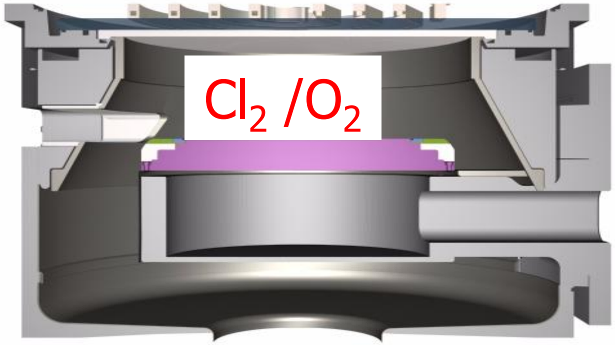
TÉCNICO LISBOA

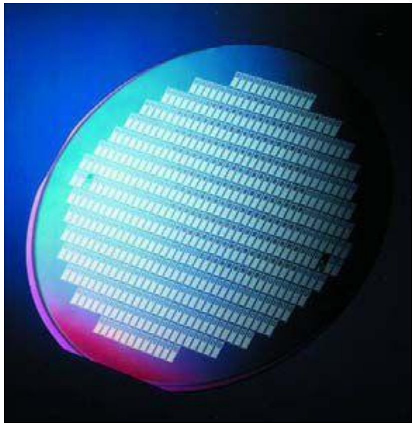
Motivation

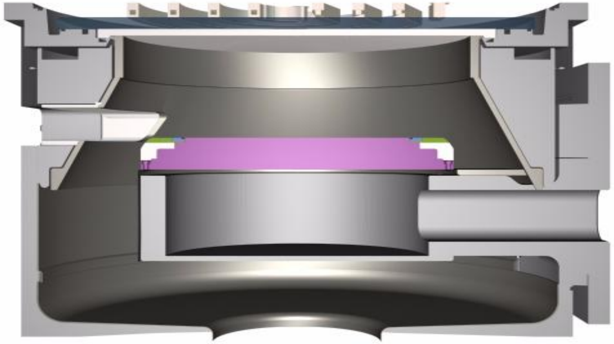
Why study low pressure RF inductive discharges in diatomic gases?

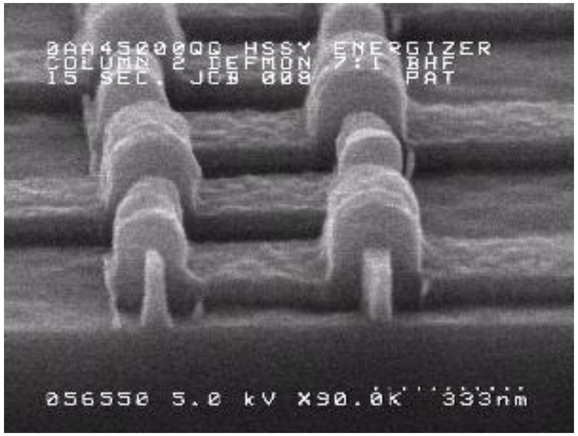


Motivation

RF plasmas in Cl_2 /O_2 (& often HBr) at low pressure widely used for selective, anisotropic etching of Si, InP etc







Motivation: understand plasmas in molecular gases

Most academic studies..

Rare gas plasmas:
Ar

⇐ ⇒

Most applications..

Mixtures of polyatomic gases:

- CF_4
- $C_4F_8/O_2/Ar$
- SiH_4/H_2
- $Cl_2/HBr/O_2$

Motivation: understand plasmas in molecular gases

LPP

Most plasma physics studies..

Most applications..

Rare gas plasmas: Ar	⇐	Diatomic gas plasmas: O_2, Cl_2, H_2...	⇒	Mixtures of polyatomic gases: •CF_4 •$C_4F_8/O_2/Ar$ •SiH_4/H_2 •$Cl_2/HBr/O_2$

Shows most of the mechanisms occuring in polyatomics:

- Dissociation, surface recombination
- Electronegativity
- Vibrational + rotational excitation

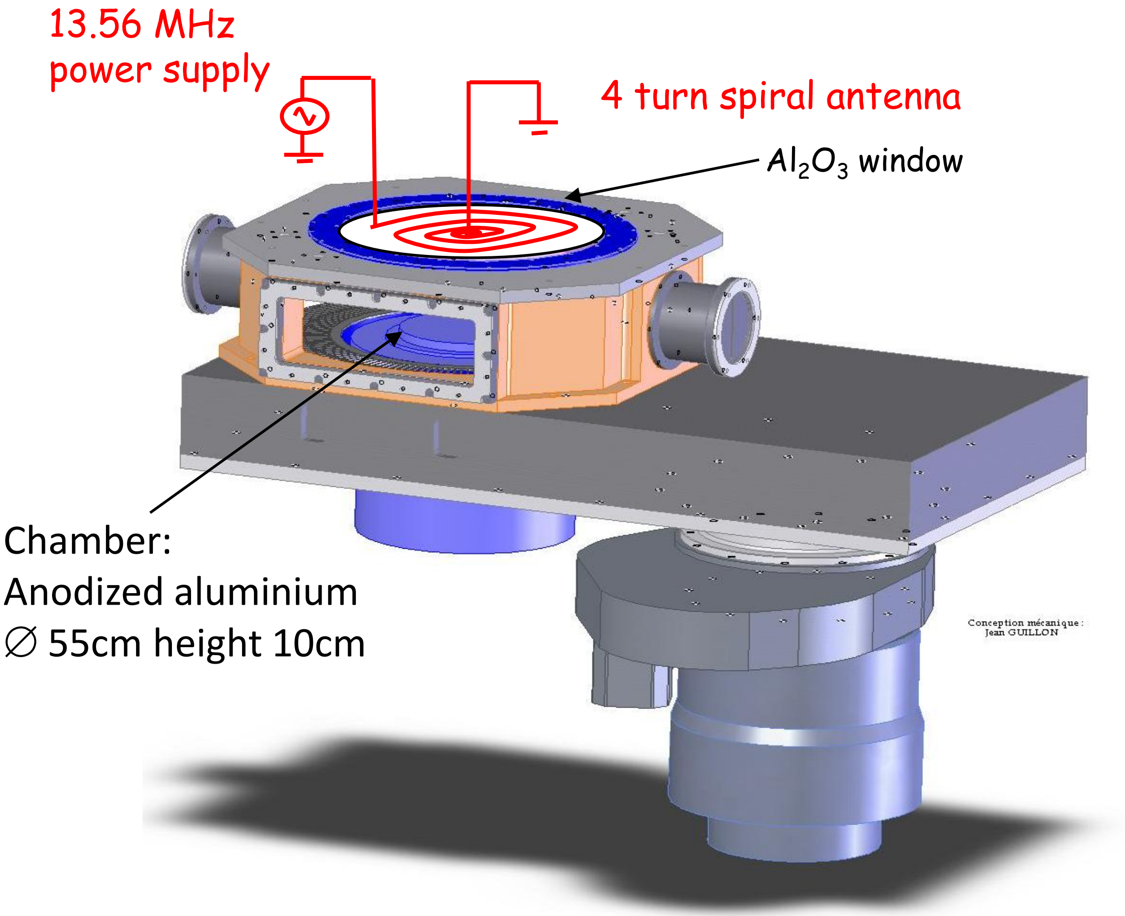
-But simpler, can measure (nearly) everything!

Test (validate) and improve Models:

-"Global" 0D models with plasma chemistry

- 2D Fluid Plasma + chemistry model : HPEM

The Inductively Coupled Plasma Reactor at LPP:



-Industrial Scale Reactor
dimension for 300mm wafers
-Industrial gases (O_2, Cl_2, HBr)

Pressure : 5-100 mTorr
Power : up to 500W

-All surfaces Al_2O_3
(no substrate)

What we can mesure?

LPP

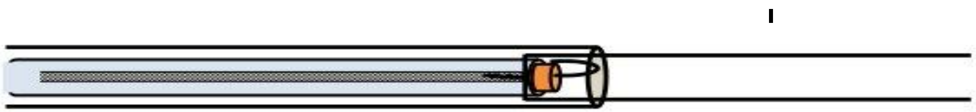
Electron density	-	Microwave resonant probe
Negative ions	-	+ laser photodetachment
O atom density	-	TALIF
Vibrational distribution	-	UV absorption spectroscopy

Gas temperature:

O_2 Trot	-	UV absorption spectroscopy
Ar^m Doppler	-	IRLAS vs IRLIF
O atom Doppler	-	HR TALIF

Electron density : Hairpin probe

LPP



¼ wave resonator : ~ 3 GHz :

- measure plasma permittivity from frequency shift with plasma
- deduce electron density from permittivity

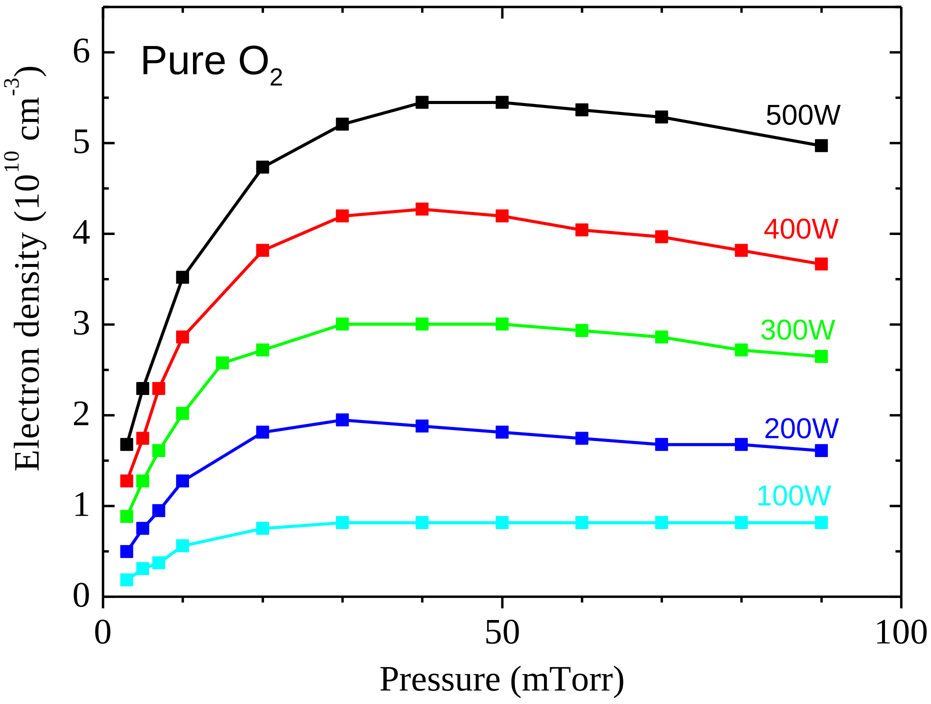
Avoids many of the problems of Langmuir probes:

- Probe contamination
- Return current path (insulating reactor walls!)
- RF compensation

Negative ions : detect electron pulse from laser photodetachment

Electron density

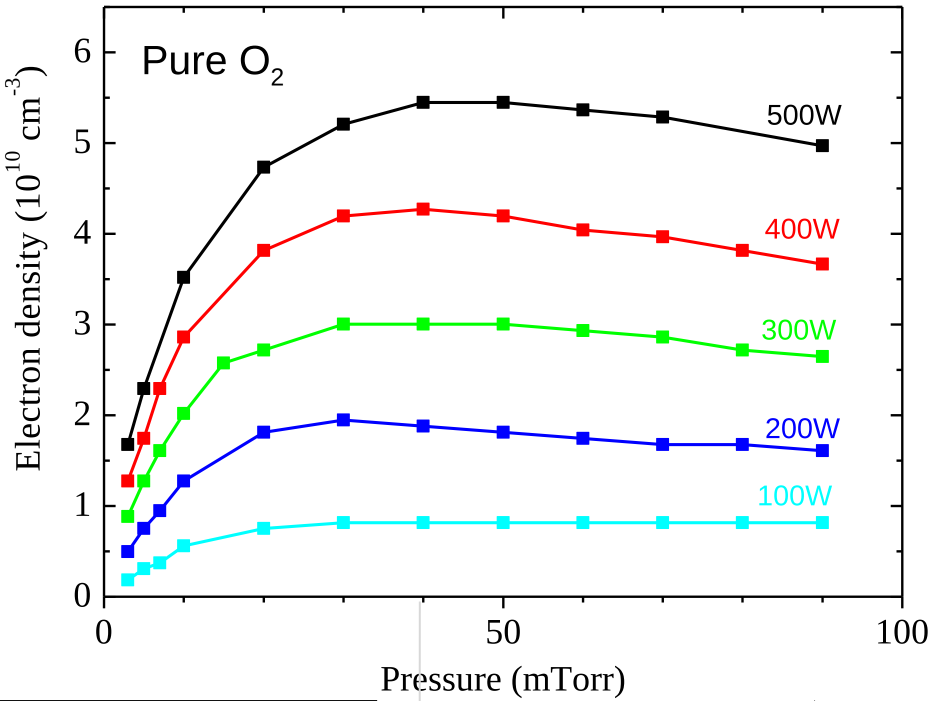
Broad maximum @ 40 mTorr



Approximately linear increase with RF power

Electron density

Broad maximum @ 40 mTorr

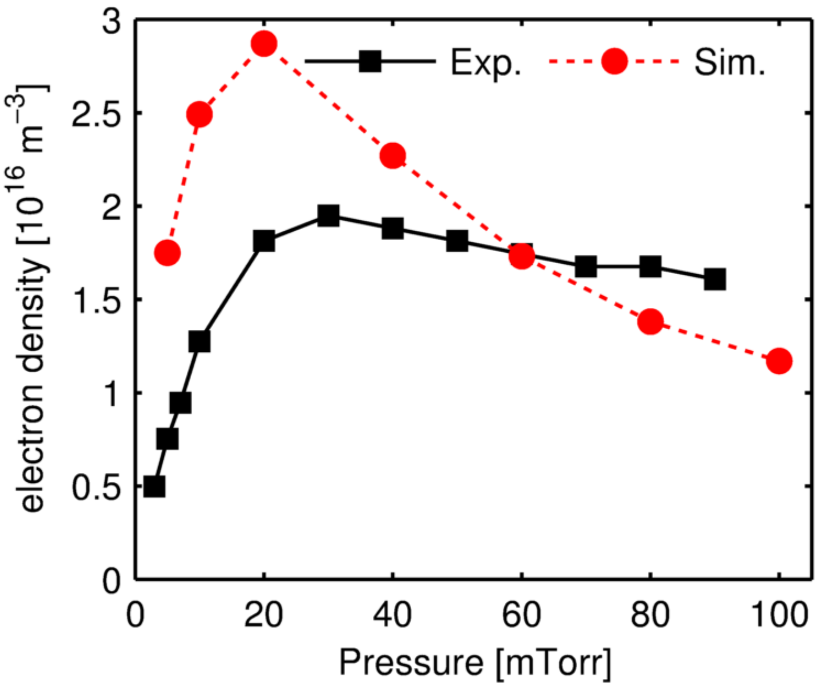


High Te, Vp:
Energy dissipated
accelerating ions
across sheath

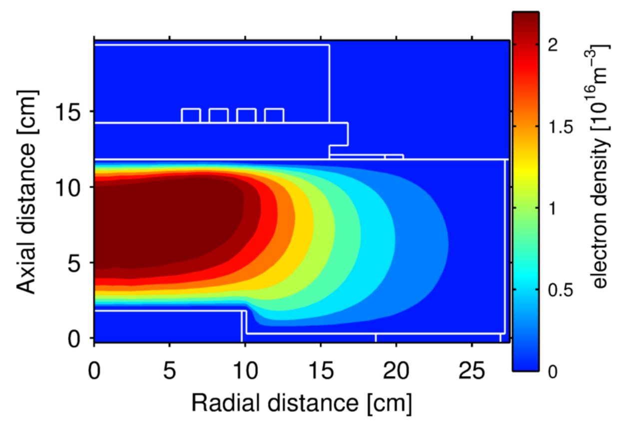
Energy dissipated in inelastic collisions

Negative ions ?

