Laser Cavity Ringdown Spectroscopy of Oxygen Plasmas:

Direct Measurement of the Densities of Oxygen Atoms, Ozone and Negative Ions and Gas Temperature

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APPLIED MATERIALS®

Acknowledgments

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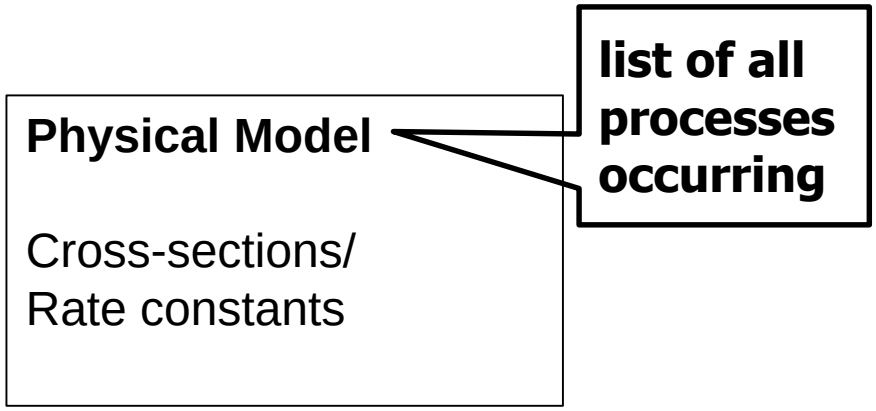
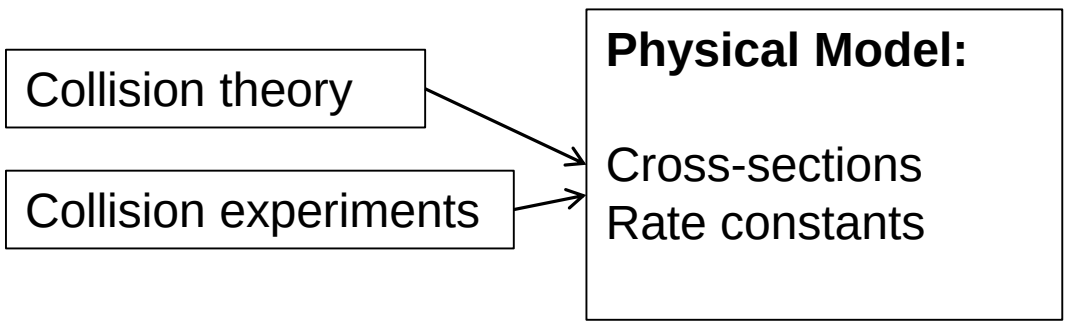
T Rakhimova, D Voloshin, Y. Mankelevich — Moscow State University

Experimental validation of models



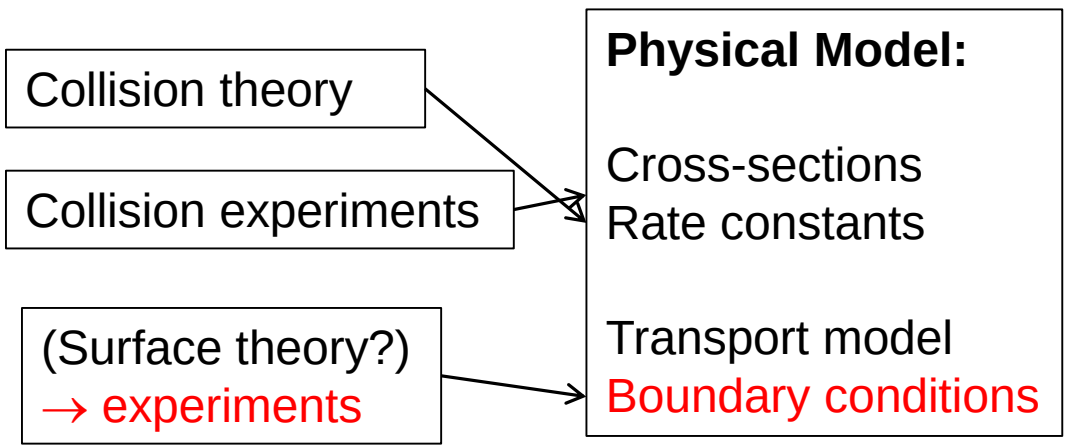
Getting this right is our goal!

Experimental validation of models



Often very incomplete
and/or inaccurate

Experimental validation of models



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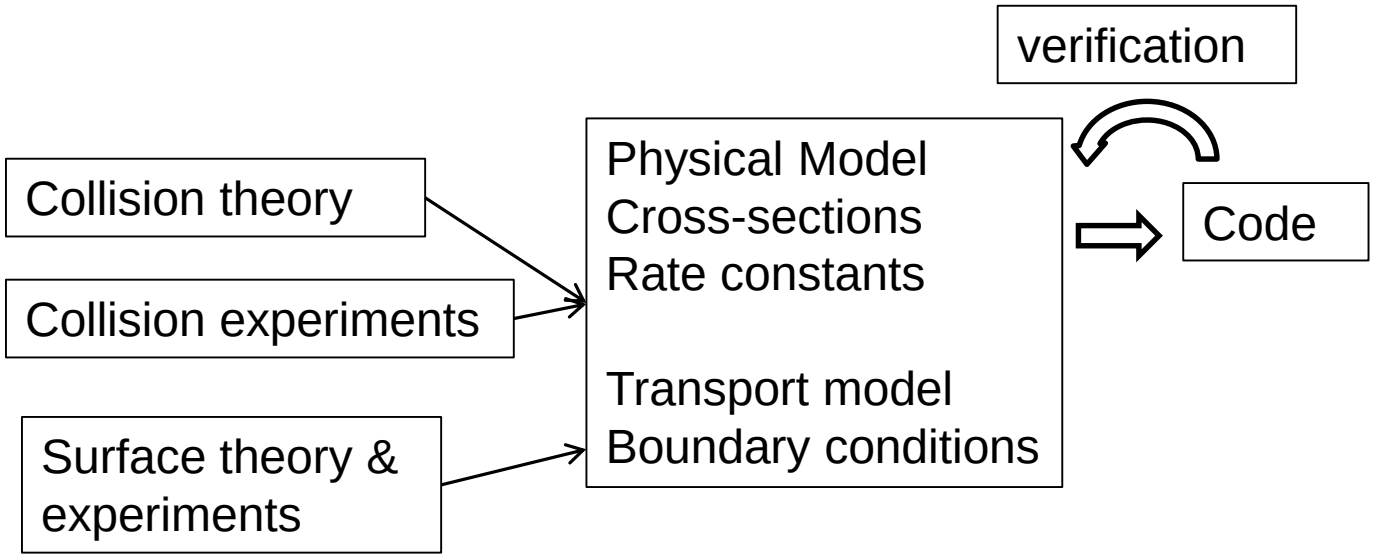

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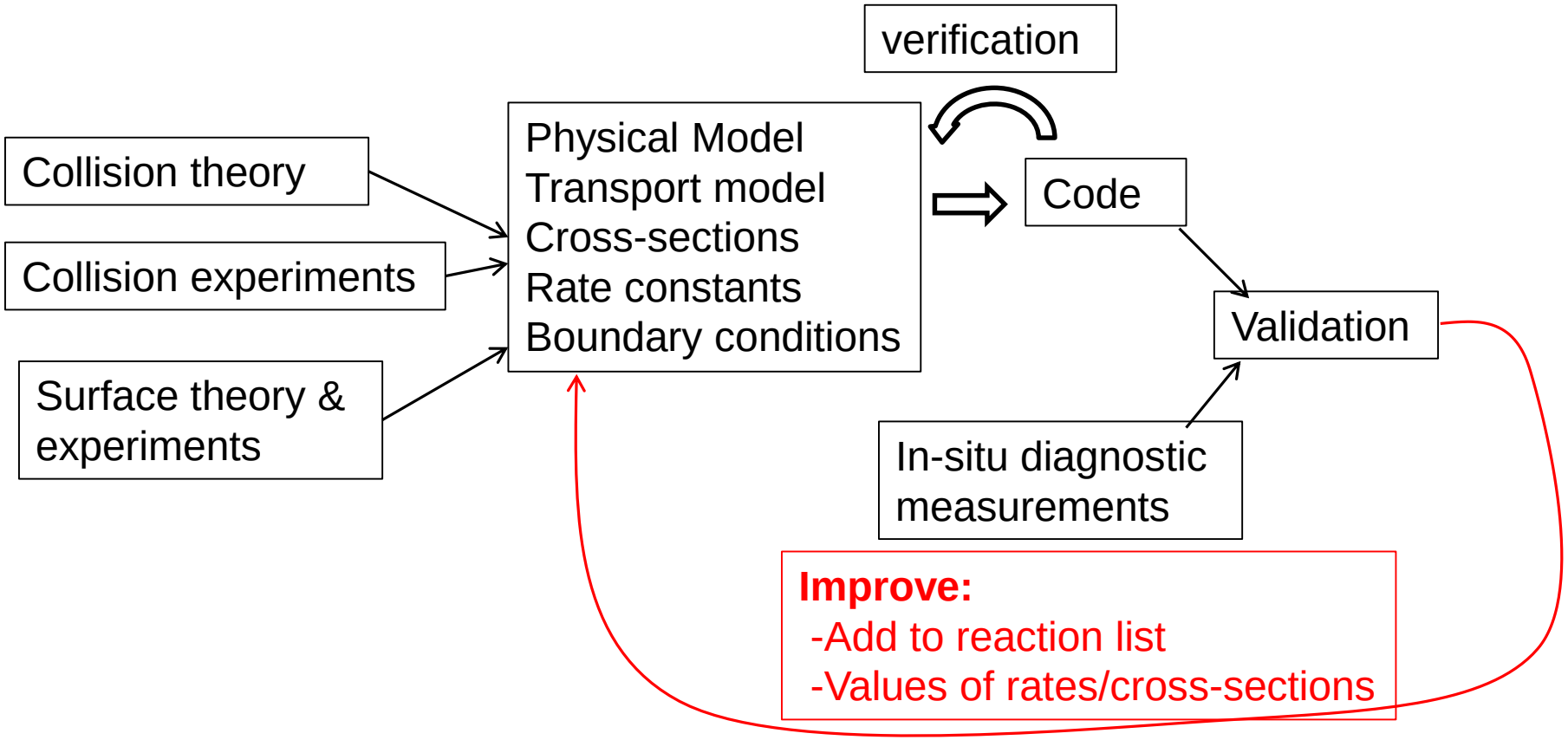
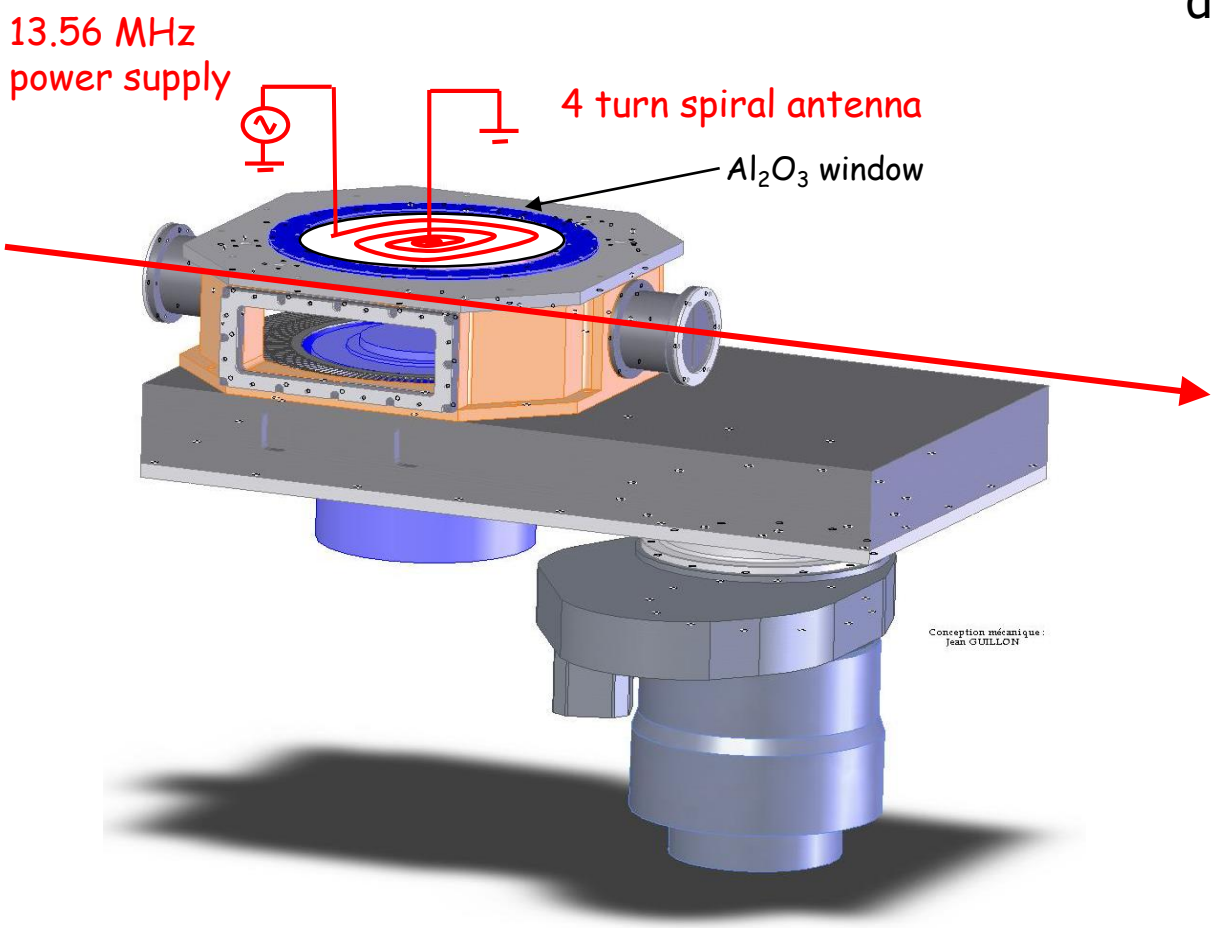