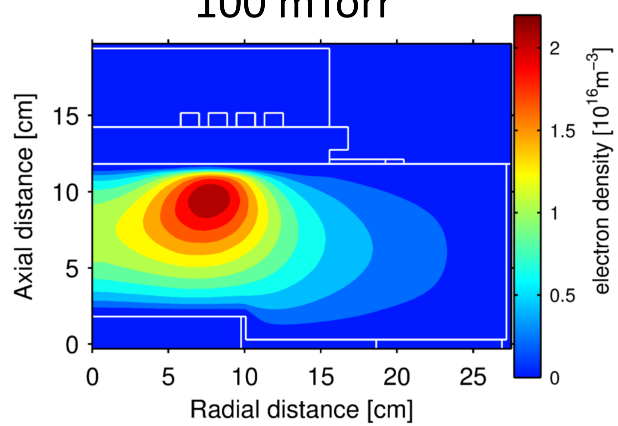
Electron density :O_2 200 W Compare to HPEM



20 mTorr



100 mTorr



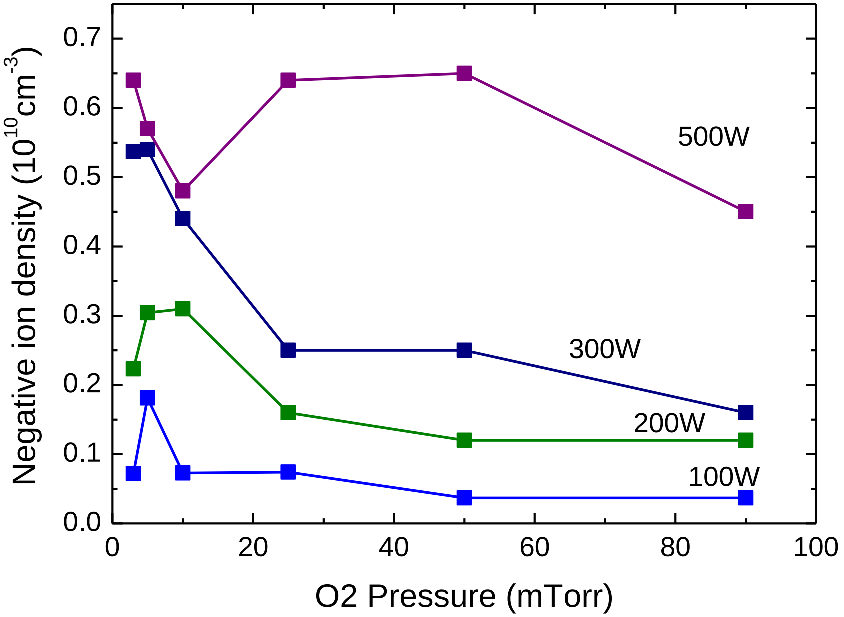
Predicts maximum at the correct pressure

High pressure trend poorly modelled

Electron density moves off-axis

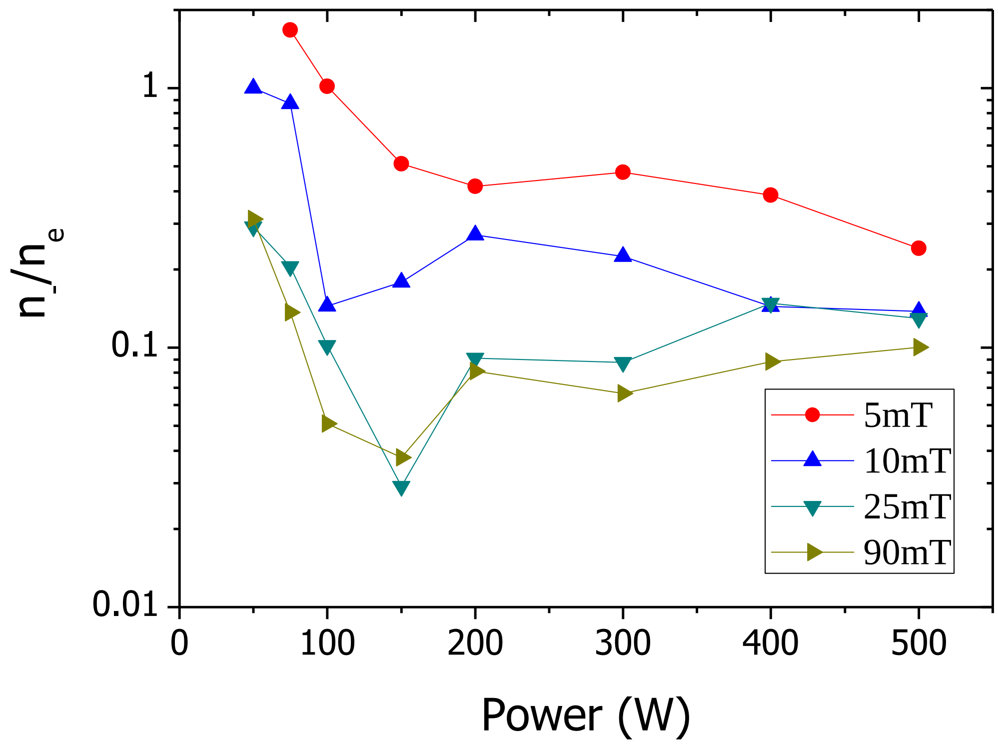
Negative Ion density

Laser photodetachment /
hairpin detection of photoelectrons



Courtesy of Nishant Sirse,
Dublin City University

Electronegativity
$\alpha = n_-/n_e$



Negative ion density lower than electron density except at **low pressure and power**

Not responsible for electron depletion

Negative ion destruction : Associative Detachment

Atoms:

$O^- + O \rightarrow O_2 + e$ (exothermic in O_2)

Metastable states : $O_2\ ^1\Delta_g$ (at ≈1 eV)

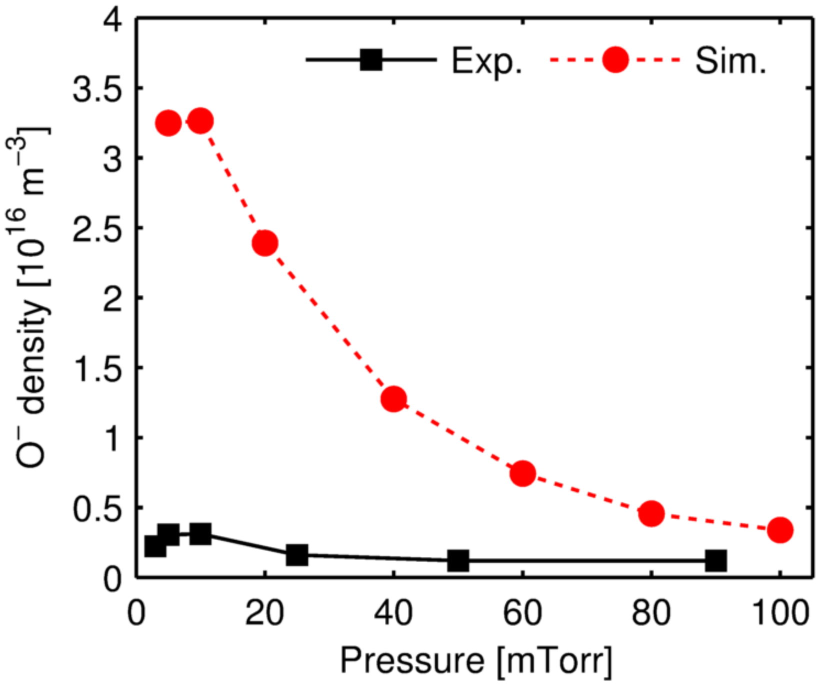
$$O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$$
$$\rightarrow O^-_2 + O_2$$
$$\rightarrow 2O_2 + e$$

Midey et al J. Phys. Chem. A ***2008, 112, 3040-3045***

As a result, O_2 plasmas have a much lower density of negative ions

Electro-negativity highest at low pressure and low power (O and $O_2\ ^1\Delta_g$ low)

Negative ion density: compare to HPEM Simulation

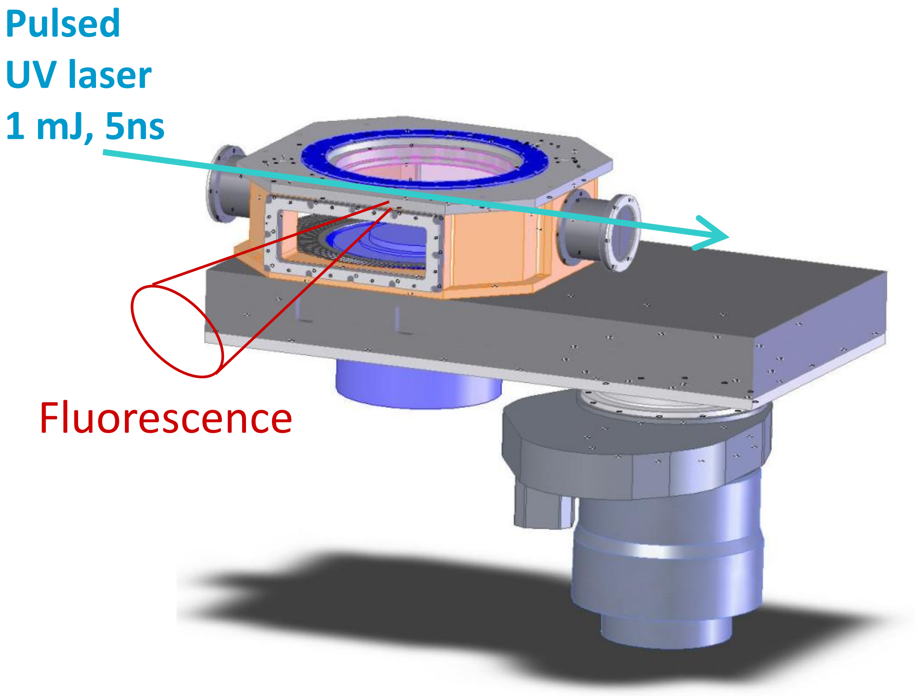


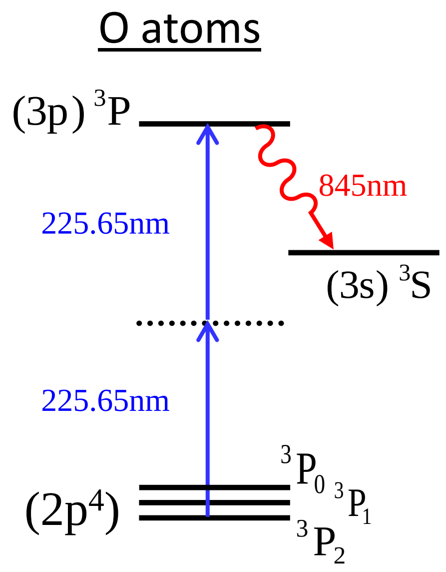
Pure O_2

Model strongly overestimates negative ion density!

Loss processes underestimated, or missing mechanisms?

Atom densities:
Two-Photon Absorption Laser-Induced Fluorescence (TALIF)

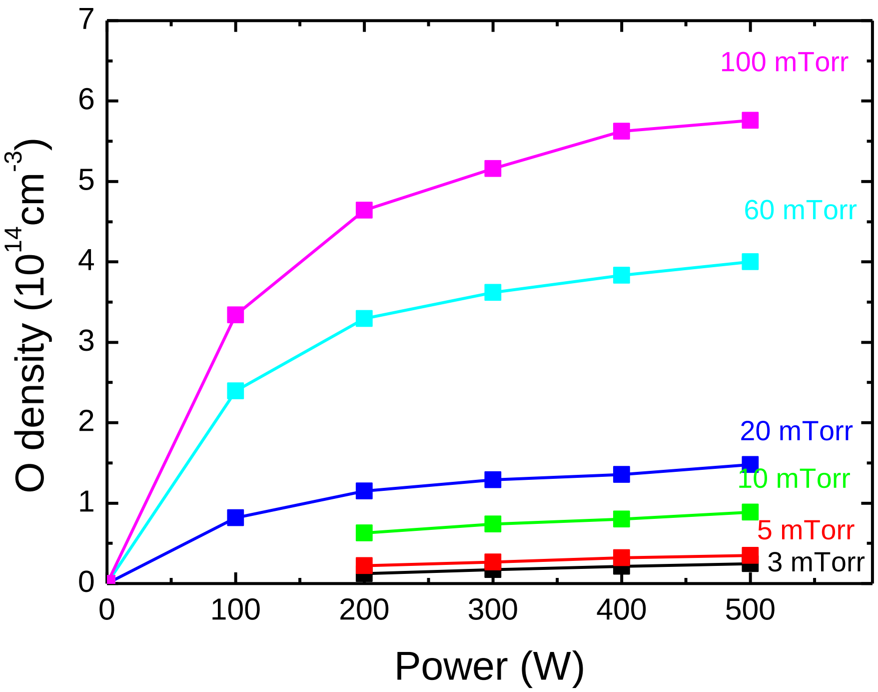




- High spatial and temporal resolution measurements
- Relative densities of ground-state O atoms
- Absolute densities: use calibration techniques

→ *Niemi et al : PSST **14**(2005) 375-386*

Pure O_2 : Atom density



O density increases:

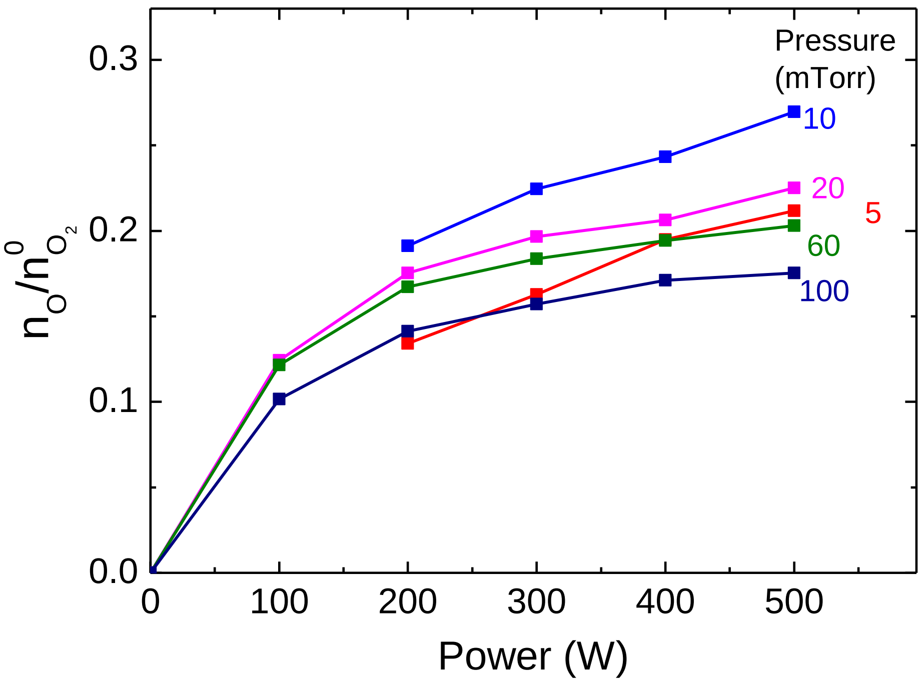
-with pressure

-with RF power :but saturates

→Dissociation fraction?

Pure O_2 : "Dissociation fraction "

Normalise to n^0_{O2} , the density of (cold) gas before plasma:



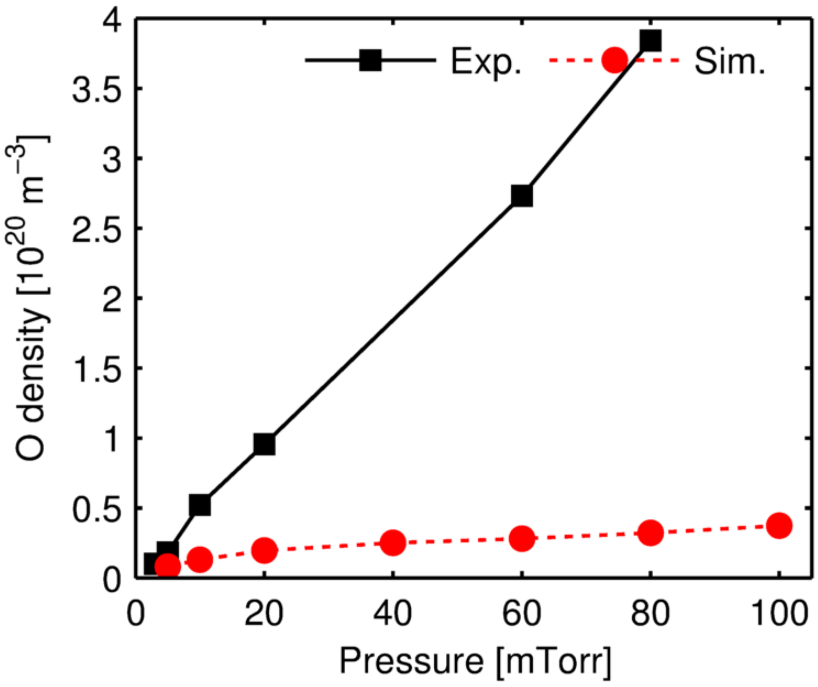
Maximal at 10 mTorr
(n_e maximum at 40 mTorr)

Dissociation saturates @ 20-30%

Why not 100% ?