Which plasma system to study?

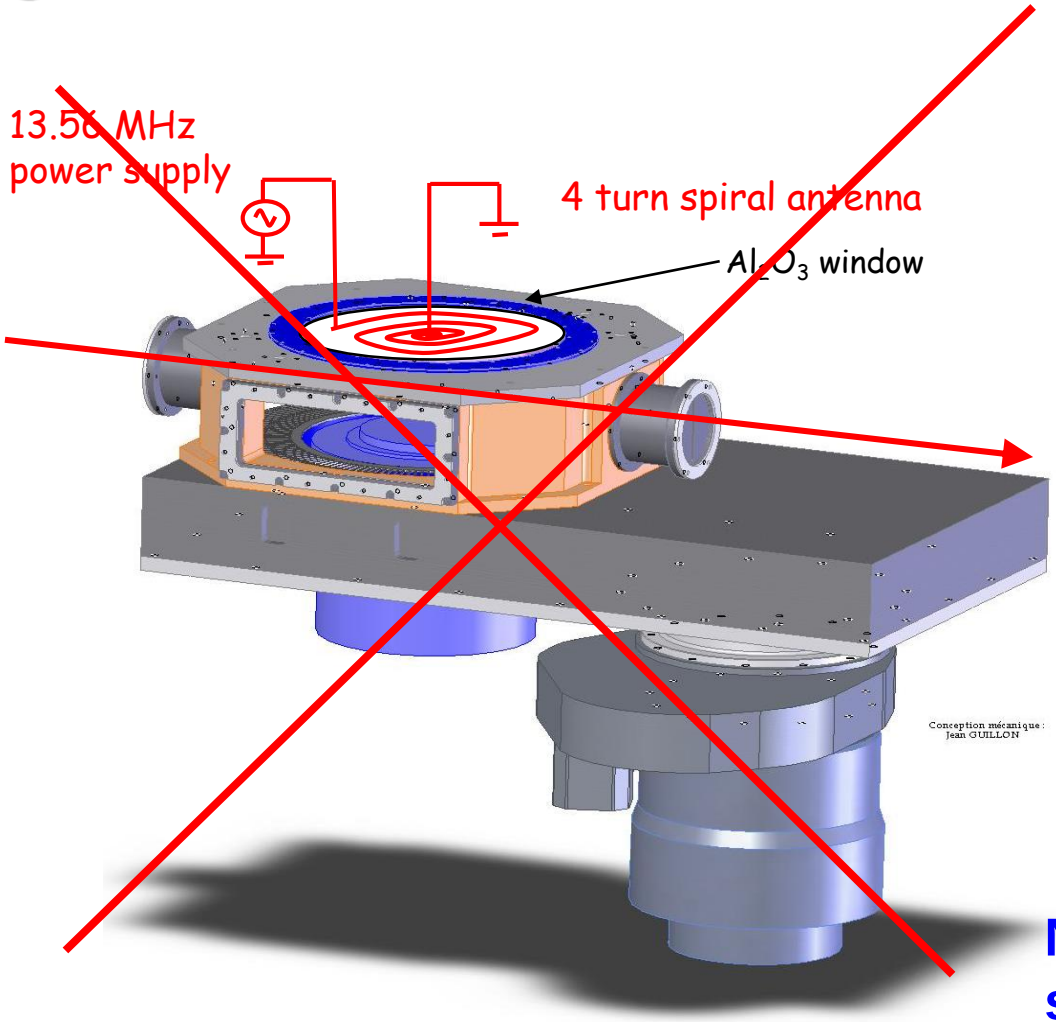
Do you want industrial funding?

Semiconductor Etching
The Inductively Coupled Plasma Reactor :

-Industrial Scale Reactor
dimension for 300mm wafers



Semiconductor Etching
The Inductively Coupled Plasma Reactor :



Poor for model validation:

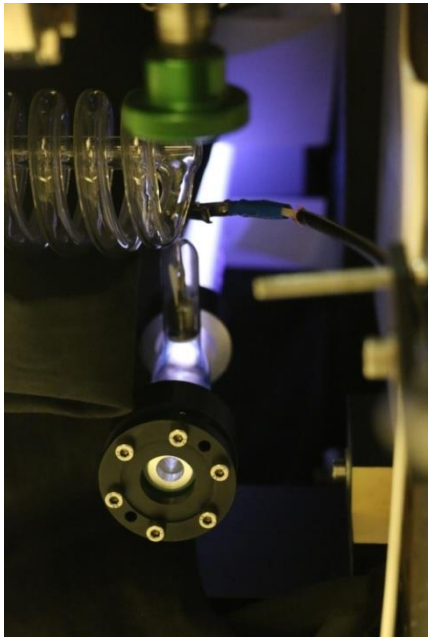
Strong radial gradients in:
Power deposition
Gas temperature
Gas density
Gas composition

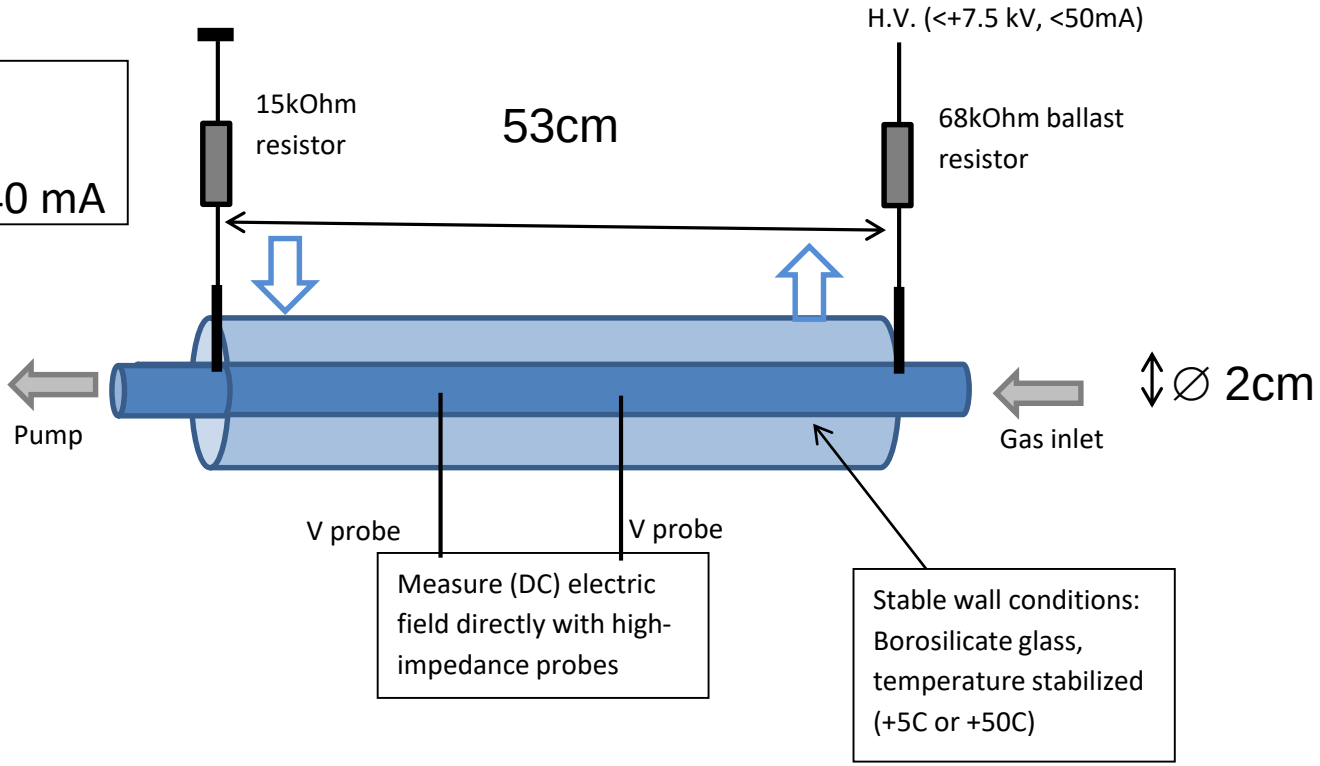
Need simpler, better controlled system for experiment/model comparison :

DC discharge in O_2 in a Pyrex tube
Ideal system for Experiment-model comparison

Pressure: 0.2 – 10 Torr

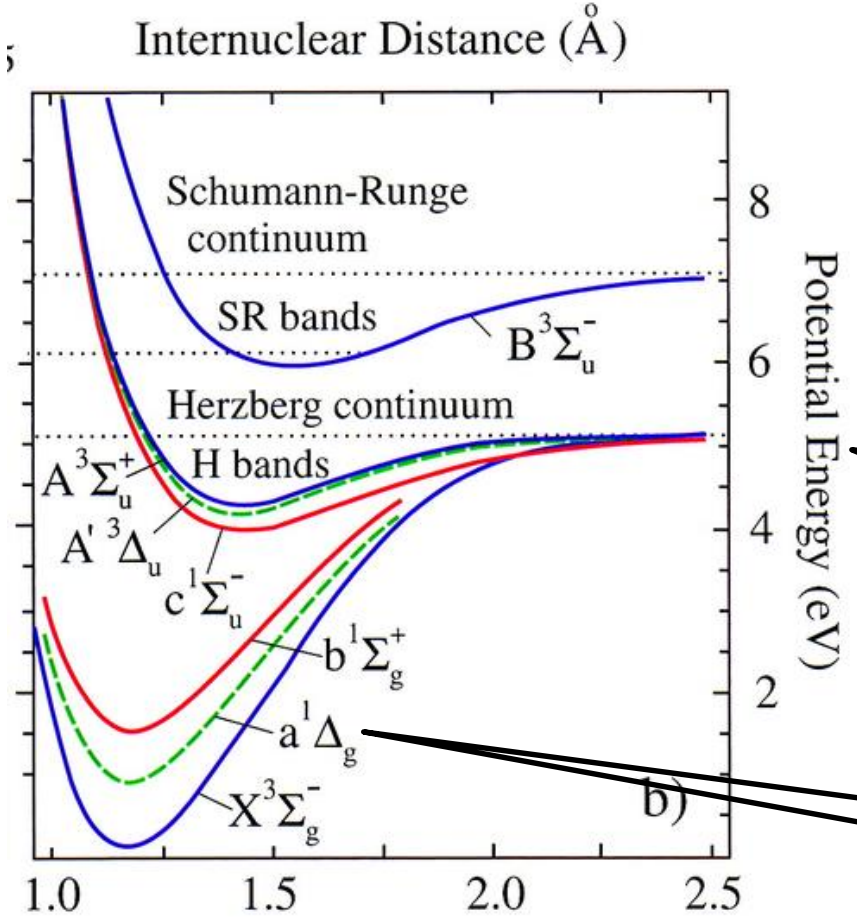
Discharge current: 10 - 40 mA





-Axially uniform,
-Constant, **measured** reduced electric field,
-Reproducible surfaces (?)

The O_2 molecule:
A simple (?) molecular system showing all processes



Dissociation to
$O\ ^3P + O\ ^1D$
8 eV

Dissociation to
$2 \times O\ ^3P$
5 eV

Metastable states at 1 and 1.6 eV

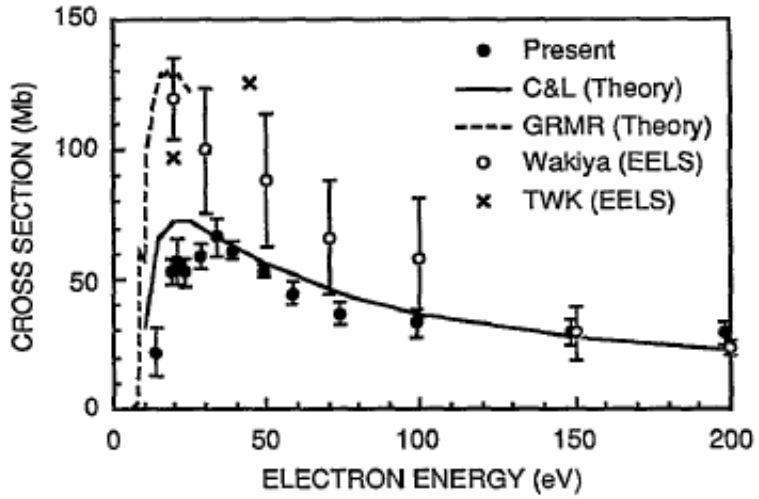
O_2 plasmas have been studied for > 100 years
-What don't we know?

Outstanding questions about O_2 plasmas

Electron impact dissociation

cross-section low energy/ rate constant at low E/N

Reliable near-threshold data non-existent!



Cosby 1993 :
No data below 15 eV!!

Outstanding questions about O_2 plasmas

Electron impact dissociation

cross-section low energy/ rate constant at low E/N

Surface recombination of O, γ_O :

Universal law for γ?

Effect of ion bombardment?

In-situ measurements :
-varying results
-drift, poor reproducibility

Outstanding questions about O_2 plasmas

Electron impact dissociation

cross-section low energy/ rate constant at low E/N

O atom surface recombination, γ :

Universal law for γ?

Effect of ion bombardment?

Metastable molecules ($a^1\Delta_g$, $b\ ^1\Sigma^+$):

Kinetics : creation, quenching (surface + gas phase)

Stepwise dissociation?

Outstanding questions about O_2 plasmas

Electron impact dissociation

cross-section low energy/ rate constant at low E/N

O atom surface recombination, γ :

Universal law for γ?

Effect of ion bombardment?

Metastable molecules ($a^1\Delta_g$, $b\ ^1\Sigma^+$):

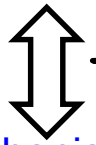
Stepwise dissociation?

Kinetics : quenching - surface and gas phase

Electronegativity

O^- : creation and loss mechanisms

Effect on charged particle transport



Complex, inter-related kinetics:

$O^- + O_2\ a^1\Delta_g \rightarrow O_3 + e$

Outstanding questions about O_2 plasmas

Electron impact dissociation

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O atom surface recombination, γ :

Universal law for γ?

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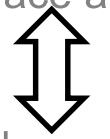


Electronegativity

negative ion creation and loss mechanisms

Temperature

Gas heating mechanisms

Surface thermal accommodation

} predictive models immature

Temperature interacts with everything!

Electron impact dissociation

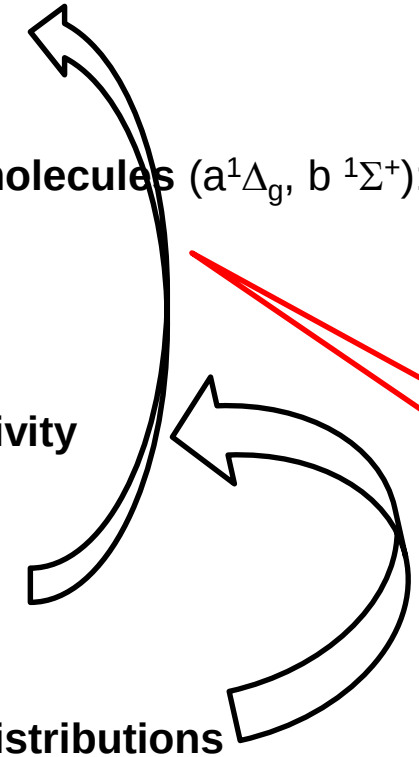
O atom surface recombination, γ :

Metastable molecules ($a^1\Delta_g$, $b\ ^1\Sigma^+$):

Electronegativity

Temperature

Vibrational distributions



Effects poorly quantified, few predictive models

Oxygen dissociation rate constant

At steady state, balance for oxygen atom density, n_O:

Production = loss

$$2 n_e n_{O_2} k_{diss O_2} = n_O . \upsilon_{loss O}$$

Oxygen dissociation rate constant

At steady state:

Determine absolute n_O

Time-resolved actinometry in partially modulated plasmas

$$k_{dissO_2} = \frac{n_O . \upsilon_{lossO}}{2 n_e . n_{O_2}}$$

From E/N, J

From pressure and temperature

Measurement techniques

Method	Implementation	Absolute densities	Time resolution	Space resolution
Optical emission (actinometry)	Cheap and simple	Model & **DATA dependent**	Good, but: Excitation model? **Not afterglow**	Deconvolution (imaging, Abel inversion)

Measurement techniques

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Optical emission (actinometry)	Cheap and simple	Model and data dependent	Good, but: Excitation model? Not afterglow	Deconvolution (imaging, Abel)
Two-Photon Laser-induced Fluorescence (TALIF)	Expensive laser Non-linear →Drifts →Noisy	Difficult calibration Accuracy?	Excellent	Excellent

Measurement techniques

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TALIF	Big laser Non-linear →Drifts →Noisy	Difficult calibration Accuracy?	Excellent	Excellent
Absorption: VUV	Vacuum optics Resolution?	Direct & accurate (line-strengths)	Excellent	Line-integrated

Measurement techniques

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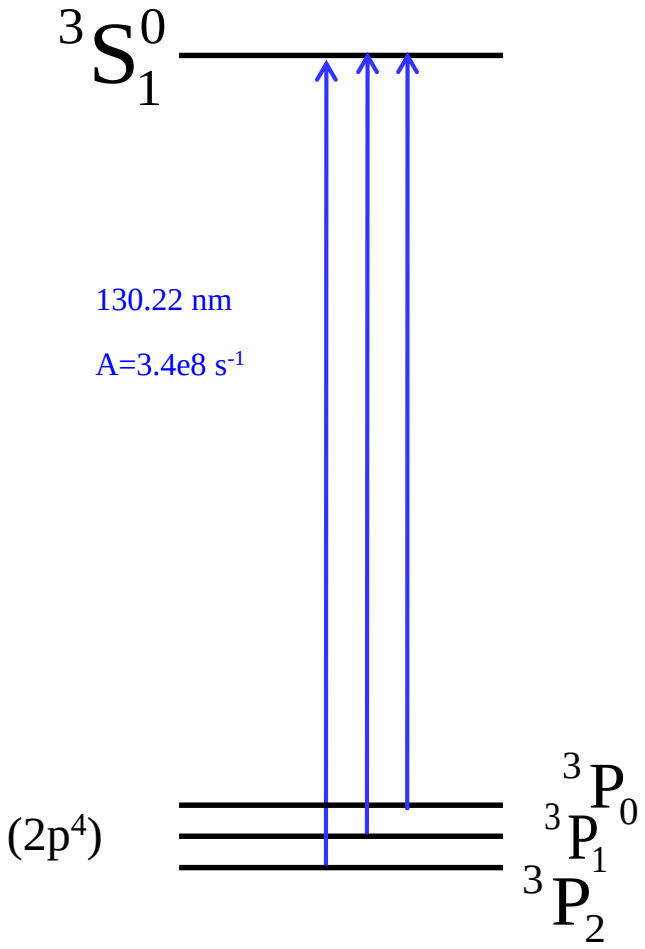
Absorption VUV	Vacuum optics Resolution?	Direct & accurate (line-strengths)	Excellent	Line-integrated
Absorption: IR	Weak transitions→ Cavity techniques	Direct & accurate	Synchronisation?	Line-integrated

O atom resonance transitions



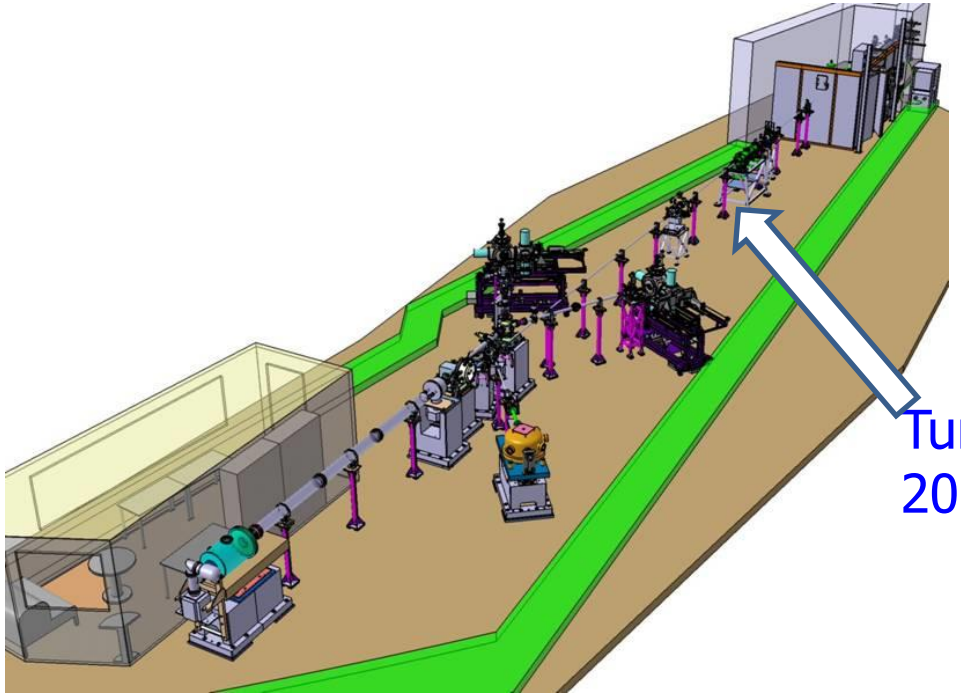
Integrated cross-section related to Einstein A coefficient:

$$\int_0^\infty \sigma_\upsilon d\upsilon = \frac{g_u}{g_l}\frac{\lambda^2}{8\pi} A_{ul}$$

Resonance absorption
using an atomic lamp:
-calculate line profile convolution
-highly questionable !