Gas temperature?

O atom density: comparison to HPEM

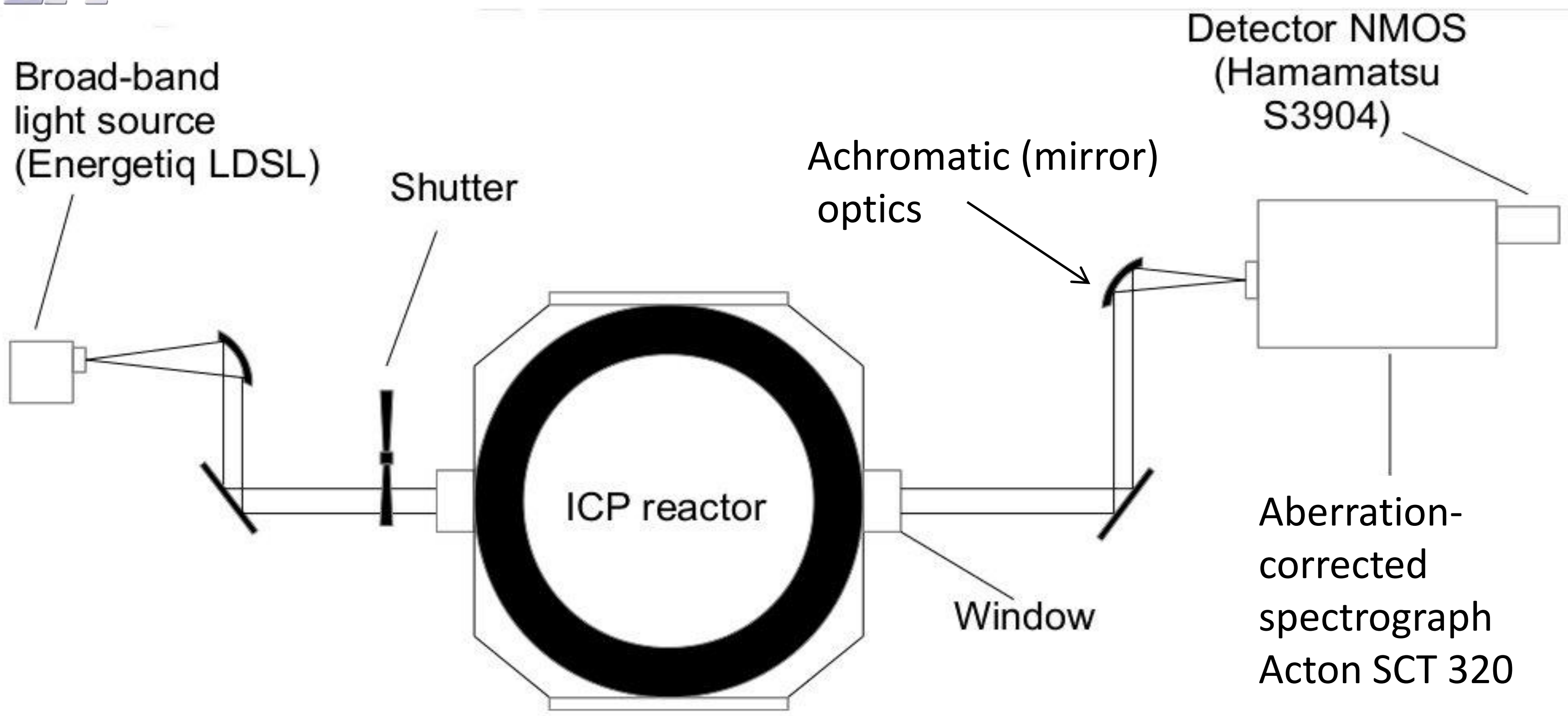


Pure O_2 200 W

Model strongly overestimates O atom density!

Error in dissociation cross-sections?

High-sensitivity ultra-broad-band Absorption spectroscopy

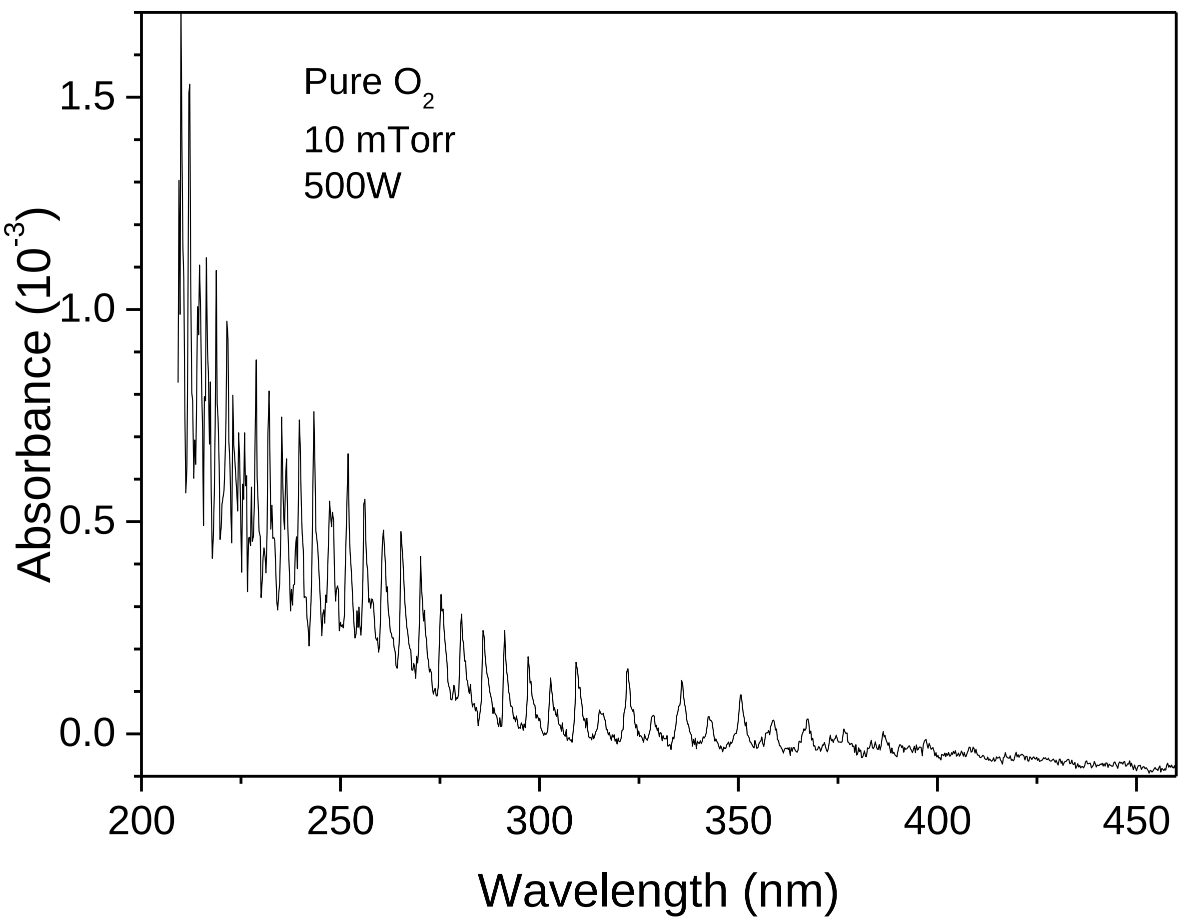


- Baseline noise ≈10^{-5} , 250nm spectrum simultaneously
- Allows whole vibrational bands to be observed

Pure O_2 plasma UV absorption

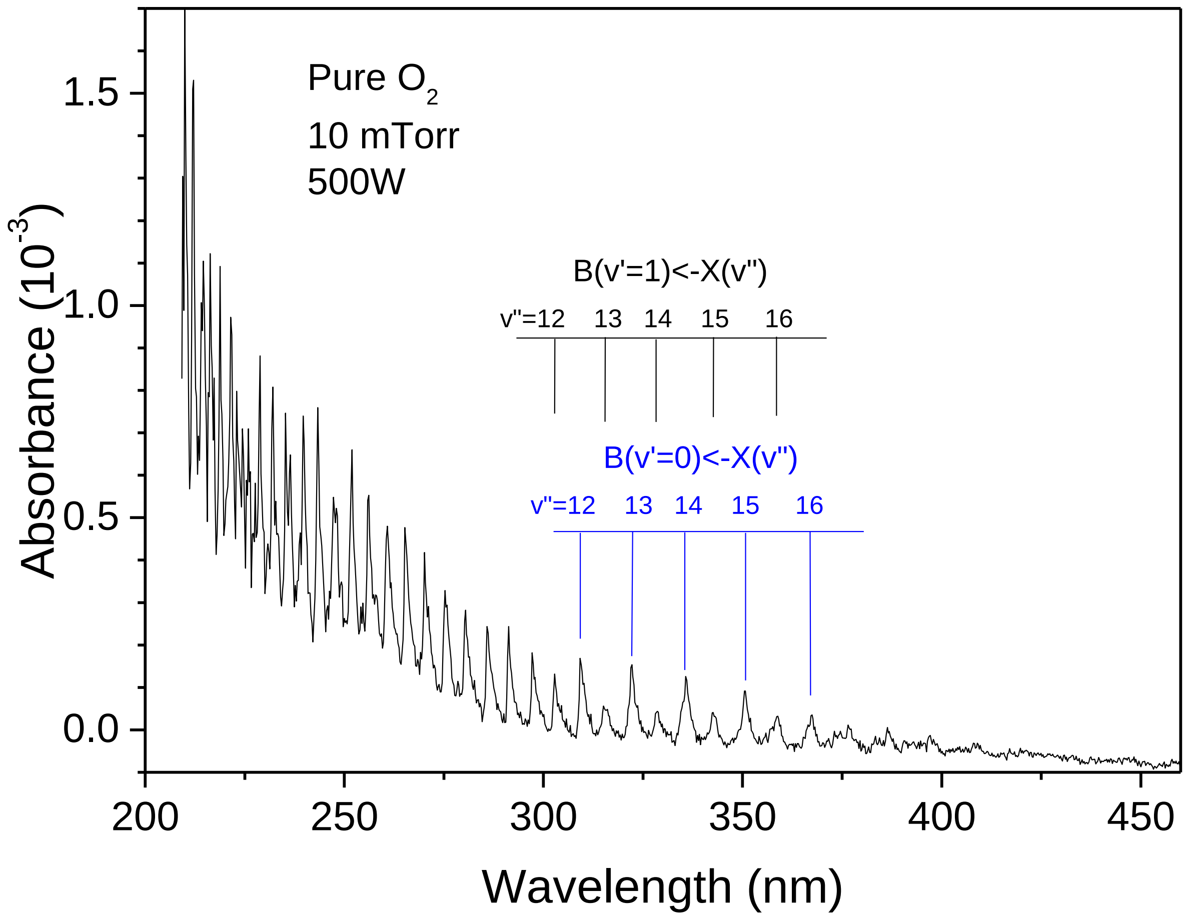
Cold O_2 doesn't absorb above ≈200 nm...

Pure O_2 plasma
UV absorption

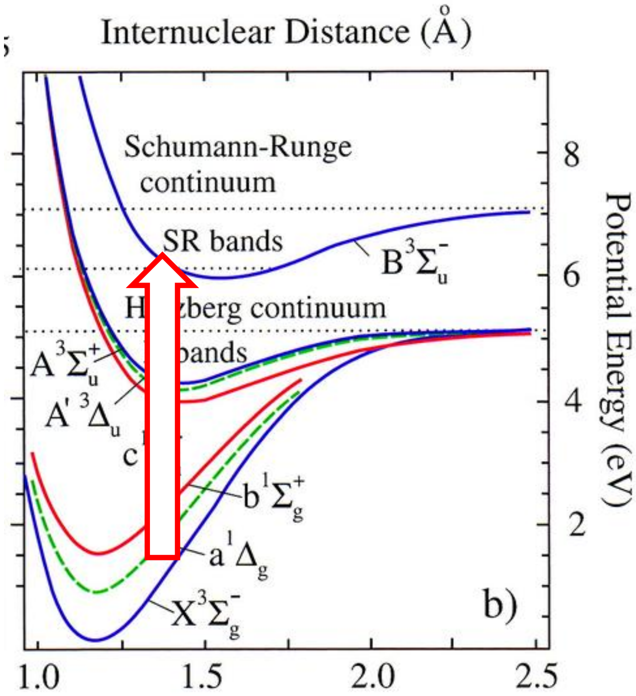


Pure O_2 plasma UV absorption

Levels up to v”≈ 18 half-way to dissociation!

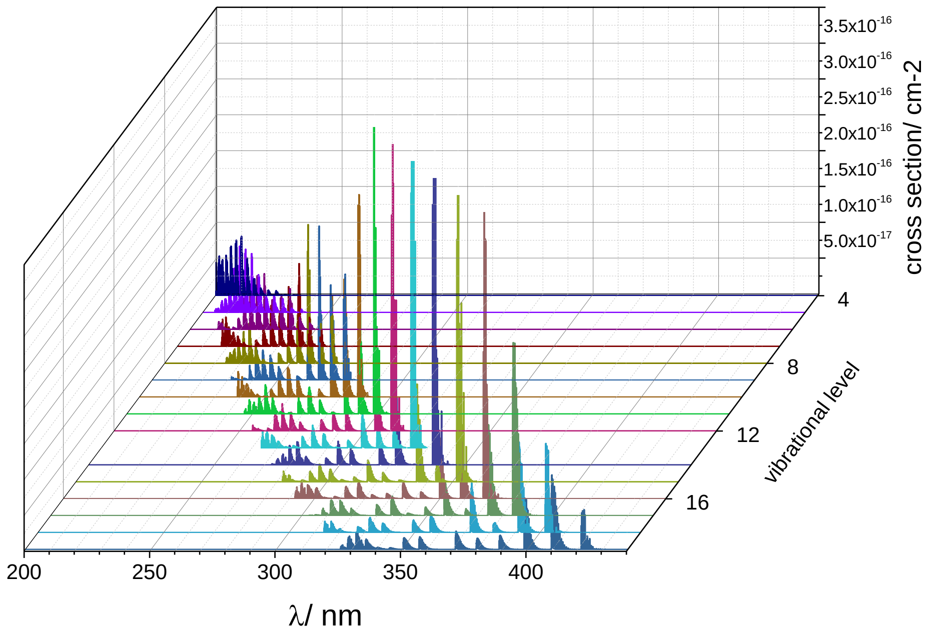


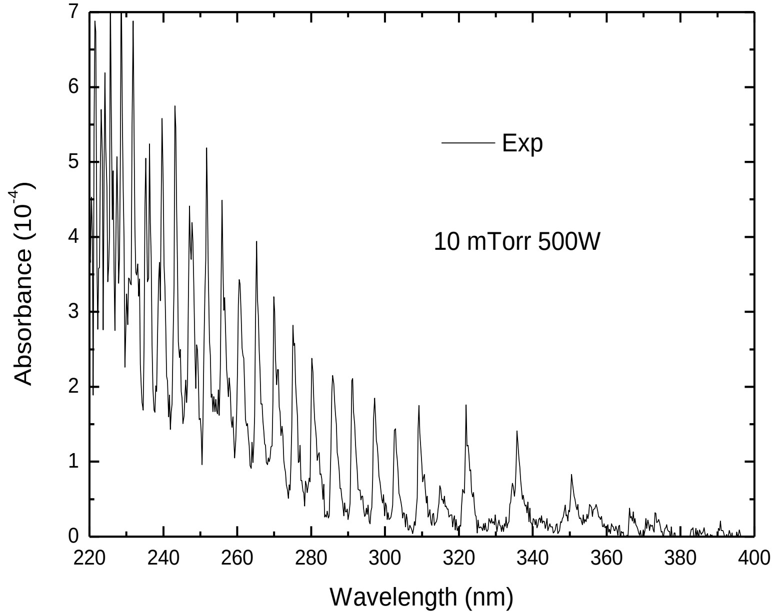
Schumann-Runge bands from highly vibrationally excited O_2



Pure O_2 : UV absorption

Vibrational-state resolved absorption cross-sections
→Extract vibrational distribution functions

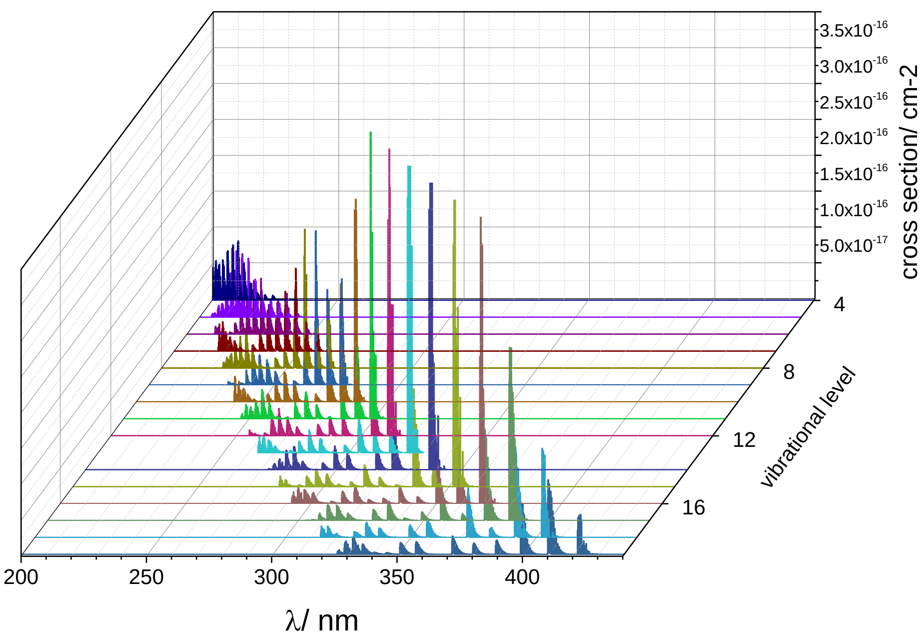




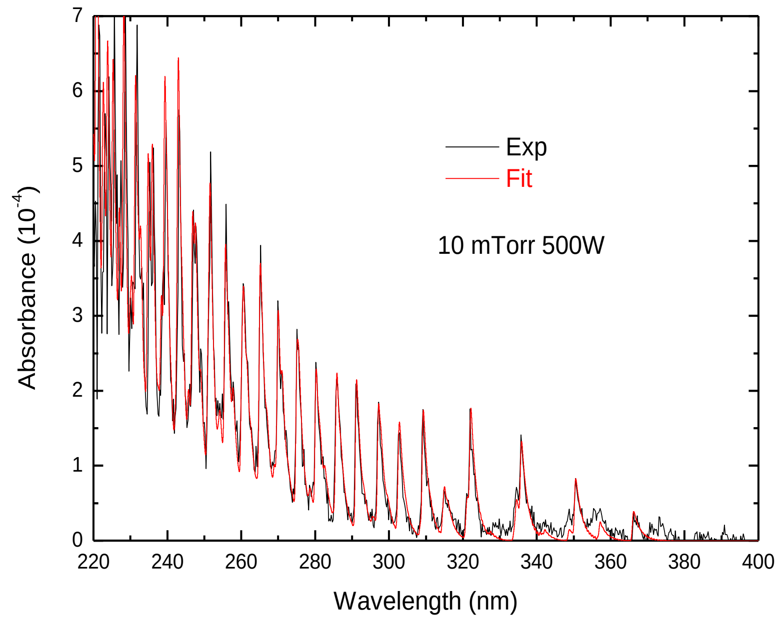
(Courtesy of Christophe Laux / Specair)

Pure O_2 :
UV absorption

Vibrational-state resolved absorption cross-sections
→Extract vibrational distribution functions

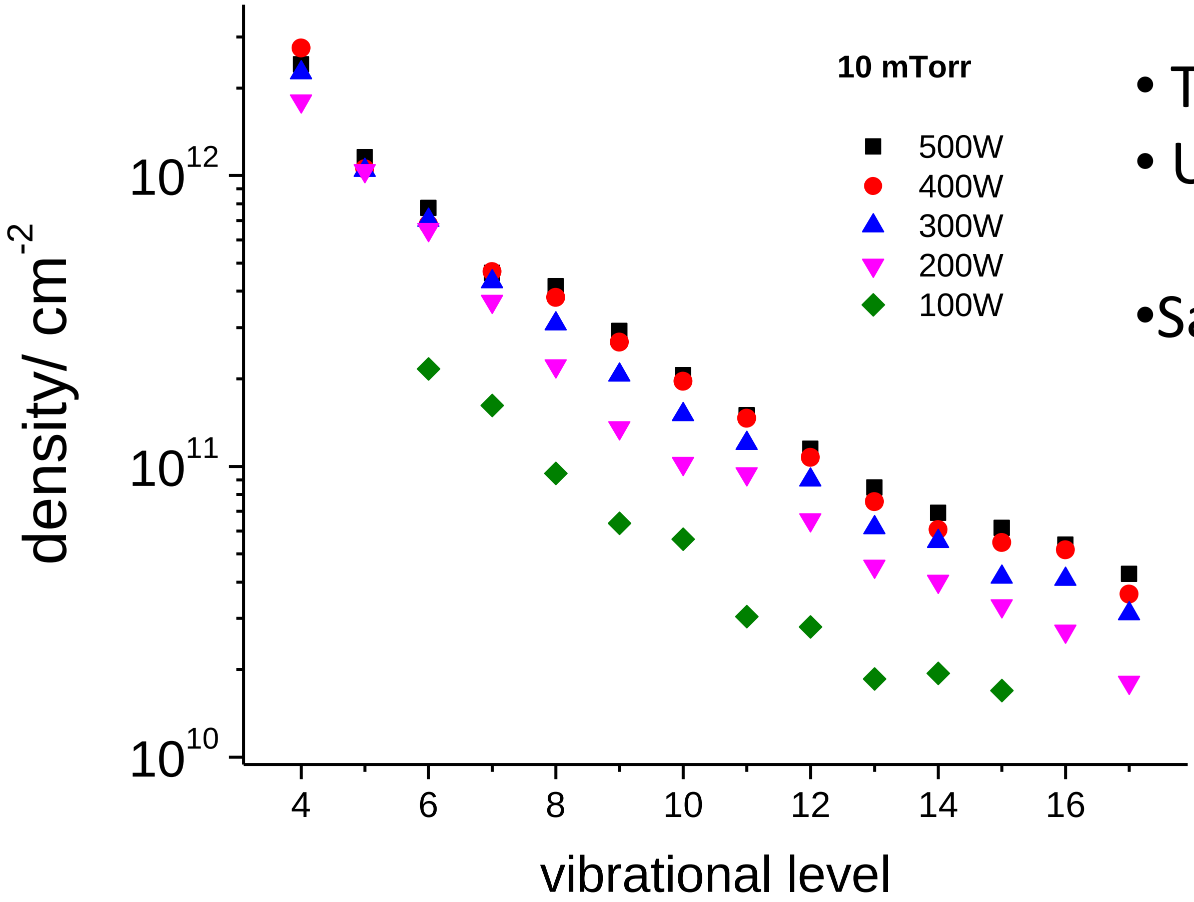


(Courtesy of Christophe Laux / Specair)



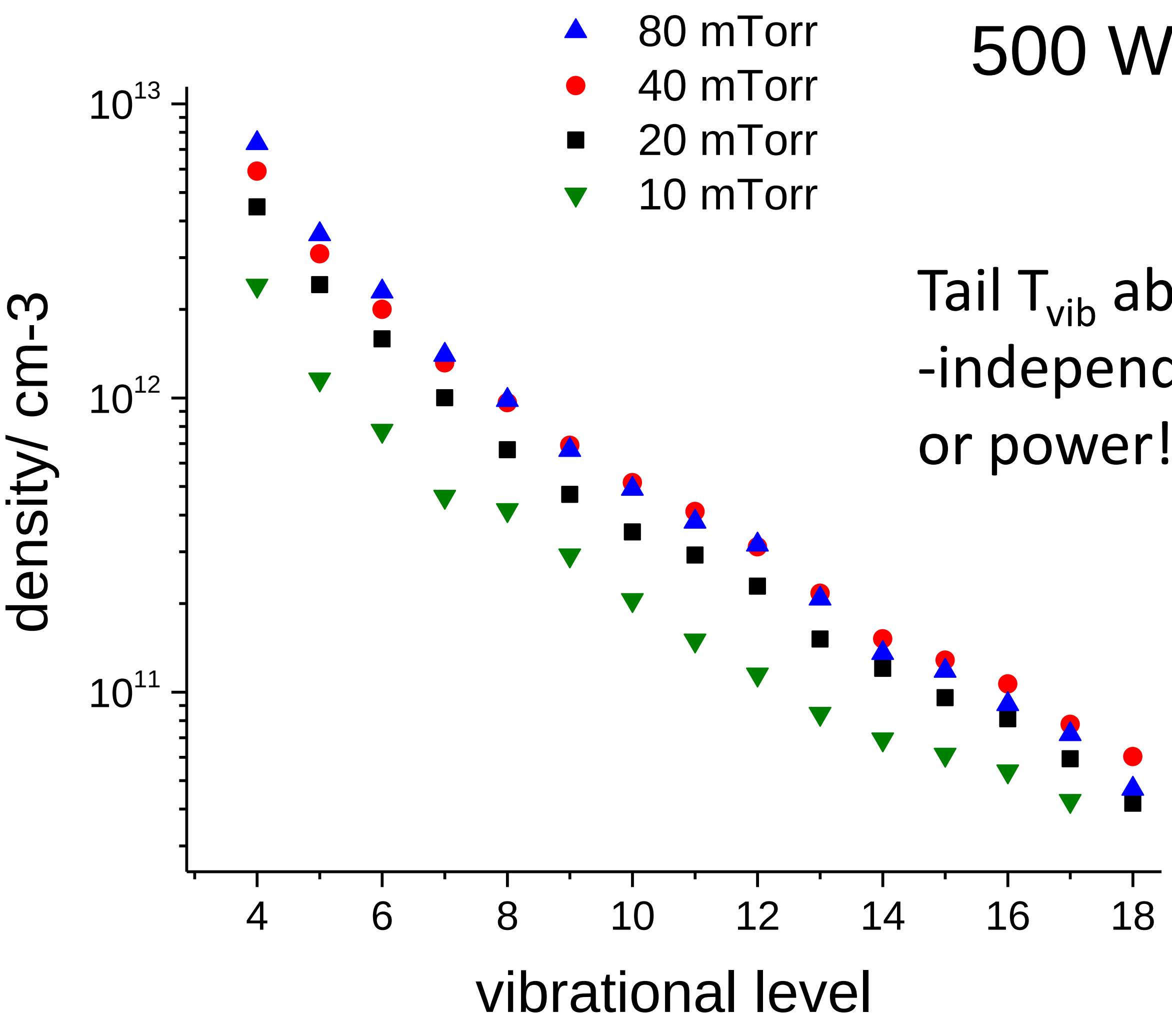
(NB cannot measure below v”=4)

O_2 Vibrational distribution functions (function of RF power :10 mTorr)



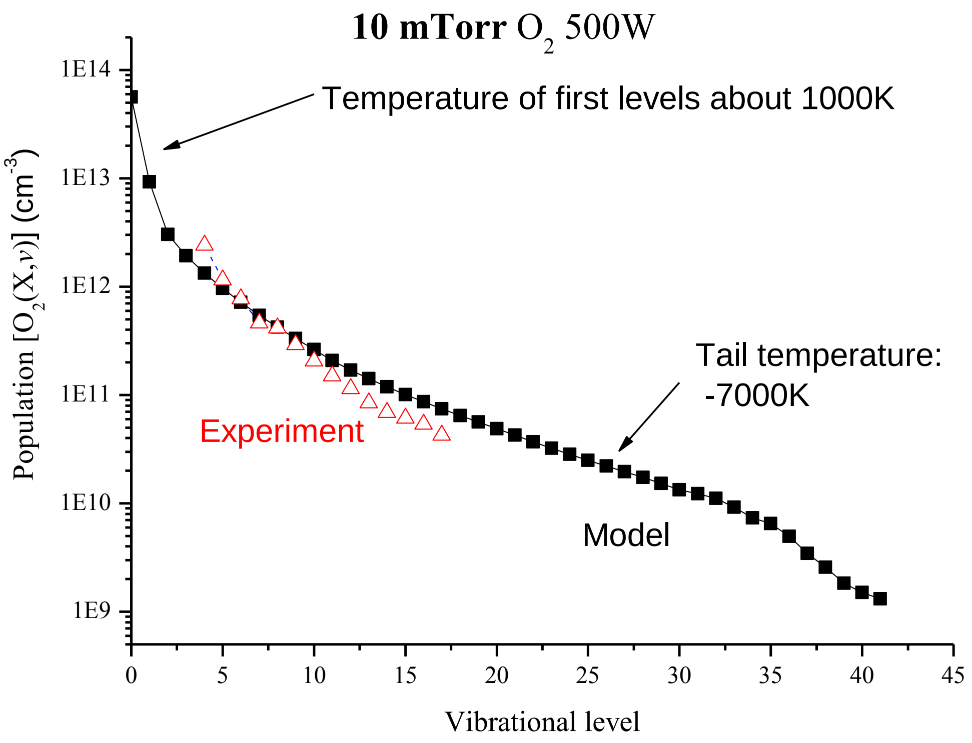
- Tail Tv ≈7000 K
- Up to 3% of O_2 in v = 4-18
- Saturates at high power

O_2 Vibrational distribution functions (function of pressure: 500W)



Tail T_{vib} about 7000K
-independent of pressure
or power!