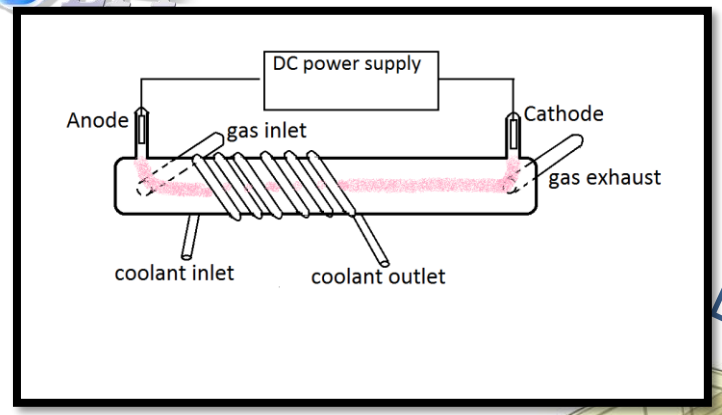
How to make Doppler-resolved measurements?

High resolution VUV absorption spectroscopy DESIRS at Synchrotron Soleil

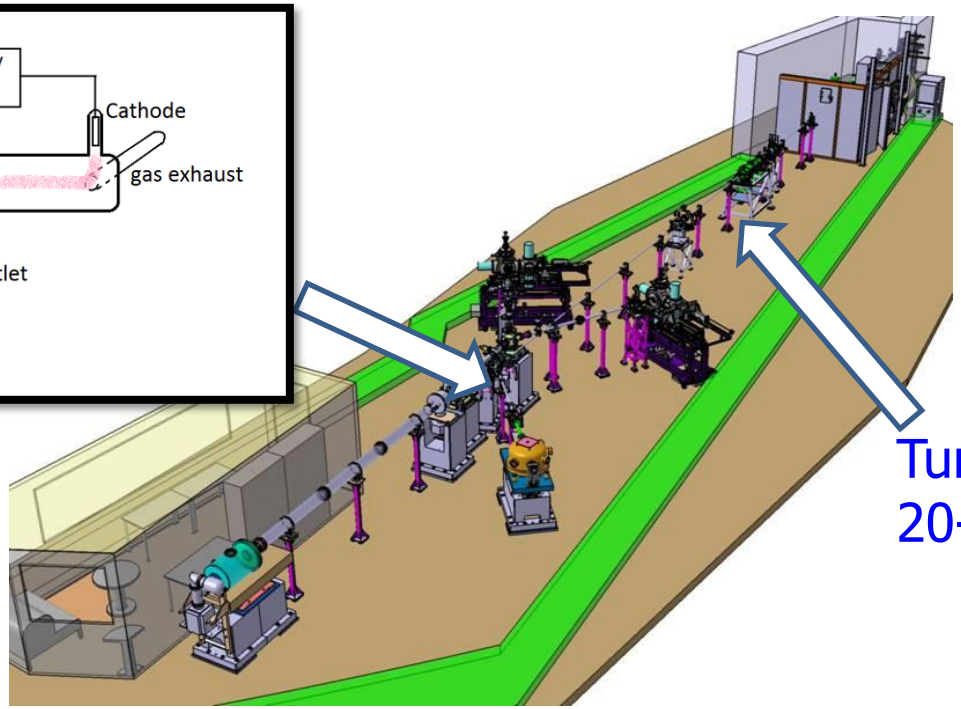


Tunable VUV beam:
20-200nm, 20nm wide

High resolution VUV absorption spectroscopy DESIRS at Synchrotron Soleil



DC discharge
MgF_2 windows



Tunable VUV beam:
20-200nm, 20nm band

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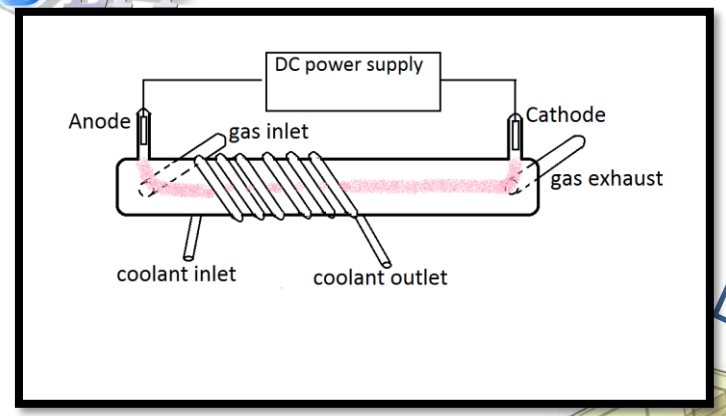

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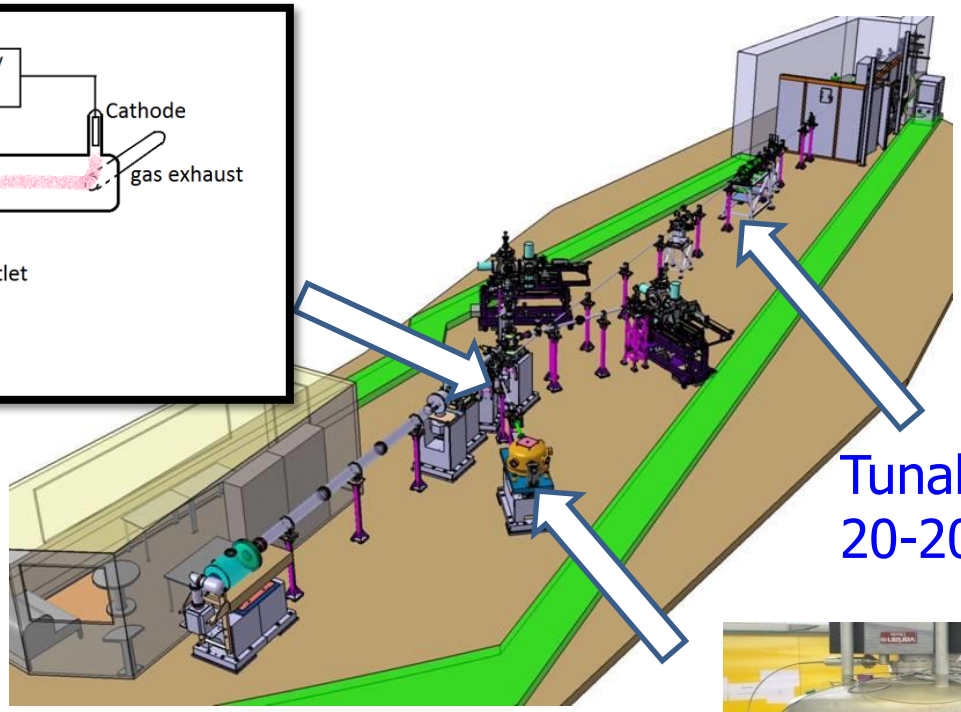

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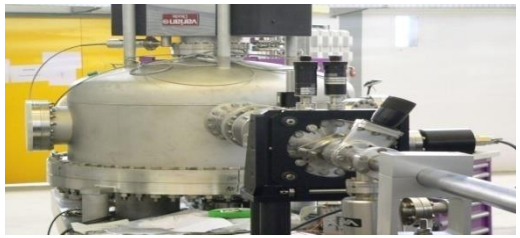


VUV Fourier-Transform Spectrometer* :
Resolution: 10^6 **(<Doppler)**

*N de Oliveira et al., *Nature Photonics* 5, 149–153 (2011)

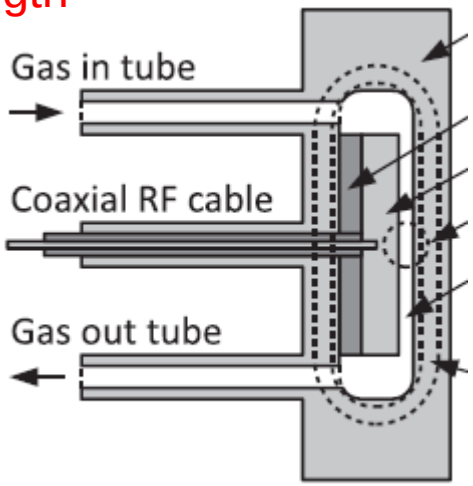
VUV absorption in an RF atmospheric plasma jet

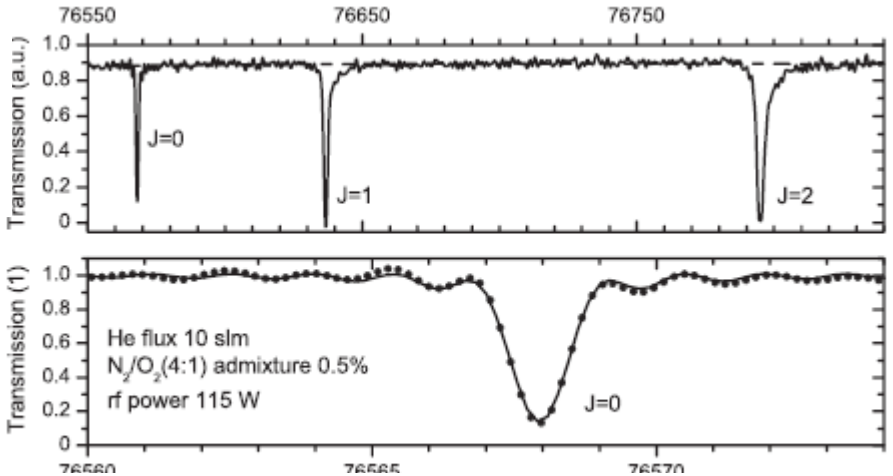
APPLIED PHYSICS LETTERS **103**, 034102 (2013)

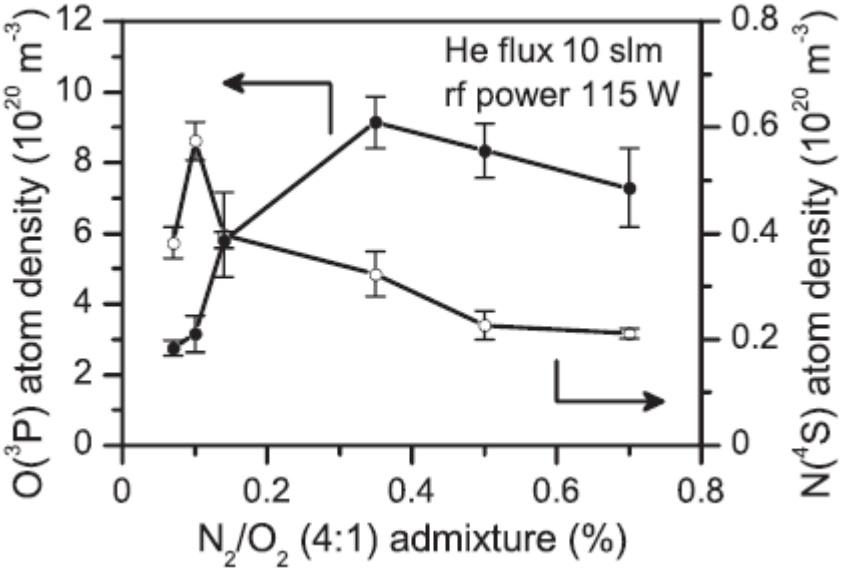
Absolute atomic oxygen and nitrogen densities in radio-frequency driven atmospheric pressure cold plasmas: Synchrotron vacuum ultra-violet high-resolution Fourier-transform absorption measurements

K. Niemi,[1,a)] D. O'Connell,[1] N. de Oliveira,[2] D. Joyeux,[2] L. Nahon,[2] J. P. Booth,[3] and T. Gans[1]

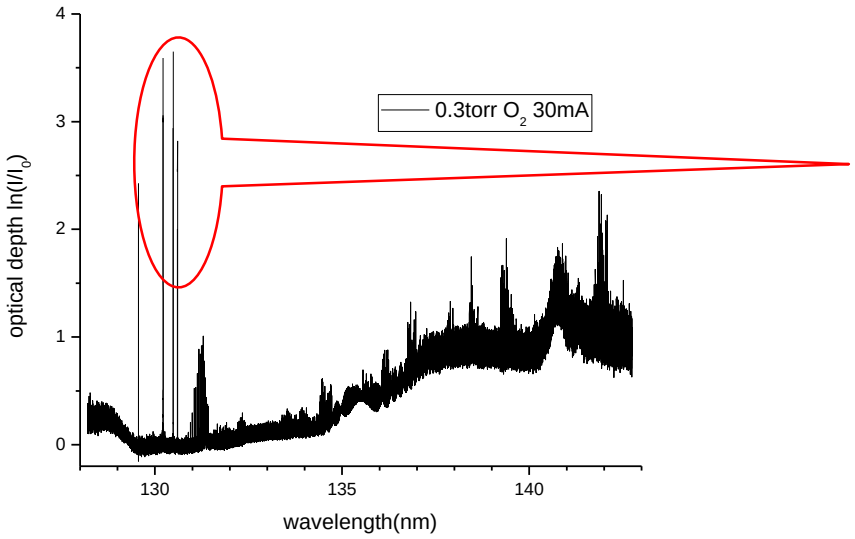
He / 0.5% N_2/O_2
13.56 MHz
10mm absorption path length

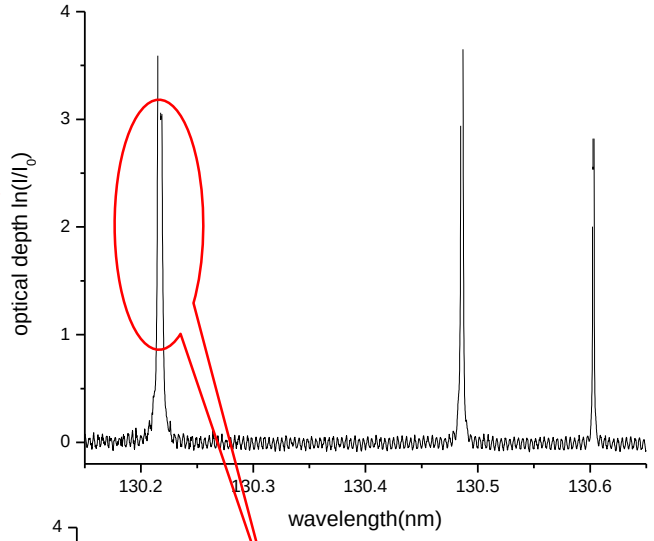


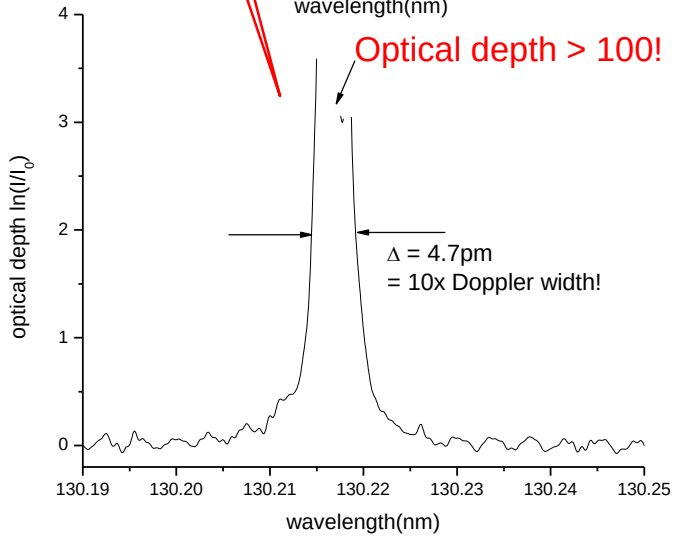




O atom resonance absorption in DC discharge

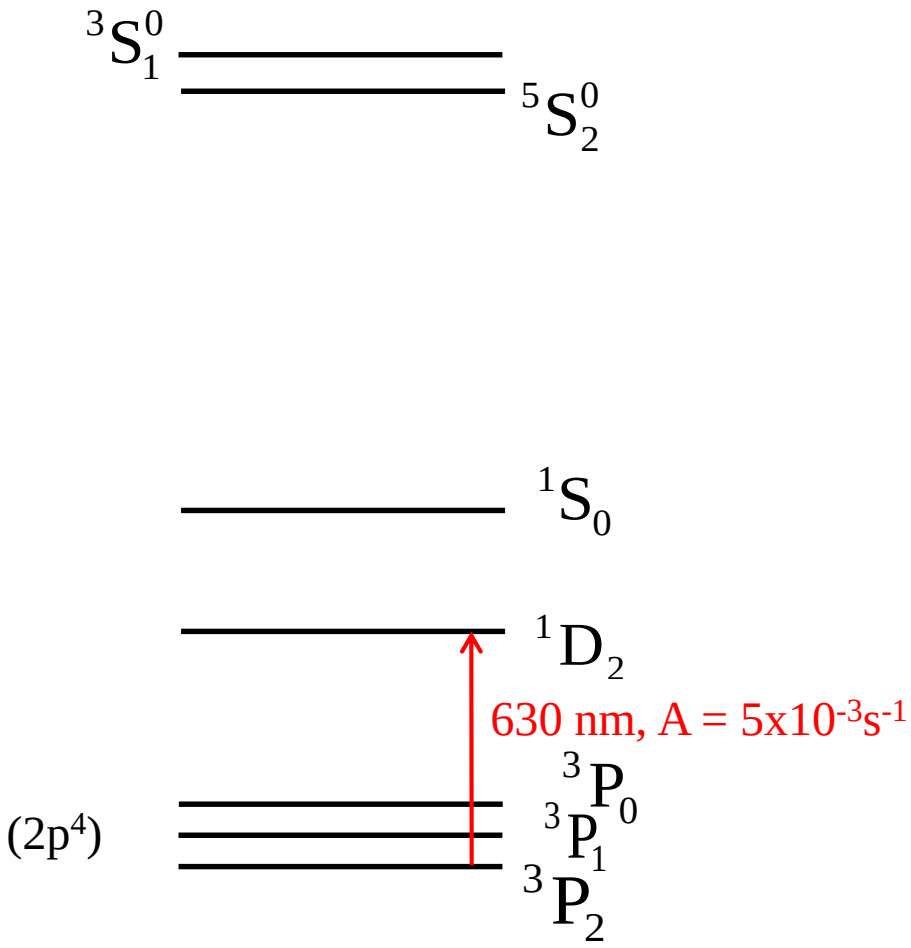






Totally saturated lines
impossible to interpret!

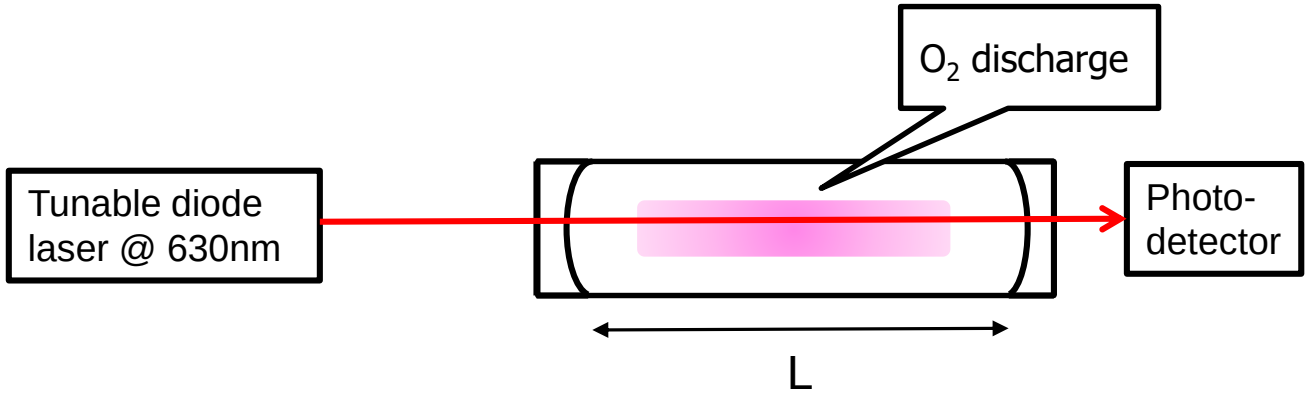
Weaker transitions?