Modelling the VDF: IST Lisbon



Lowest levels in equilibrium with T_{gas}

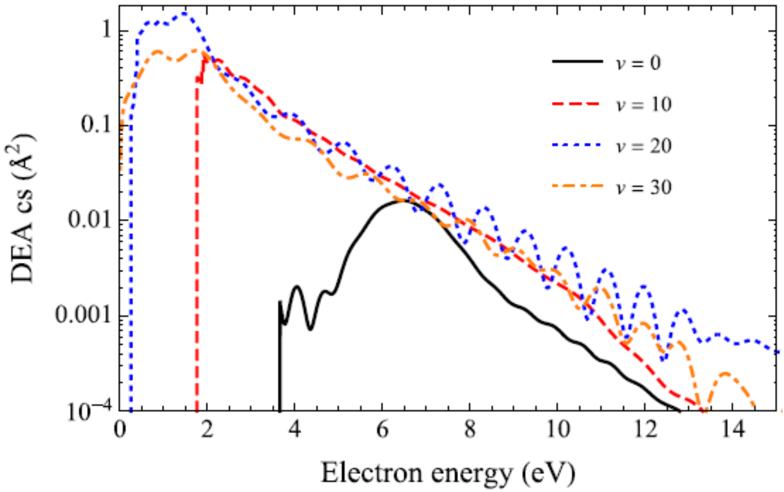
Higher levels much hotter

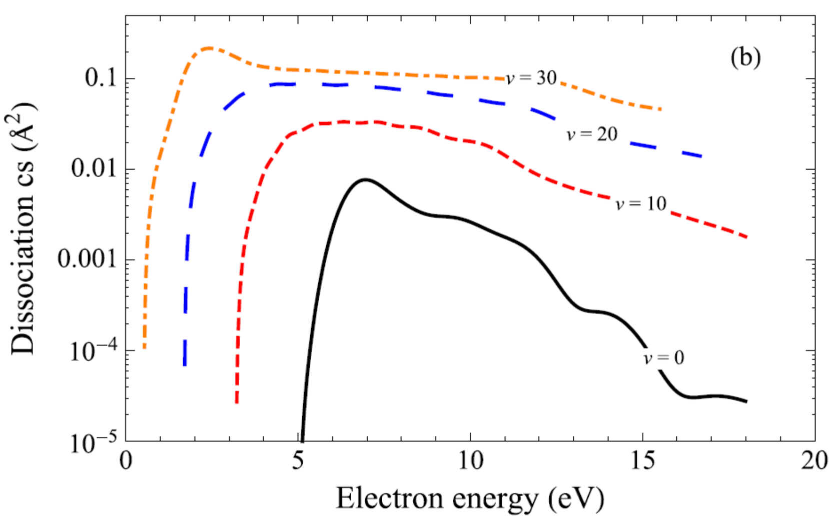
VDF determined by:

-electron impact excitation

-V-T O_2 - O

Effect of vibrational excitation on electron-induced processes



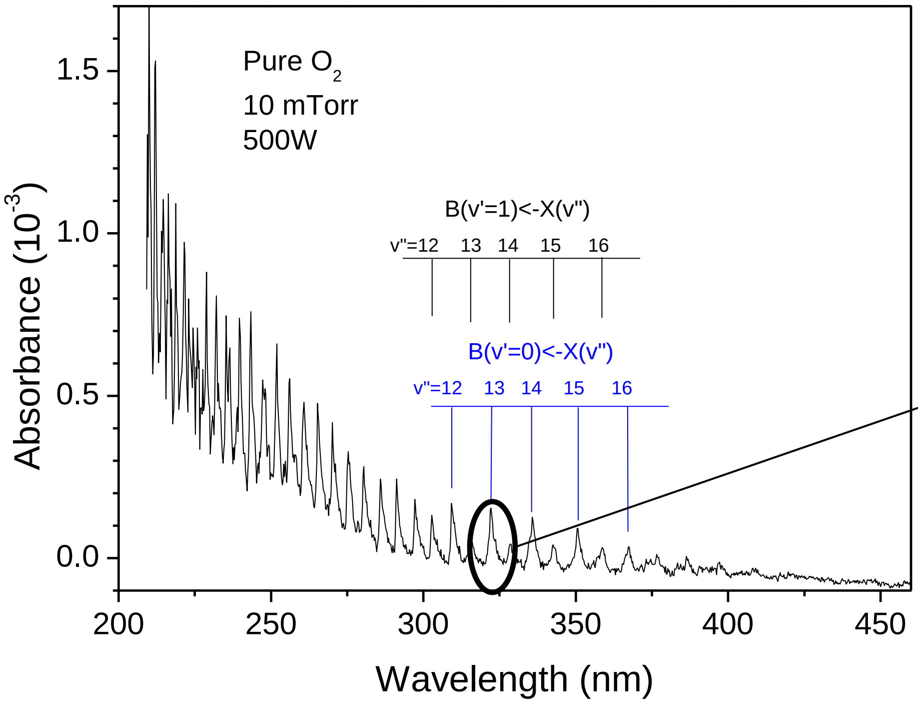


Excitation to >v=10 has a strong effect on both cross-sections:

- Lower threshold
- Higher cross-section

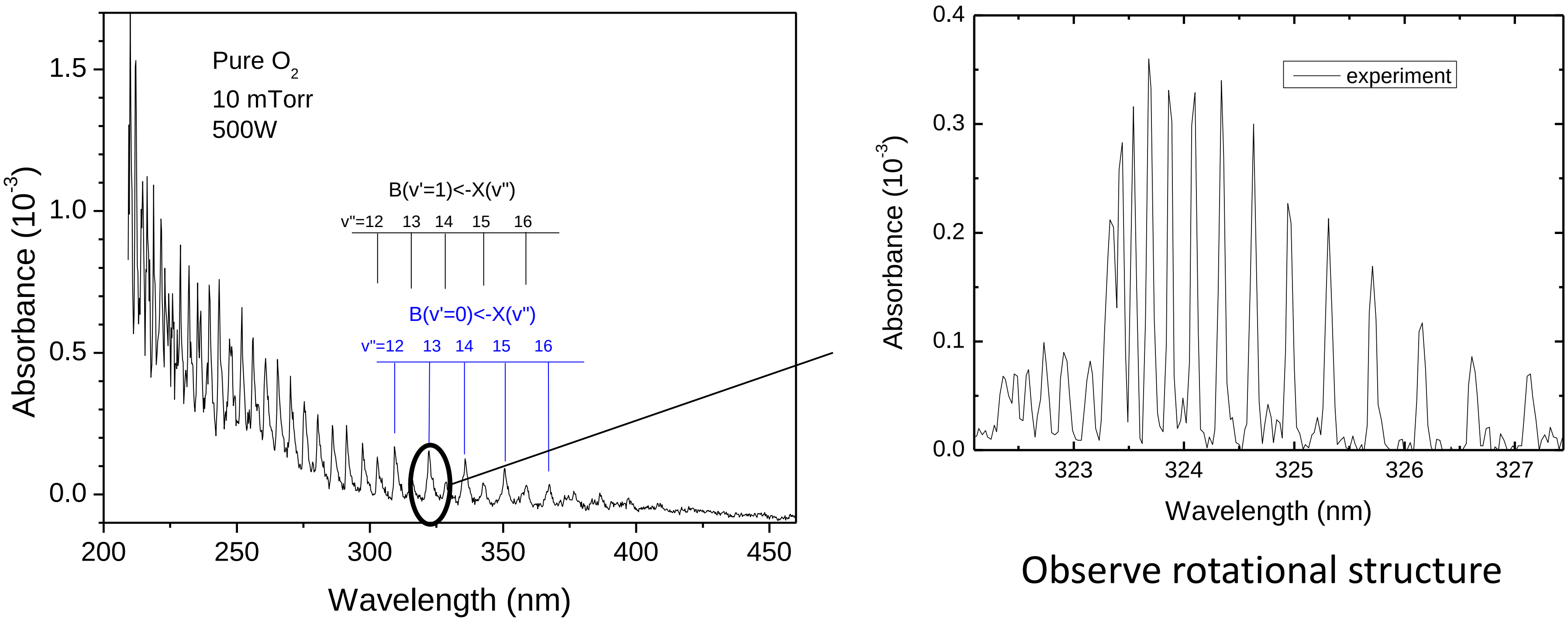
Dissociation and negative ion production significantly enhanced

Gas temperature:
Absorption spectra at higher resolution:



Look at one band in higher resolution :
Change grating 300l/mm to 2400l/mm:

Absorption spectra at higher resolution:

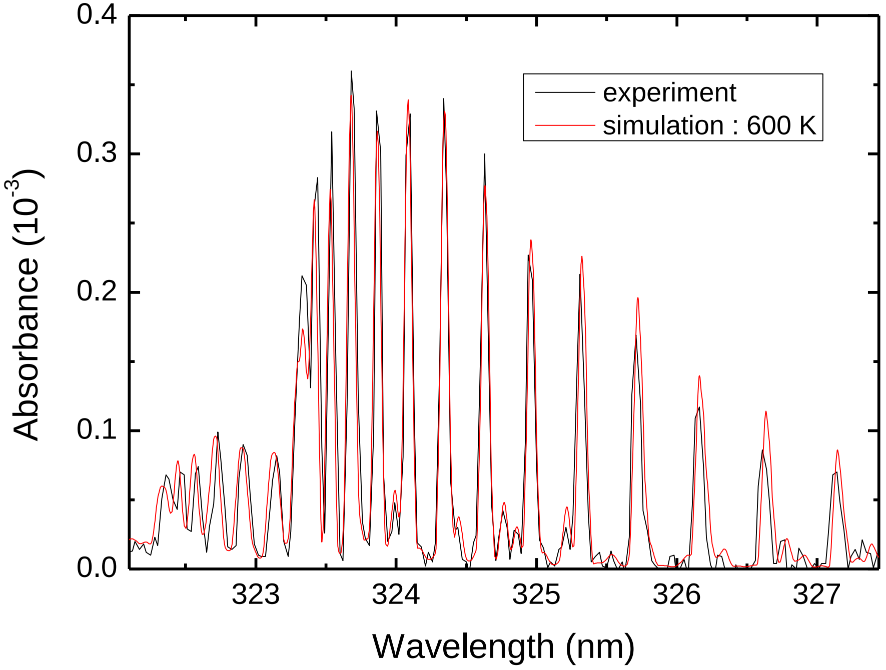


Observe rotational structure

At these pressures $T_{trans} \approx T_{rot}$ << T_{vib}

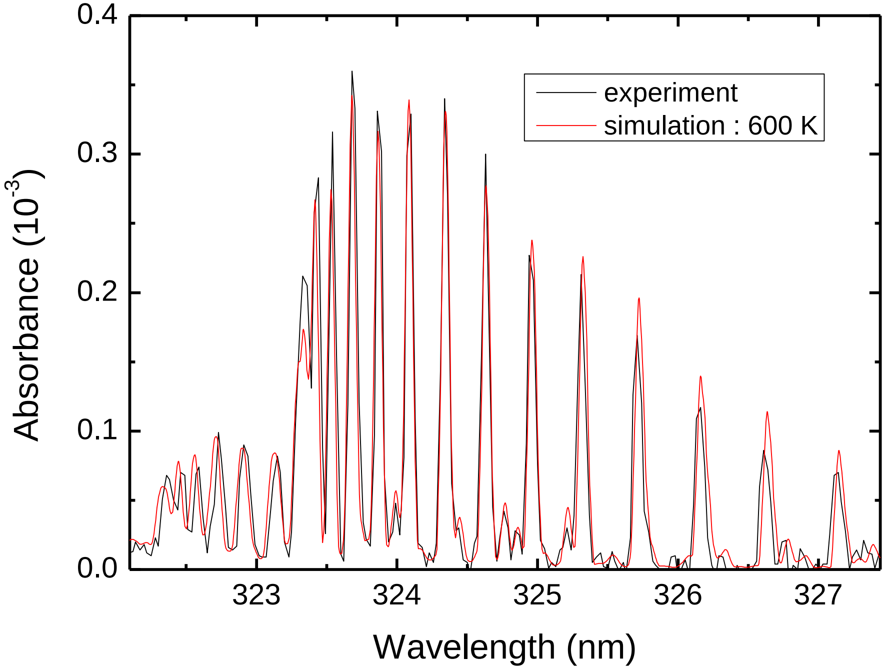
Absorption spectra at higher resolution:

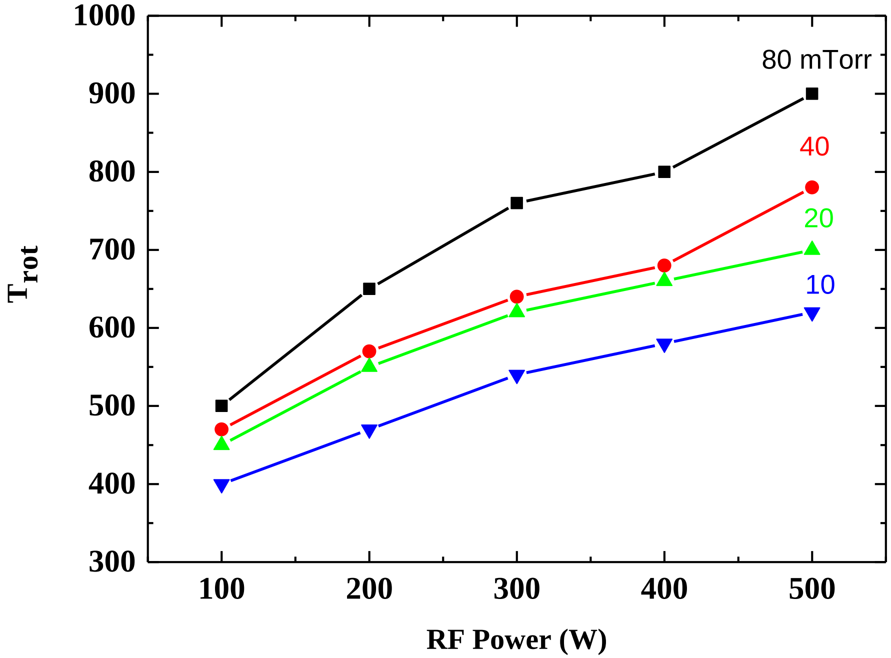
Fit to simulated spectra to determine T_{rot}:



O_2 rotational temperature

Fit to simulated spectra to determine T_{rot}:





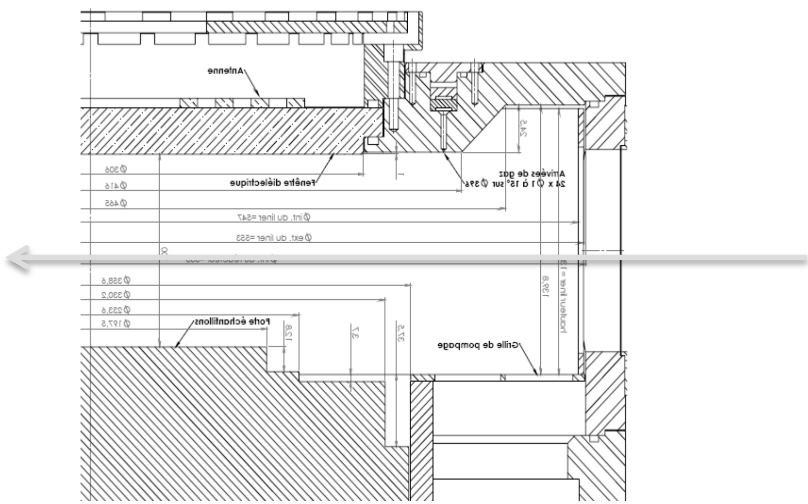
T_{rot} up to 900K!

Explains why O atom density does not exceed 30% of initial gas density

Gas temperature from Ar^m IRLAS Doppler width

Add 10% Ar
Determine temperature from Doppler width of Ar metastable absorption at 772nm

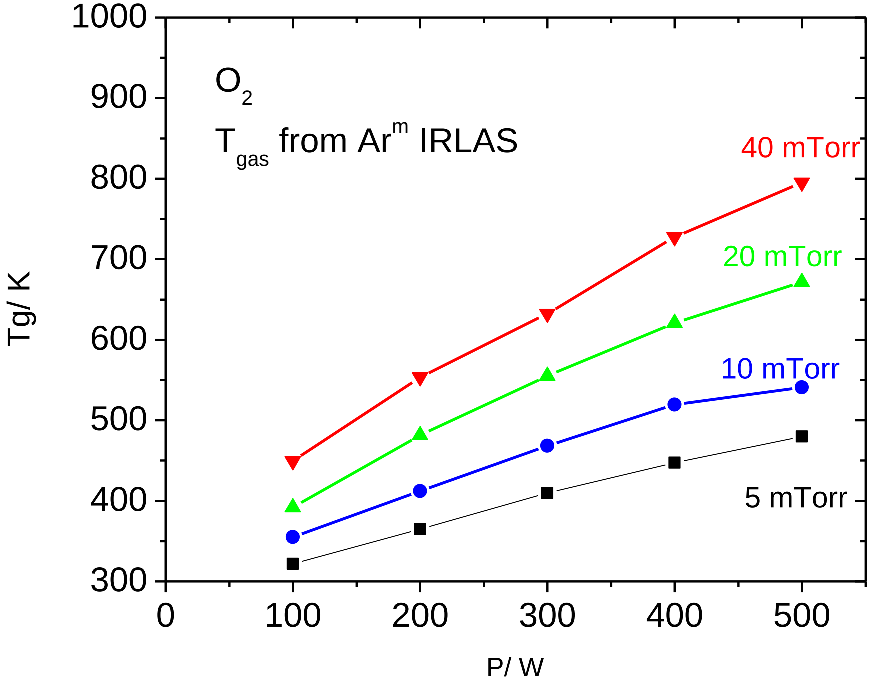
Laser beam at reactor mid-plane:



NB measurement integrated over the reactor diameter, weighted by the Ar^m density profile

Gas temperature from Ar^m IRLAS Doppler width

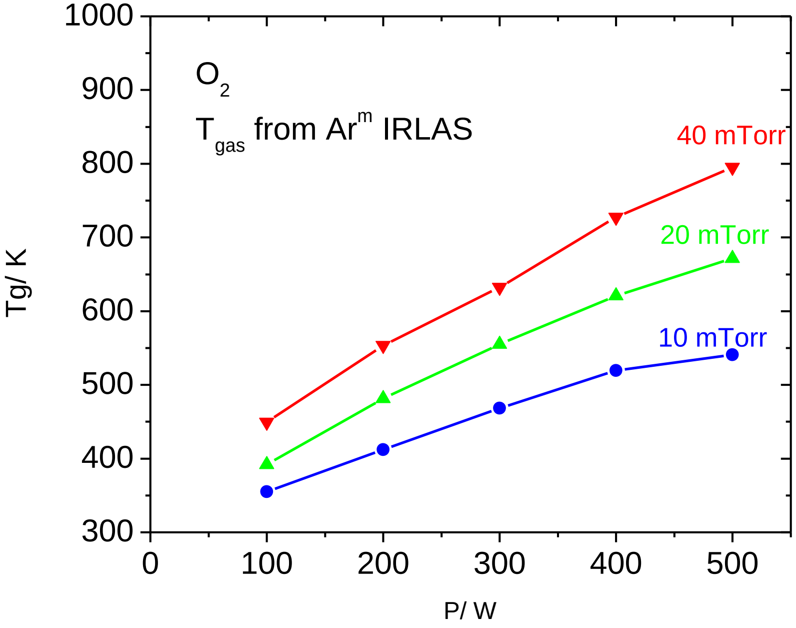
From Ar^m IRLAS



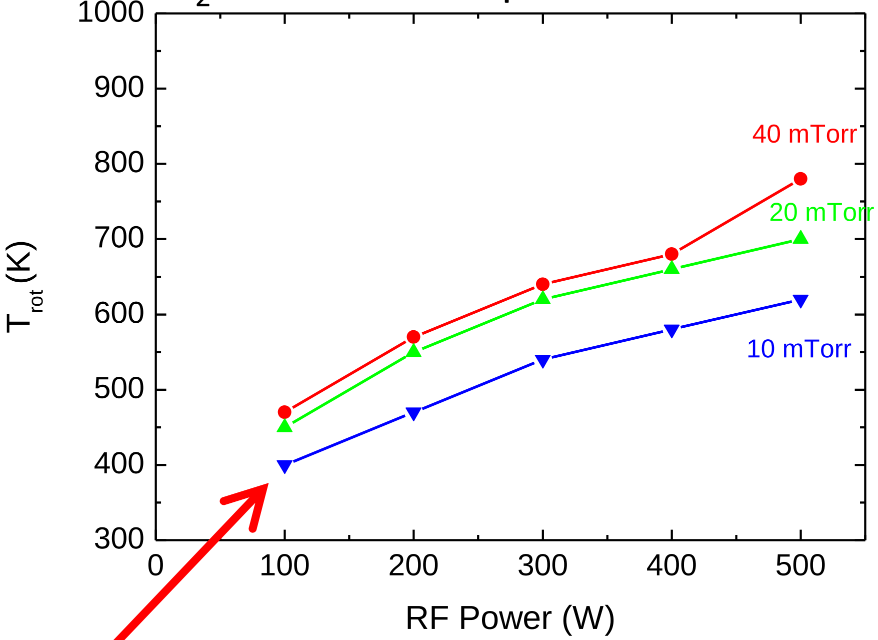
Is thermal equilibrium $T_{trans} = T_{rot}$ established at the lowest pressures?

Compare the two techniques:

Ar^m Doppler temperature;



O_2 rotational temperature:



Reasonable qualitative agreement

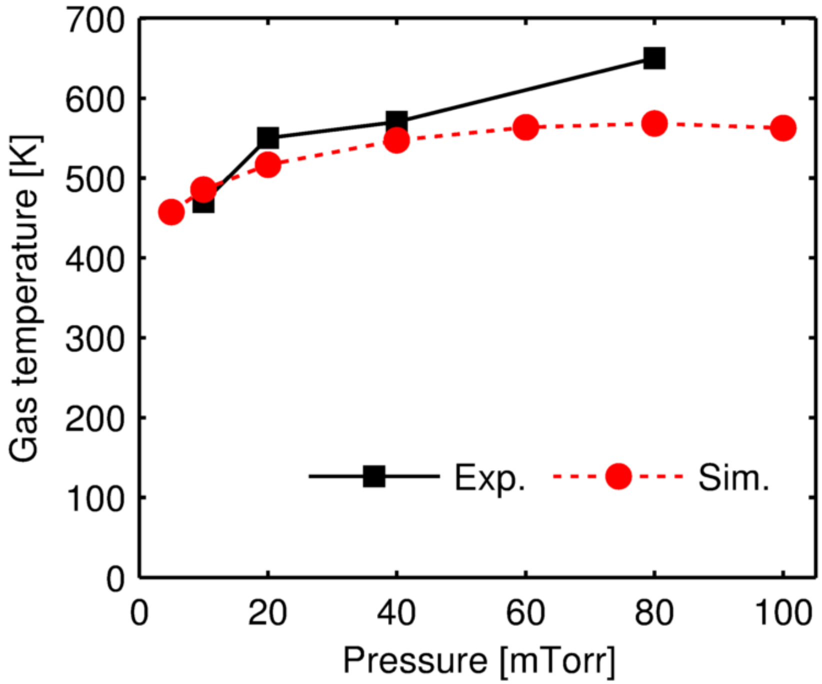
-but at low pressure, IRLAS is cooler than O_2 T_{rot}

Can we directly measure translational temperature of O atoms?

-with time and space resolution

-probe energy relaxation rates (surface and gas phase)?

Simulated gas temperature (300W)



Reasonable trend but underestimated heating:

-underestimated energy release from dissociation?

-neglected heating mechanisms?

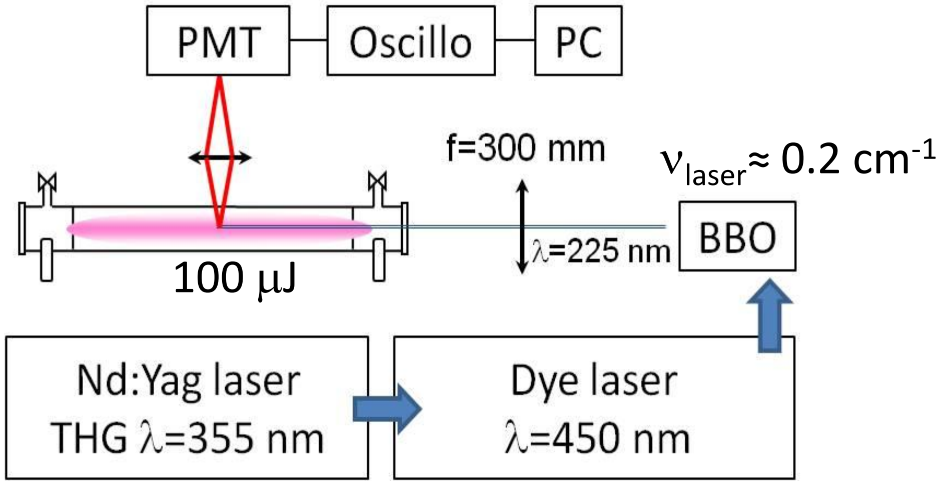
-overestimated thermal accomodation at walls?

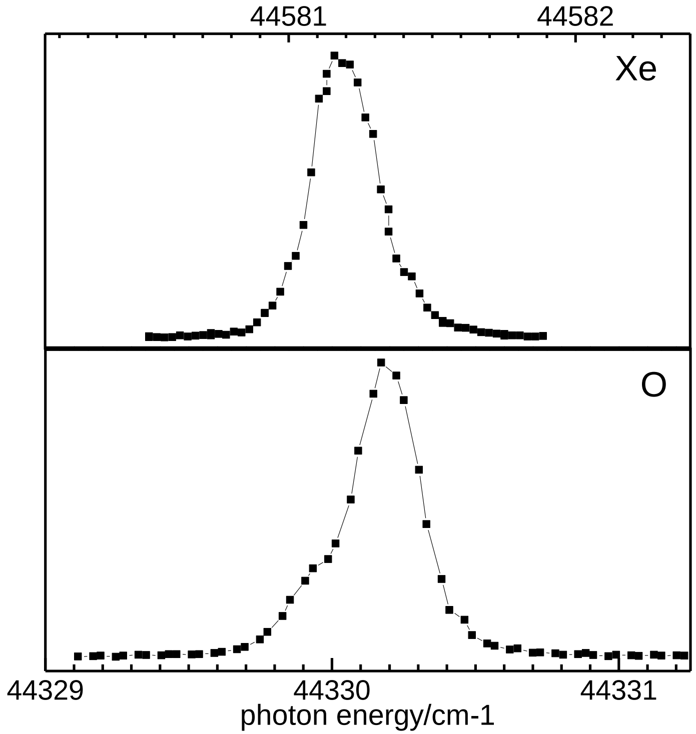
High resolution TALIF for O atom temperature

D. Marinov, O. Guaitella, M. Foucher, JP. Booth
(LPP)

C. Drag, C. Blondel
(Lab Aime Cotton)

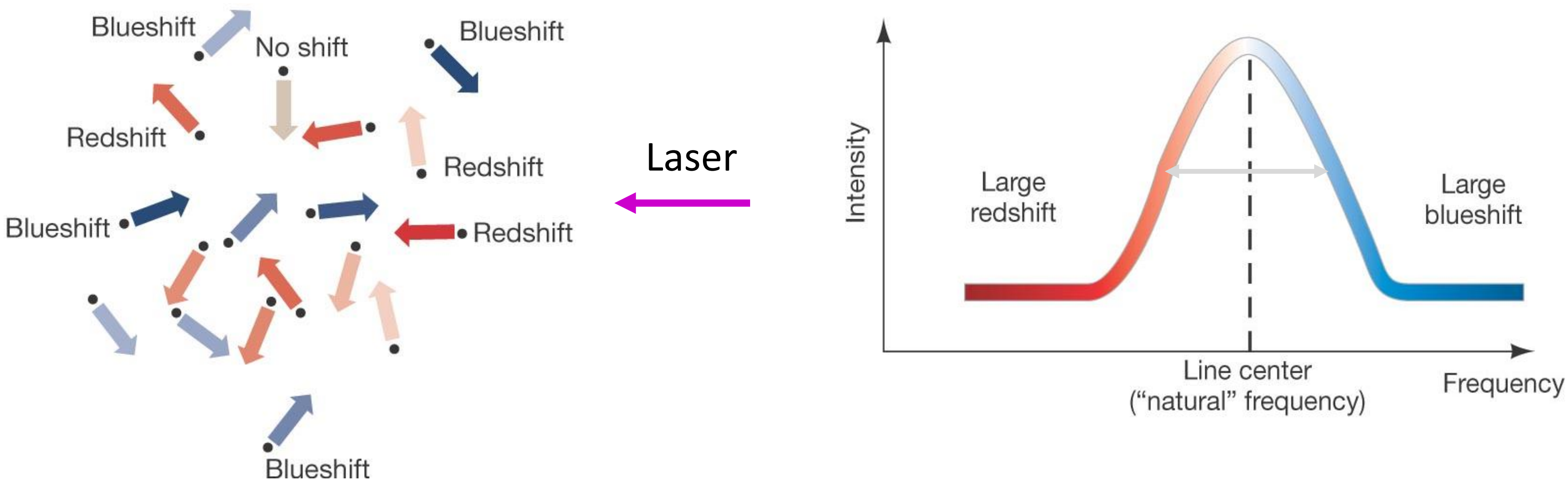
Standard TALIF





- **A lot of information is hidden in the line shape!**
- **But it is not accessible because of the broad and often unknown laser line profile.**

Doppler line width – a direct measure of the translational gas temperature

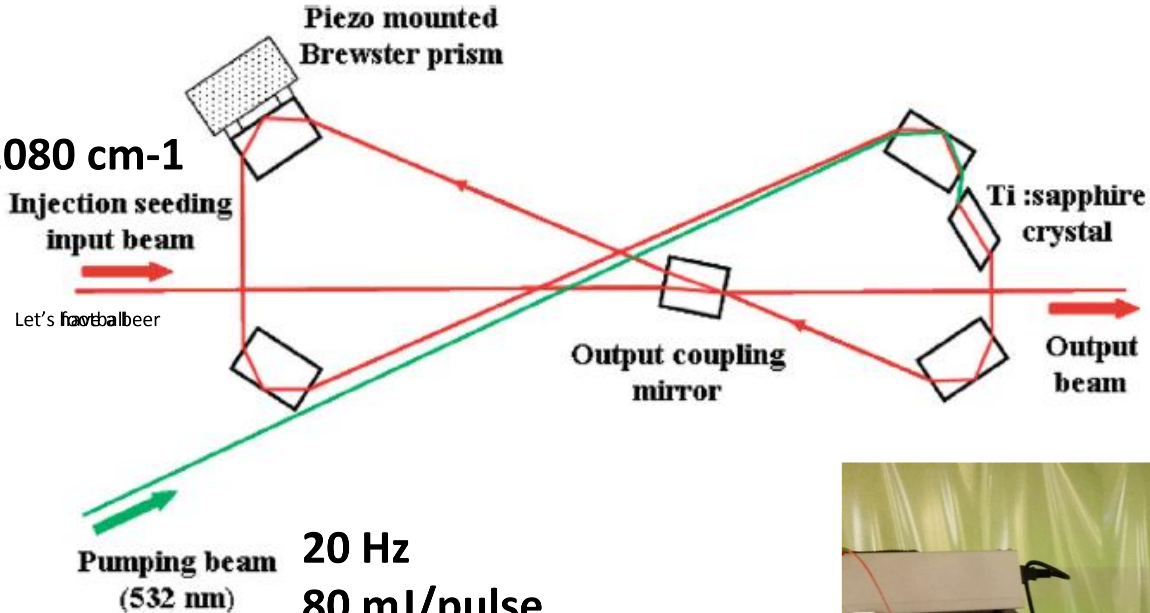


$$\frac{\Delta \nu_{FWHM}}{\nu_0} = \sqrt{\frac{8kT \ln 2}{Mc^2}}$$

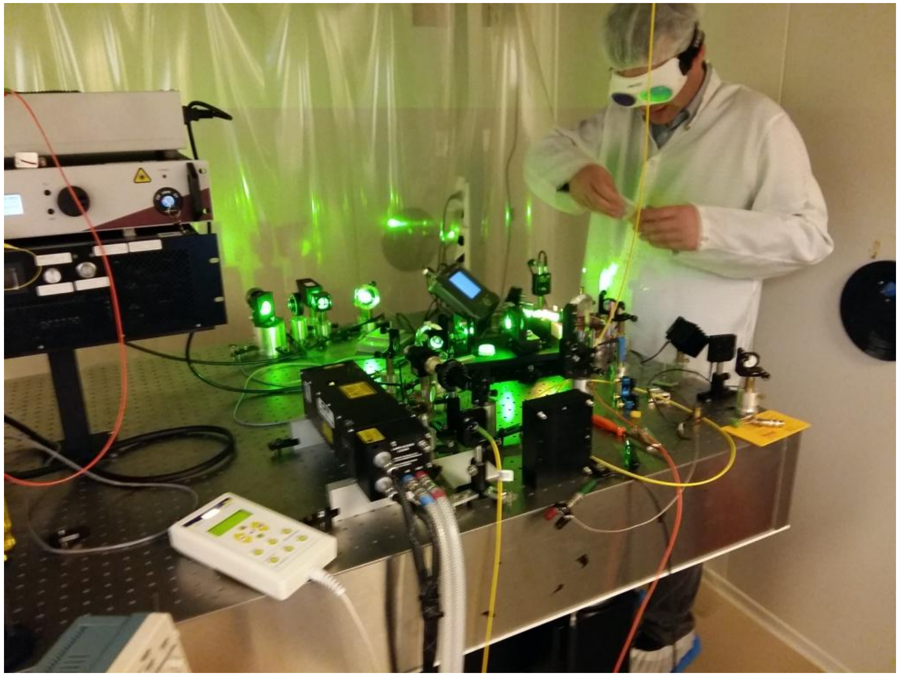
At 300 K $\Delta\nu_O = 0.3\ \text{cm}^{-1}$

Single mode pulsed laser (Aimé Cotton)