Spin-forbidden:
10^{11} times weaker!
Single pass absorption $\approx 10^{-4}$

$\Rightarrow$Multipass techniques necessary

Cavity ringdown spectroscopy with a monomode diode laser

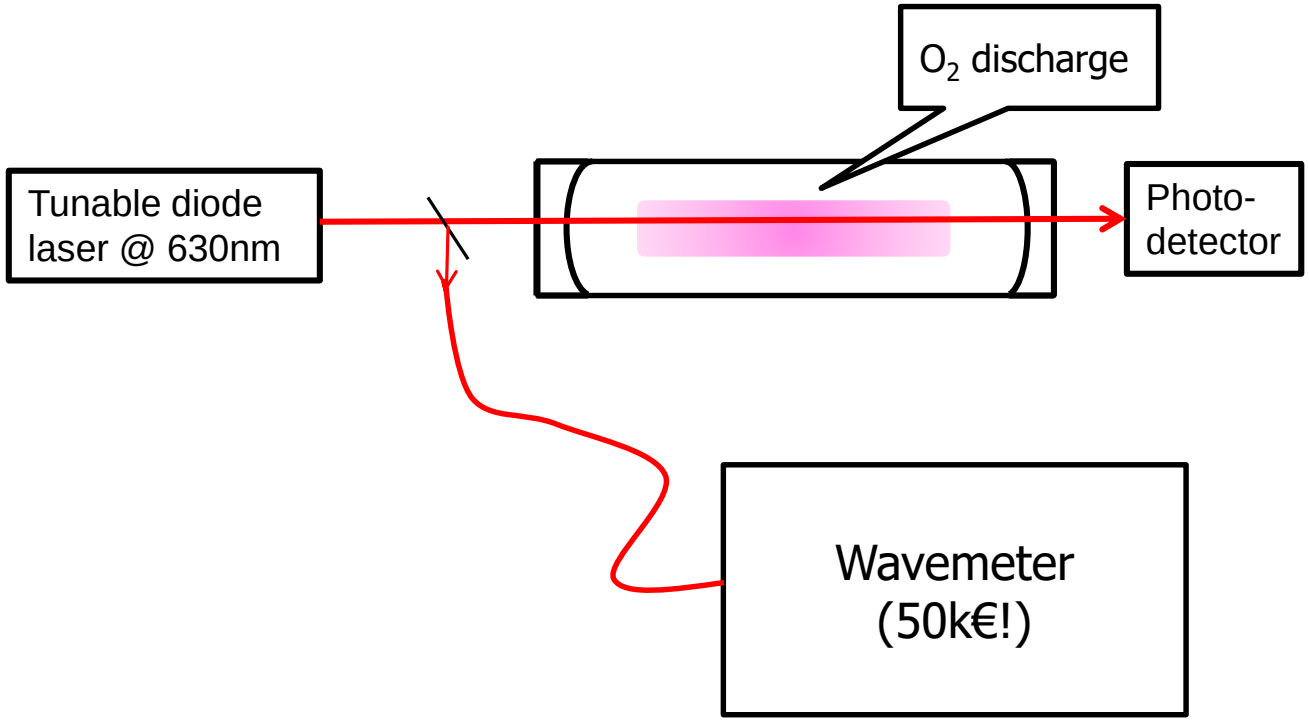


Commercial external-cavity grating controlled diode laser

(Toptica DL100)

~10 mW

Cavity ringdown spectroscopy with a monomode diode laser



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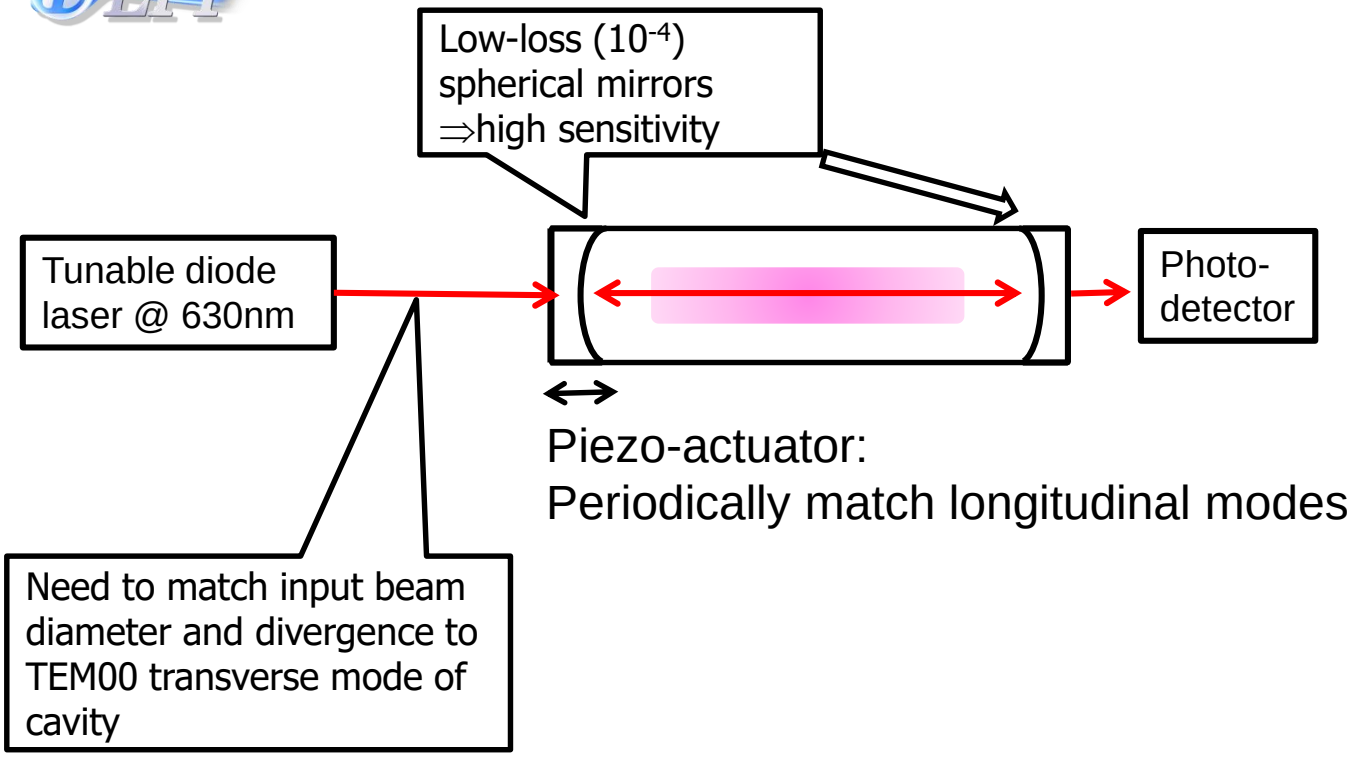

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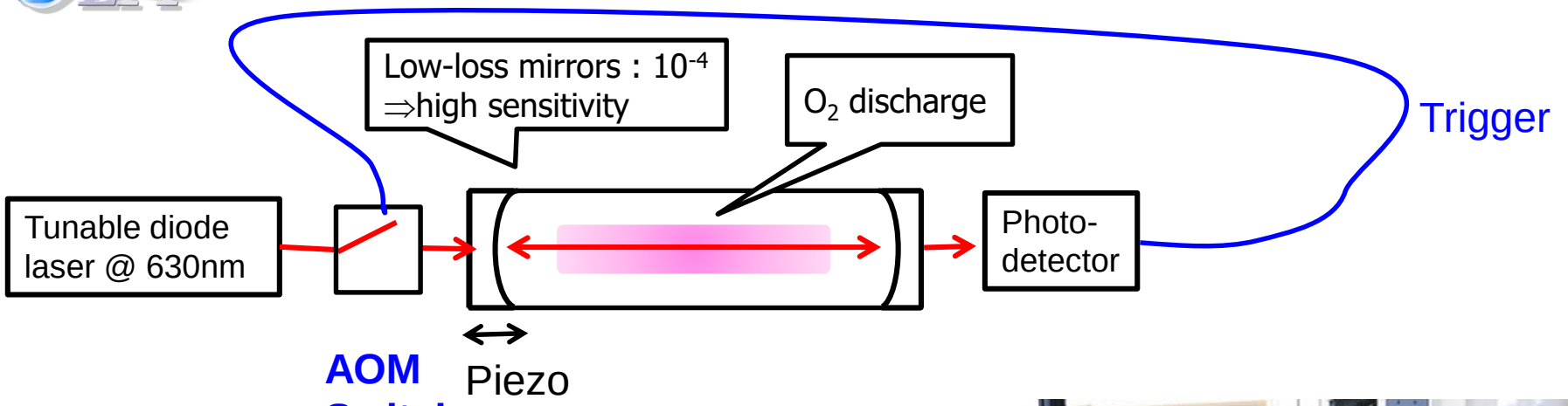
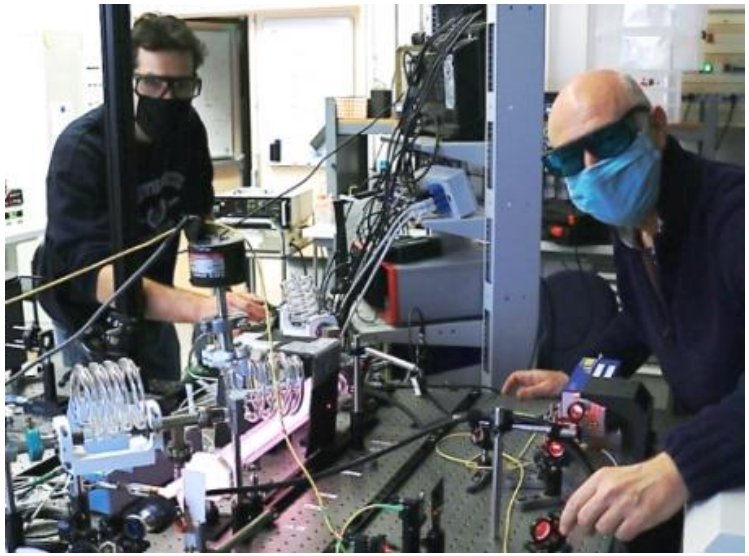


AOM Switch:

Stop laser when longitudinal mode is matched and intensity in cavity is adequate.
-measure exponential decay rate



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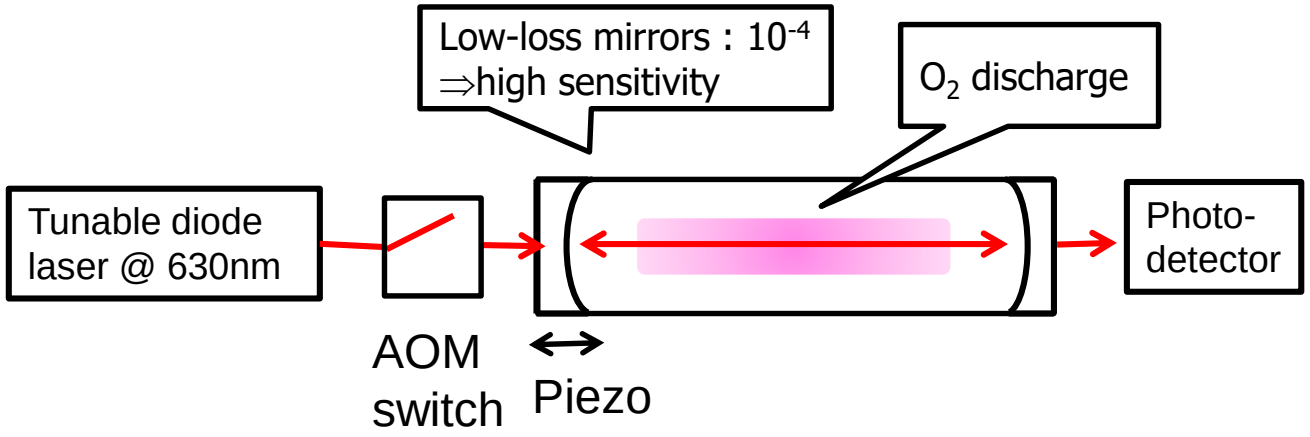
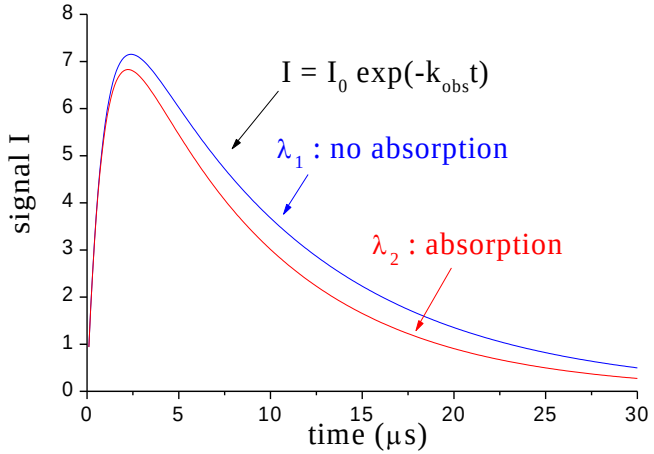