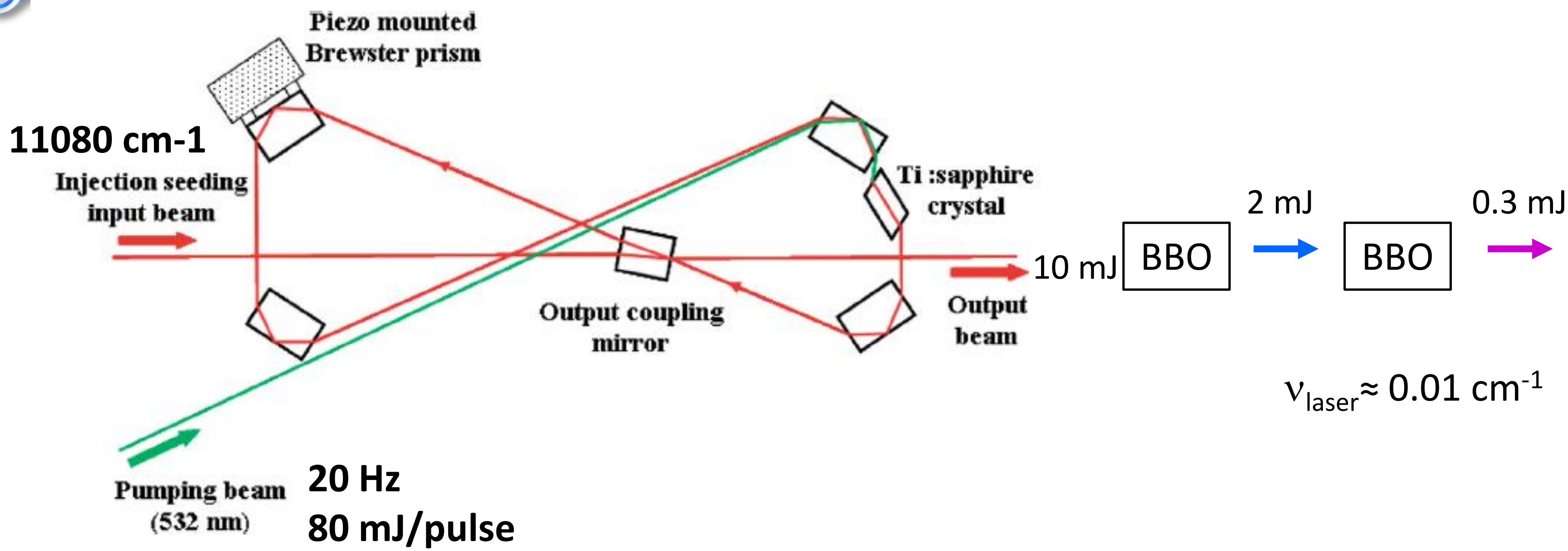
11080 cm-1



20 Hz
80 mJ/pulse



Single mode pulsed laser (Aimé Cotton)



$\nu_{laser} \approx 0.01\ cm^{-1}$

- **Doppler and sub-Doppler line profiles can be accurately measured.**

Laser performance

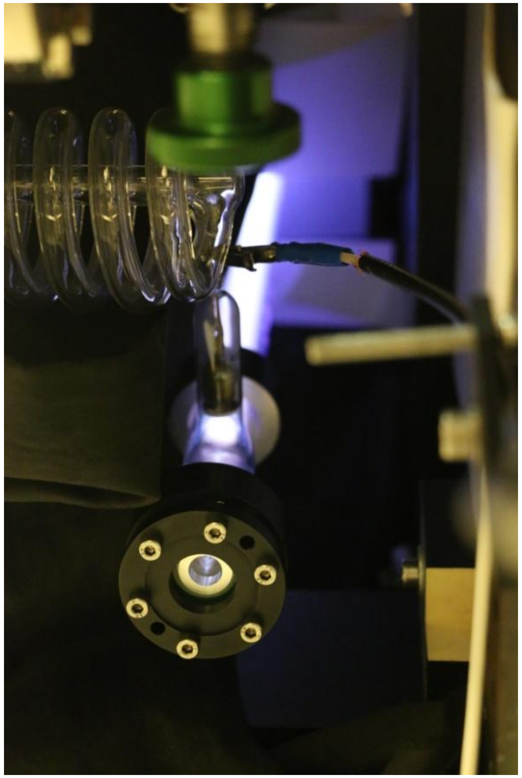
Fundamental line width: determined by Fourier transform of pulse duration (22MHz) + locking jitter (25MHz)

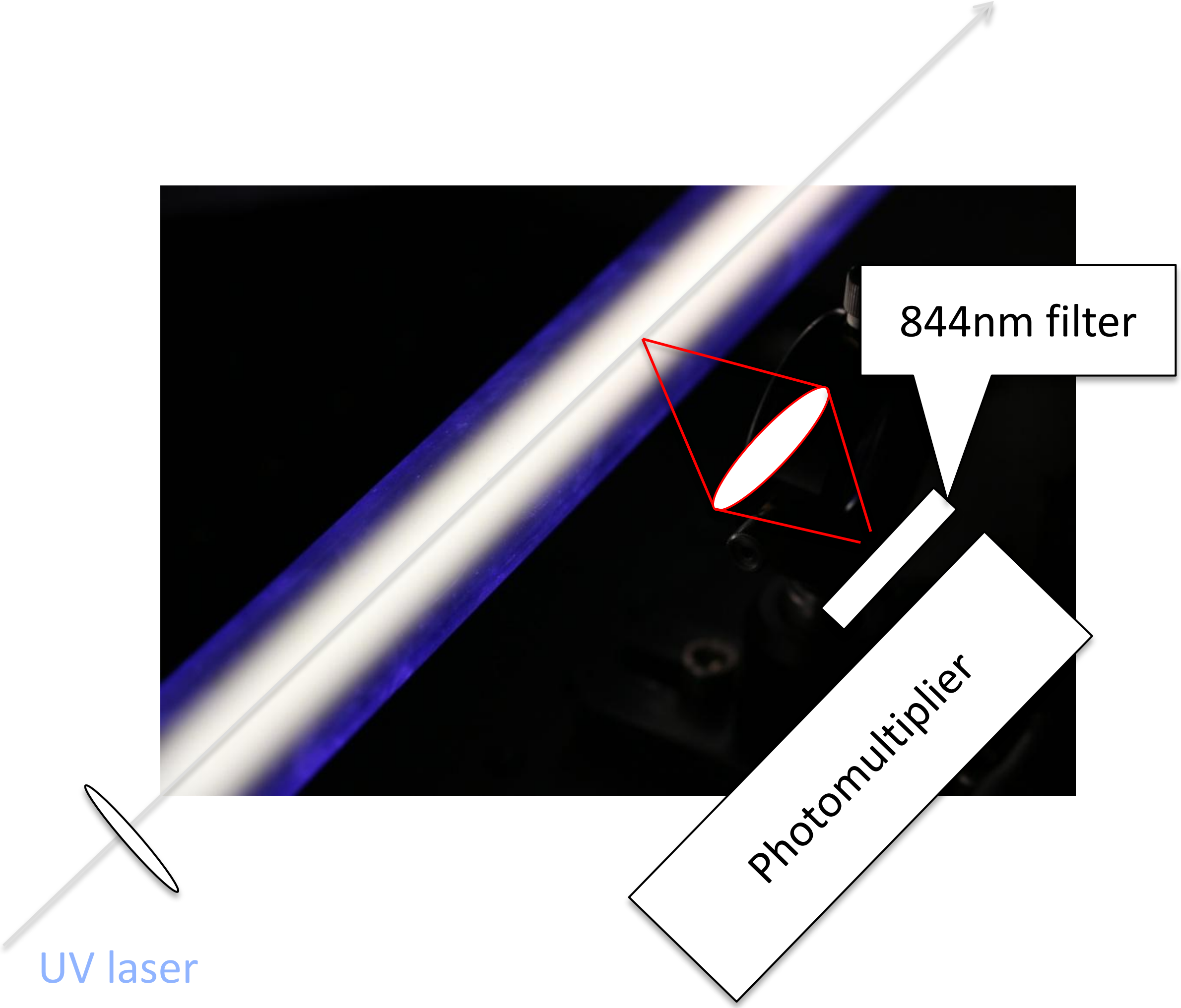
	Wavelength (nm)	Laser energy (mJ)	Estimated line width
Fundamental	902.32	10	47 MHz
Frequency doubled	451.16	2	
Frequency quadrupled	225.58	0.25	188 MHz ($0.01 cm^{-1}$ @ 2 photon)

30x narrower than a dye laser!

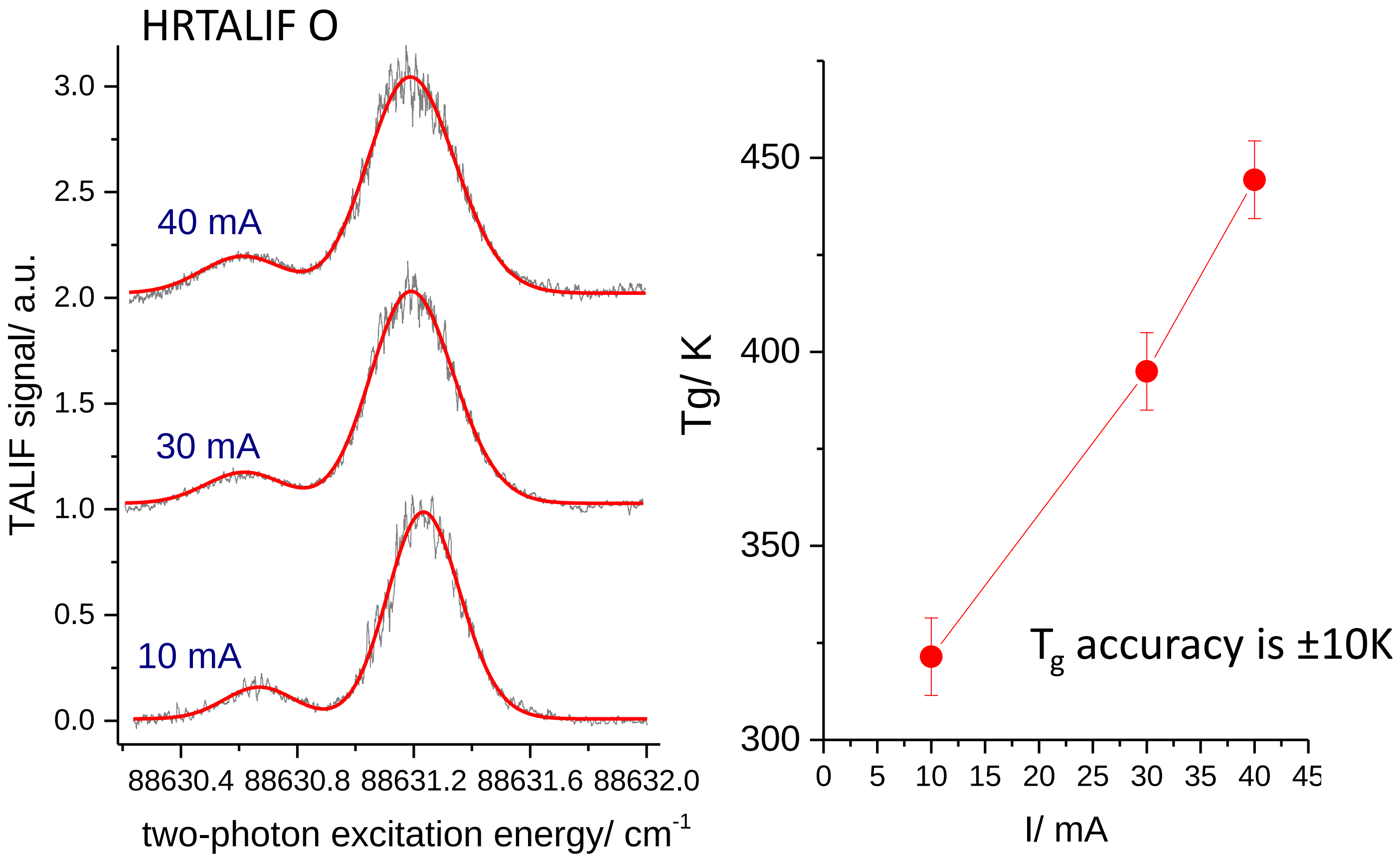
O atoms in an O_2 DC discharge

1-4 Torr O_2 in a 2cm diameter tube
5-40 mA current



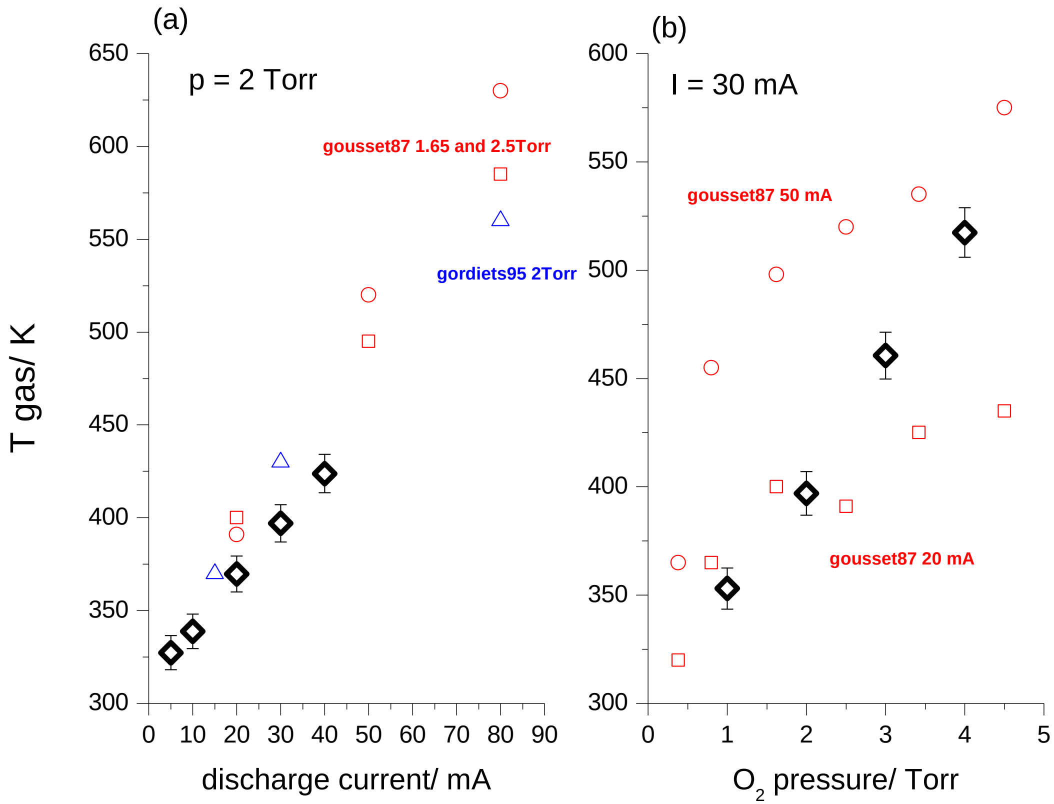


Gas temperature measurements in a low pressure dc glow discharge



O_2 dc discharge 2 Torr – collisional broadening is negligible

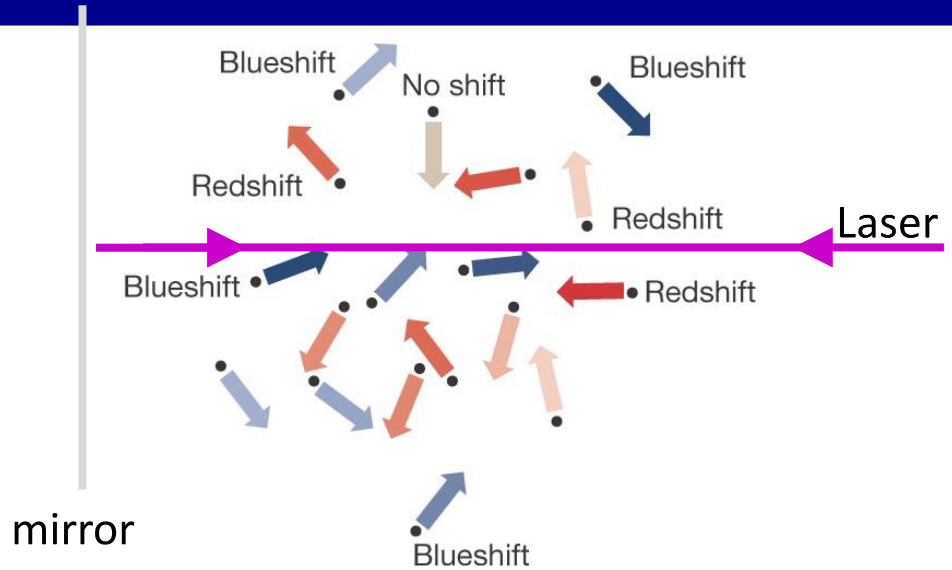
Comparison to previous measurements

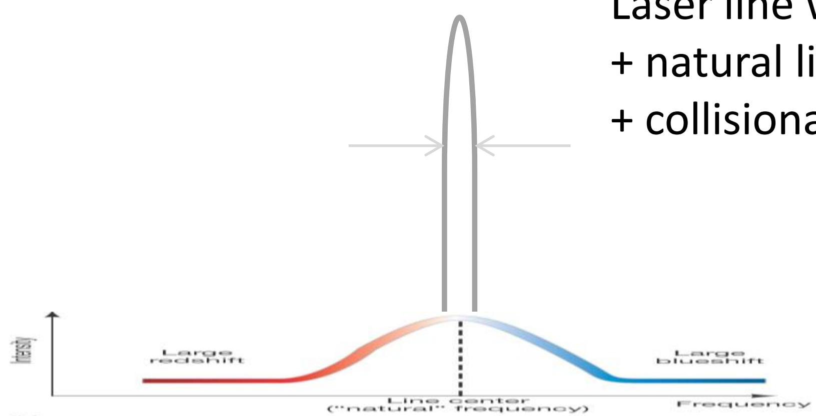


(T deduced from O_2 density : VUV absorption)

Good agreement within errors of previous measurements

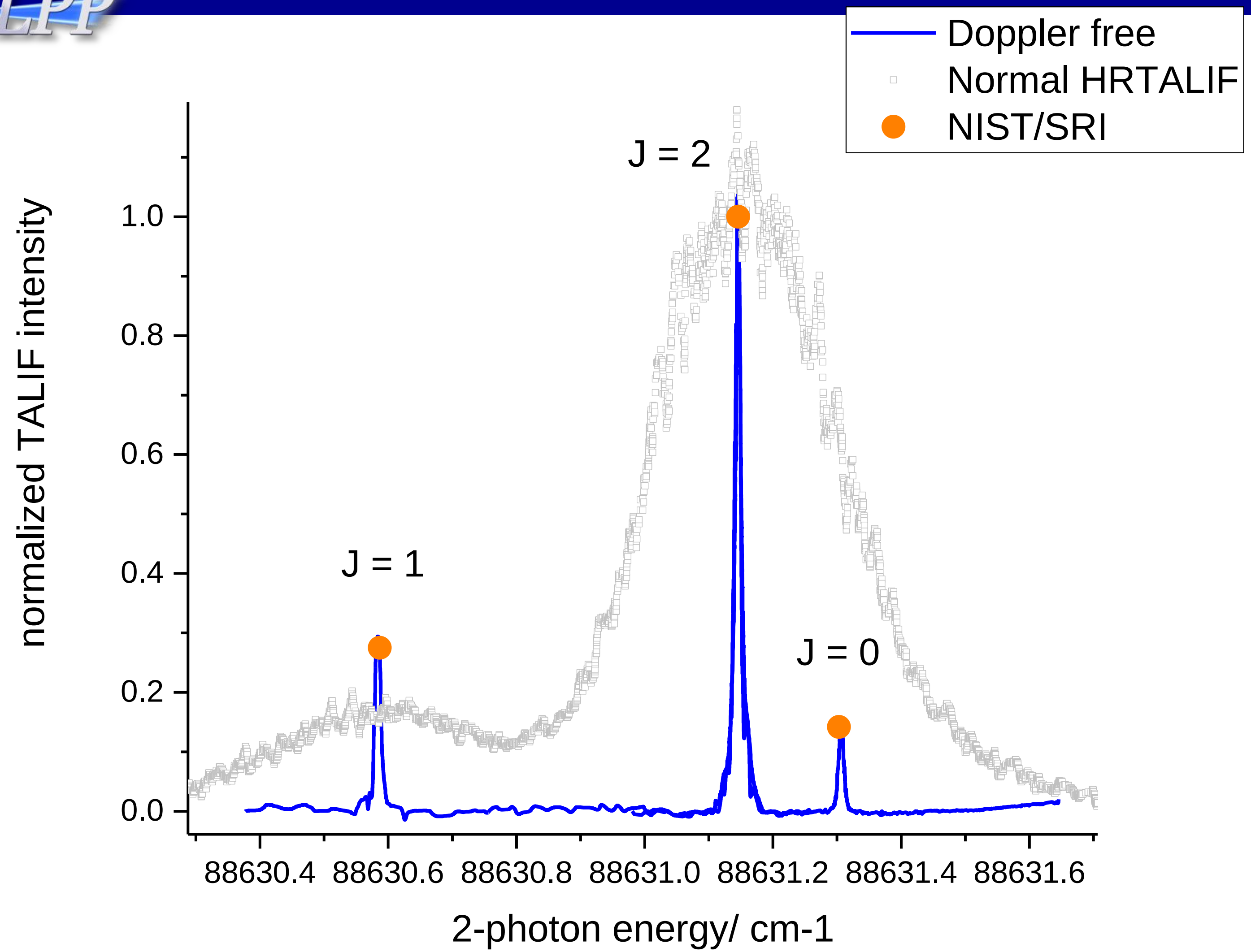
Doppler-free TALIF spectroscpy

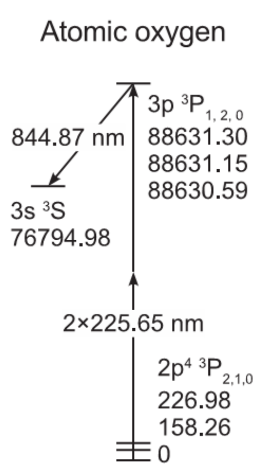




Laser line width
+ natural line width
+ collisional broadening

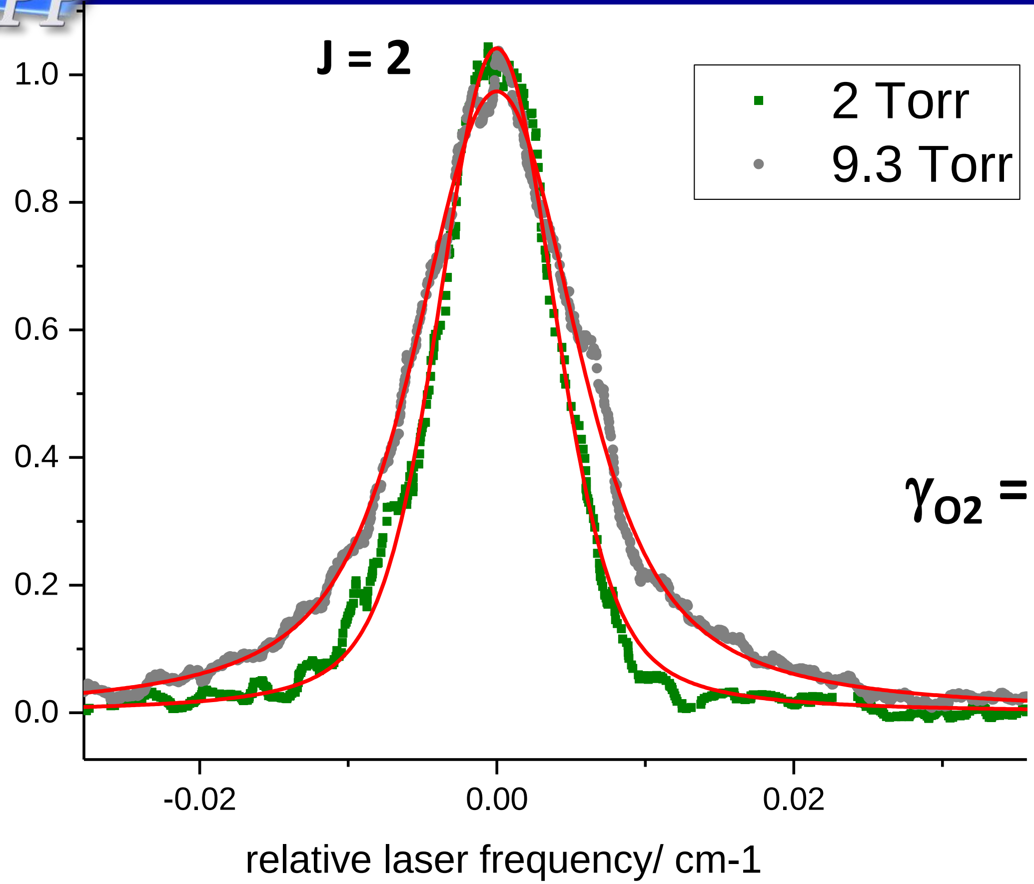
Doppler-free measurements of the fine structure components of O^3P





O_2 dc discharge 2 Torr

Measurements of the collisional broadening coefficients in the Doppler-free configuration

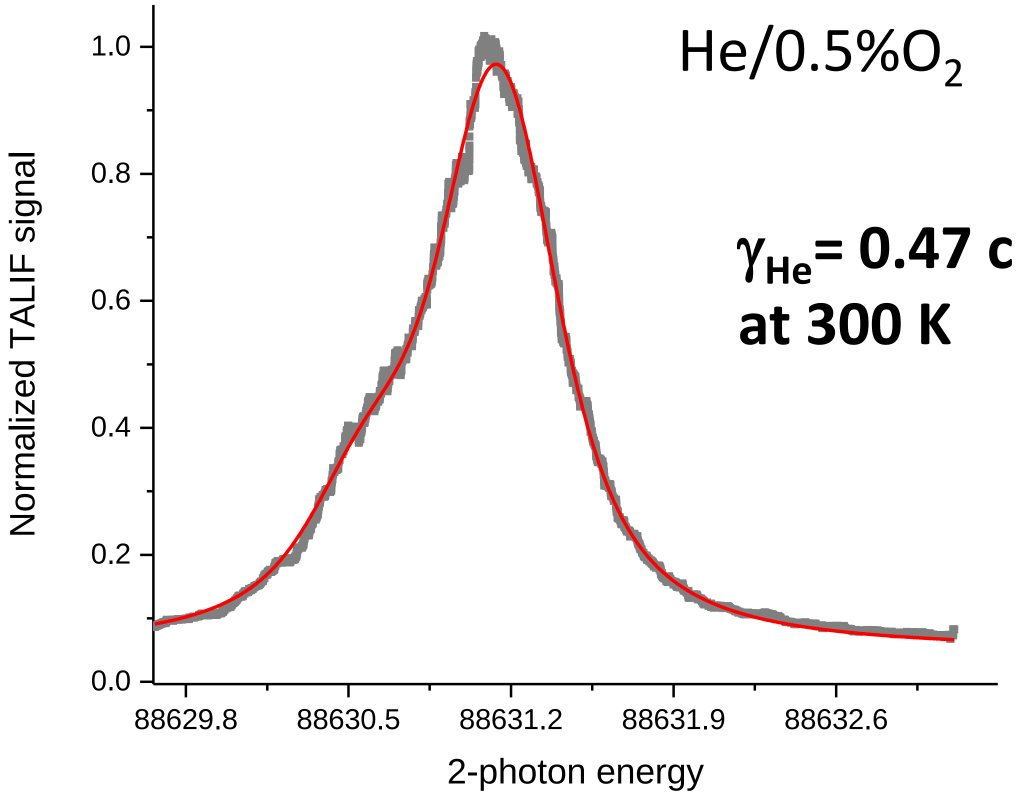


γ_{O2} = 0.38±0.08 cm-1/atm

The only literature value[1] $\gamma = 0.42\ cm^{-1}/atm$ in a O_2/CH_4 flame at 2500 K

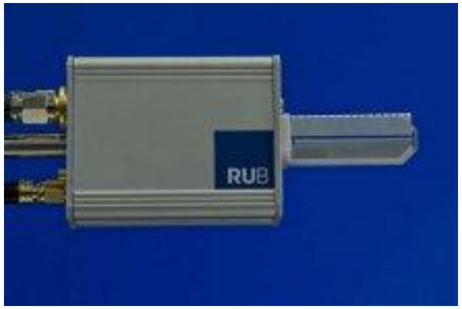
[1]Dyer et al., Opt. Lett. **14**, 12-14 (1989)

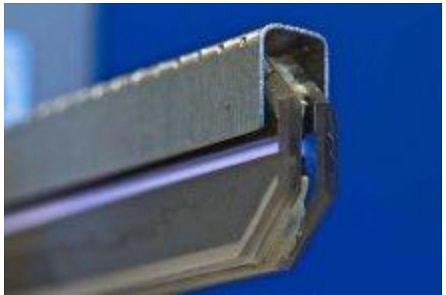
Pressure broadening in the μAPPJ (normal TALIF configuration)



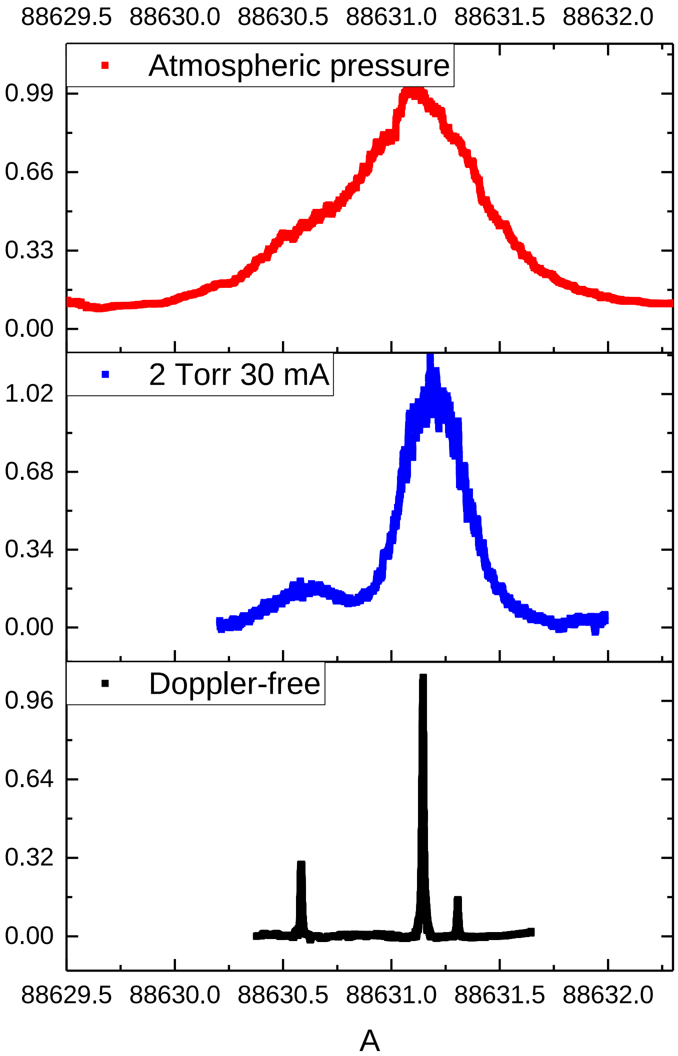
He/0.5%O_2

γ_{He}= 0.47 cm-1/atm at 300 K





Summary of HR TALIF



- atm pressure:
  - -Pressure broadening
- Low pressure Doppler:
  - Translational gas temperature
- low pressure sub-Doppler
  - -Pressure broadening
  - -Fine structure
  - -Atomic physics

Conclusions

Comprehensive data set to test models of Oxygen plasmas

-Atom densities and kinetics

-Molecule densities and energy distributions

-Electron (& negative ion) densities,

-Gas temperature

Even for the simple case of pure diatomic gases, state-of-the-art models are unable to correctly predict trends with gas pressure

-Fundamental collision data is lacking or innaccurate

-Gas heating is very significant and remains to be fully understood

-Vibrational excitation can be significant and may play a large role

Future work:

High resolution TALIF – in ICP reactor

-time and space resolution to understand relaxation kinetics

FUNDING :