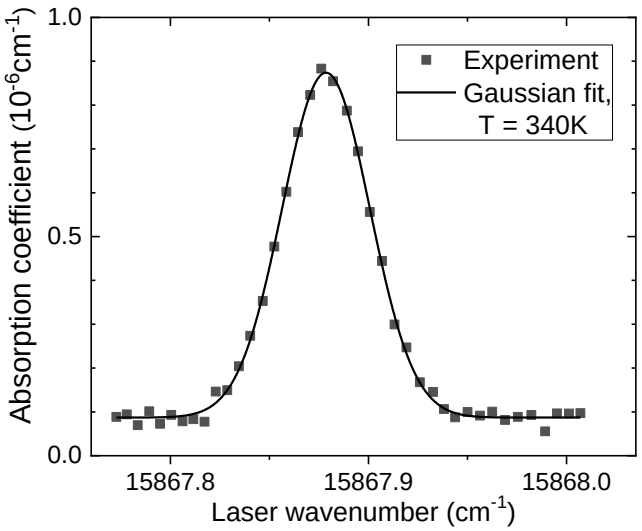


$$\frac{k_{obs}.L}{c} = (1-R) + n\sigma L$$

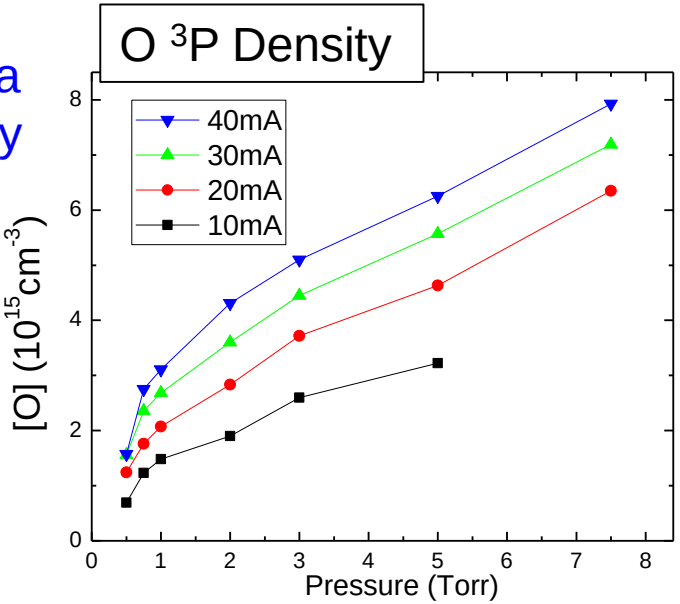
Cavity losses (constant)

Line-integrated absorption

CRDS in an O_2 DC positive column: O number density

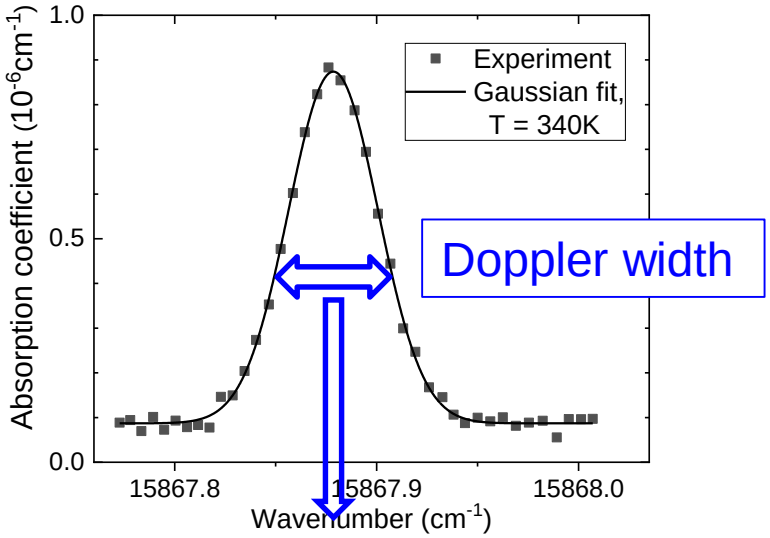


Integrated area
$\propto$ O $^3P_2$ density

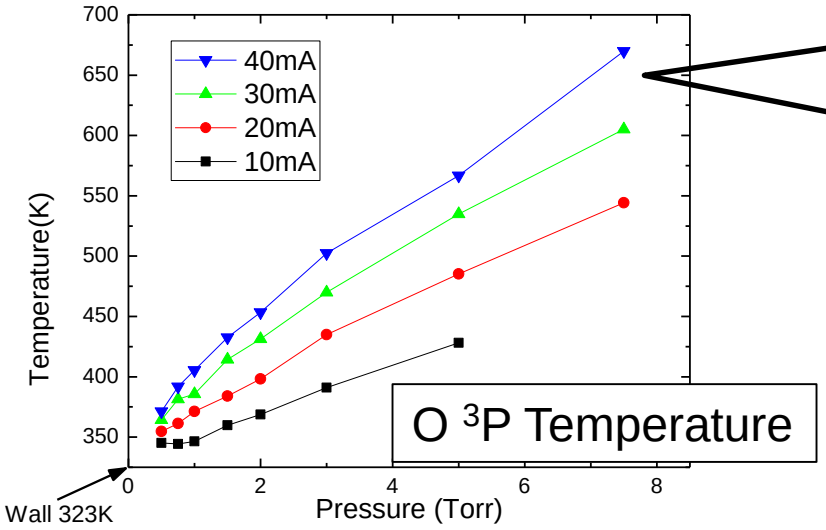


(add density of $^3P_1$ and $^3P_0$ assuming Boltzmann population)

CRDS in an O_2 DC positive column: Gas temperature



Doppler width



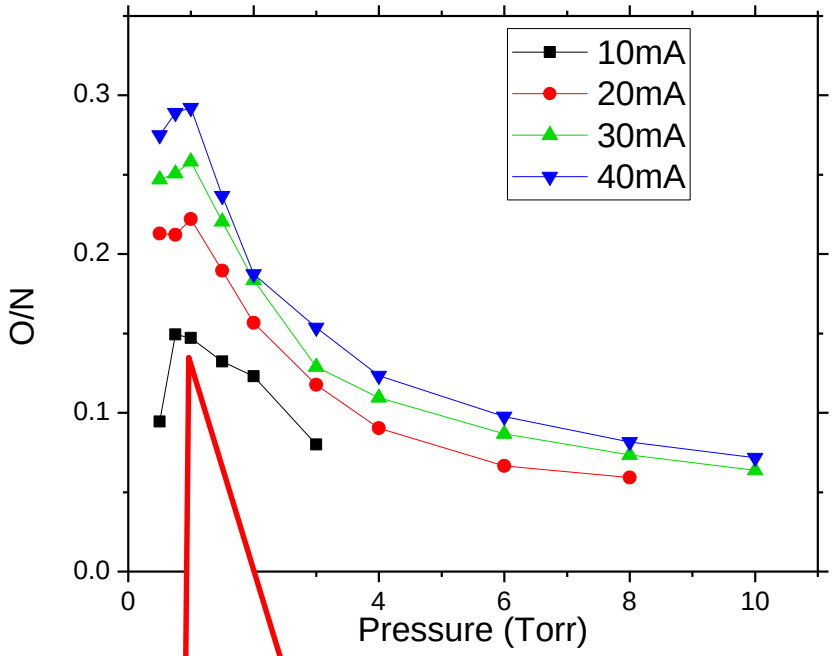
O ^{3}P Temperature

up to 700K:

Radial gradient in
-temperature
-gas density
-E/N
-Makes modelling more difficult

Combine [O] and temperature measurements ⇒

O atom mole fraction



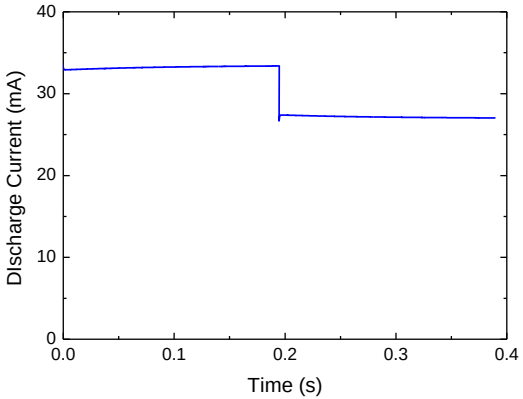
Up to 30% of gas is O atoms!

Passes through a maximum at ~1 Torr.

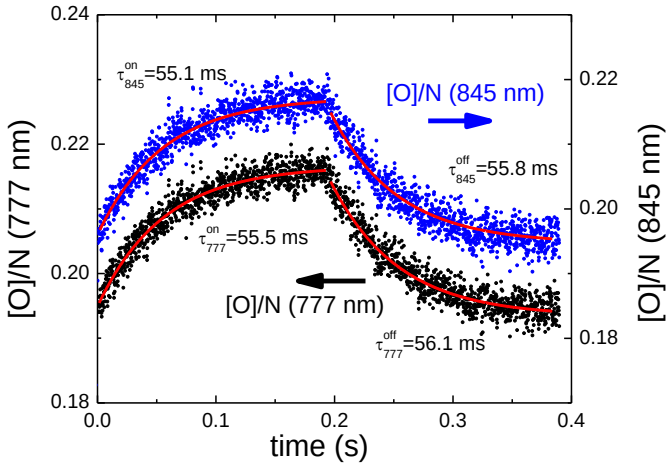
⇨ Why? Probe atom loss kinetics:

Oxygen atom loss kinetics: surface recombination

Modulate Current (electron density)
→ response of atom density



Actinometry : I_O/I_{Ar}



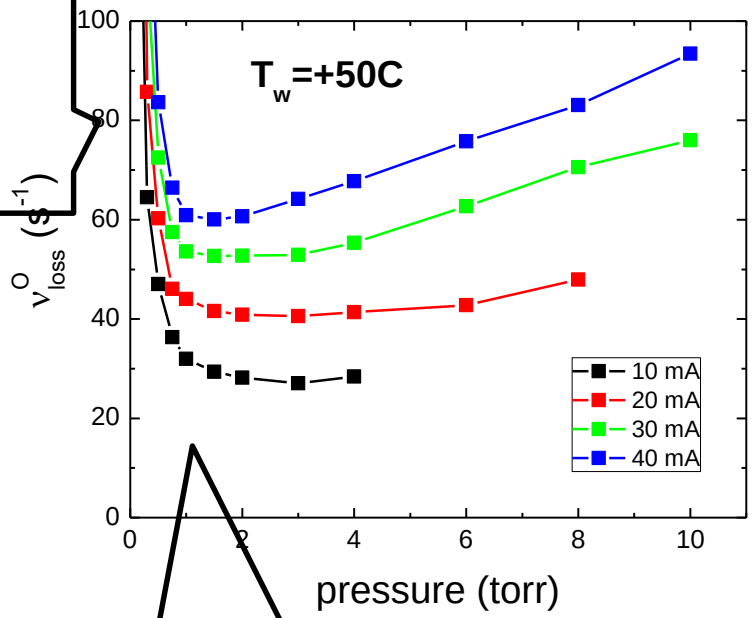
15% current modulation

Exponential decays / rise
-two emission lines

} all give similar loss frequencies, ν_{loss}

O atom loss frequency vs pressure and current

-Loss rate increases strongly at low pressure: Energetic ions!

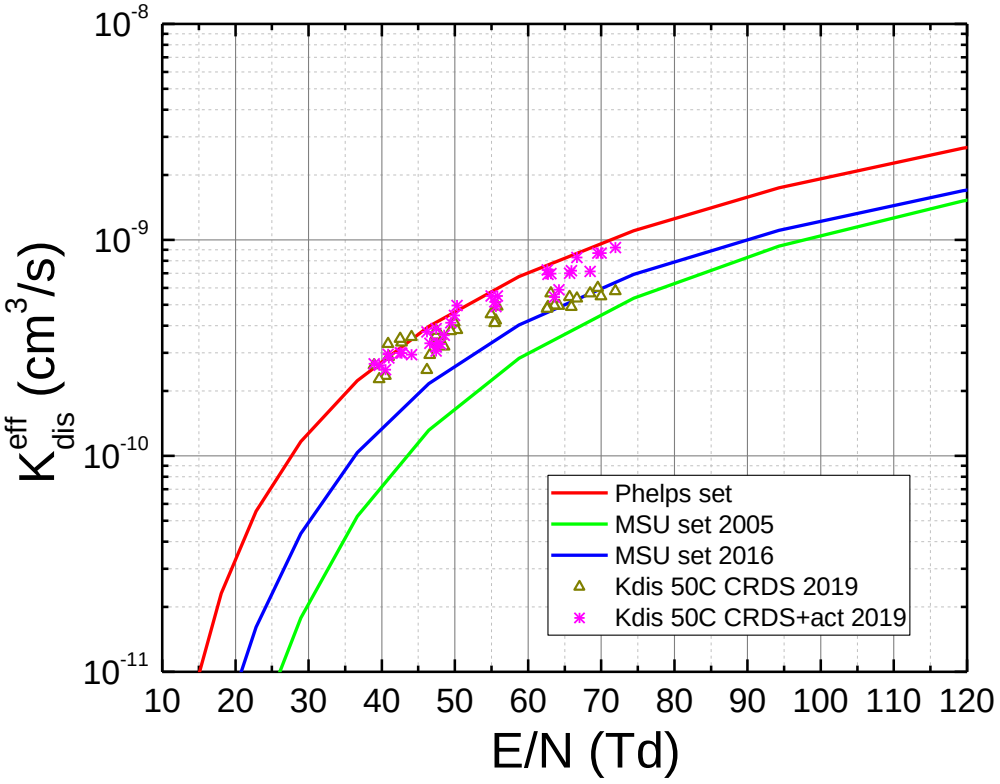


Maximum in O fraction corresponds to minimum in surface loss rate

Oxygen (^3P) atom recombination on a Pyrex surface in an O_2 plasma, Booth at al. Plasma Sources Sci. Technol. 28 (2019) 055005

O_2 dissociation rate constant

$$K_{dis}^{eff} = \frac{\nu_{loss}^{O}}{n_e} \frac{[O]/2N}{(1-[O]/2N)}$$



Best agreement with Phelps cross-section set (from electron energy loss spectra)

-significantly bigger than that obtained from the Cosby (1993) cross-section used in most models.

Work in Progress:
-surface condition drift
-effect of radial gradients
etc

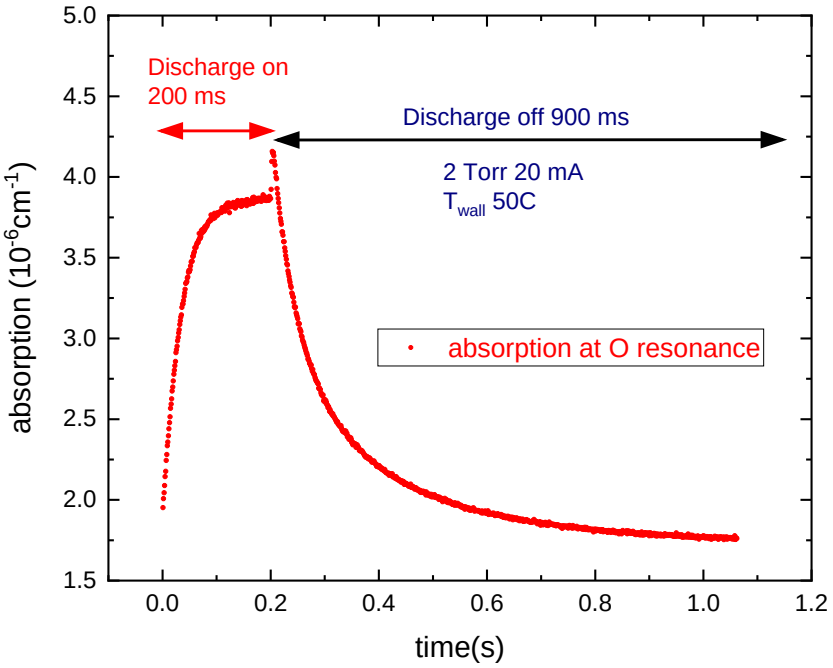
What happens in the afterglow (full current modulation)?

Actinometry not possible in afterglow (no electrons)

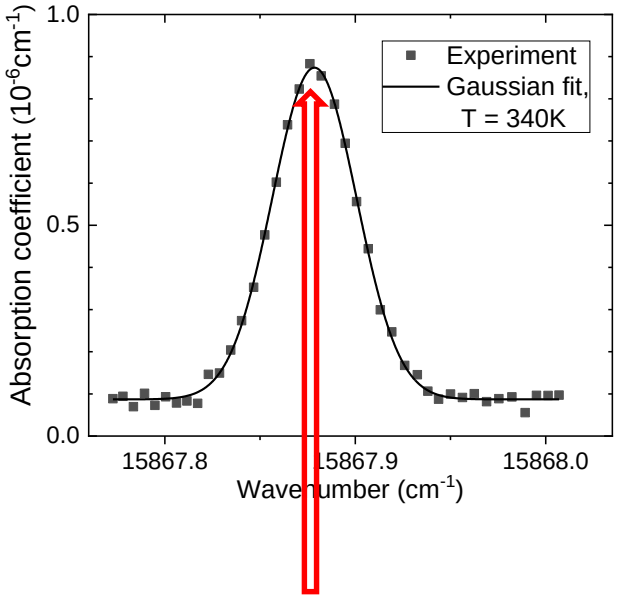
CRDS : cannot synchronise ringdown events to pulsing

$\Rightarrow$ let CRDS free-run during modulation
$\Rightarrow$ record phase delay for each event
$\Rightarrow$ put events into time-bins

Time-resolved CRDS with 100% modulation

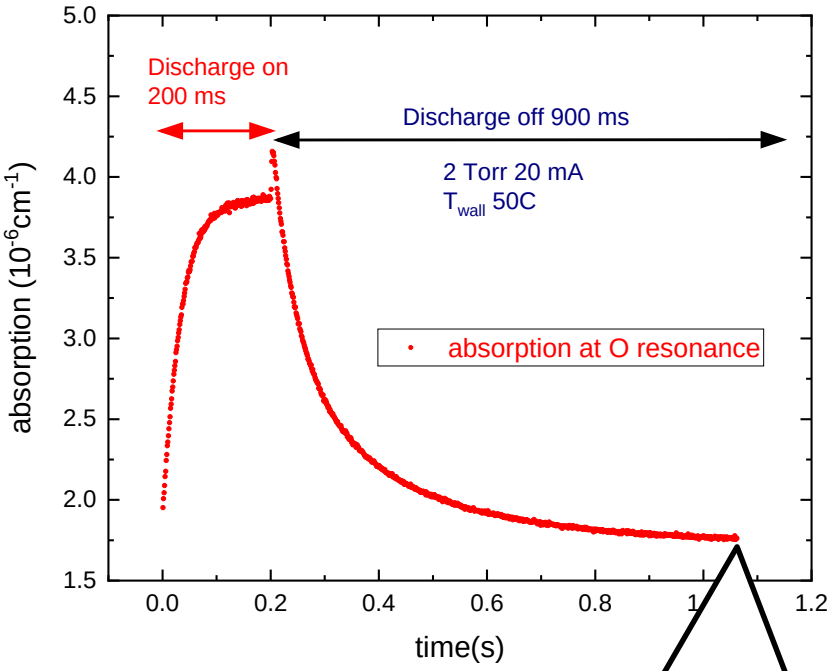


O atom kinetics are slow enough for time-resolved CRDS (~10 μs)

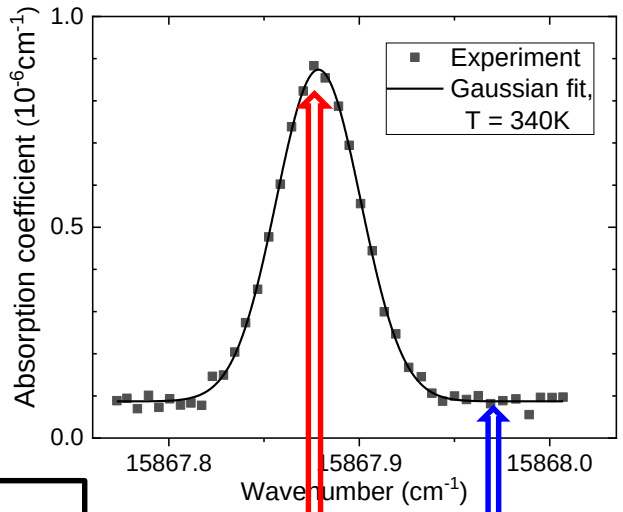


On-resonance

Time-resolved CRDS with 100% modulation



O atom kinetics are slow enough for time-resolved CRDS

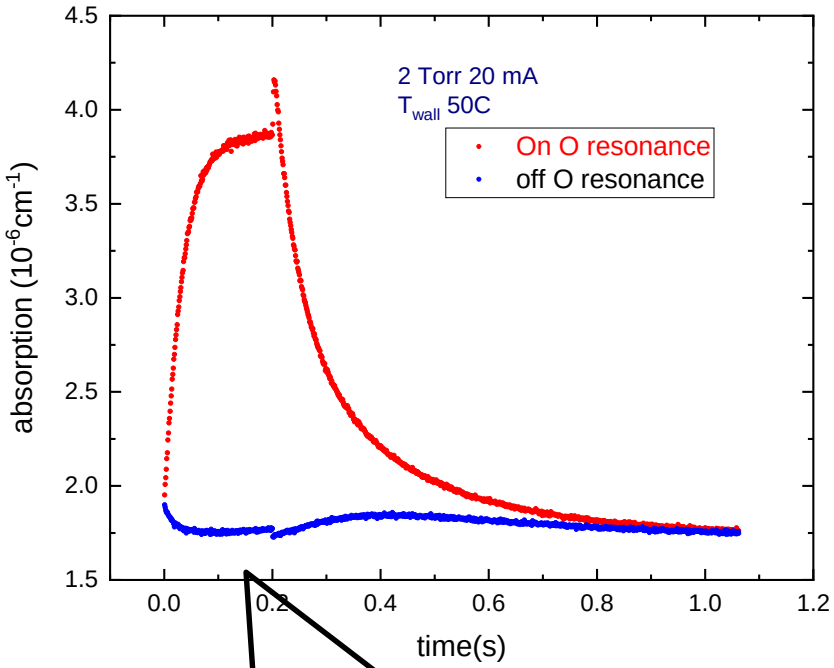


What about baseline?
-tune laser off-resonance ⇒

On-resonance

Off-resonance

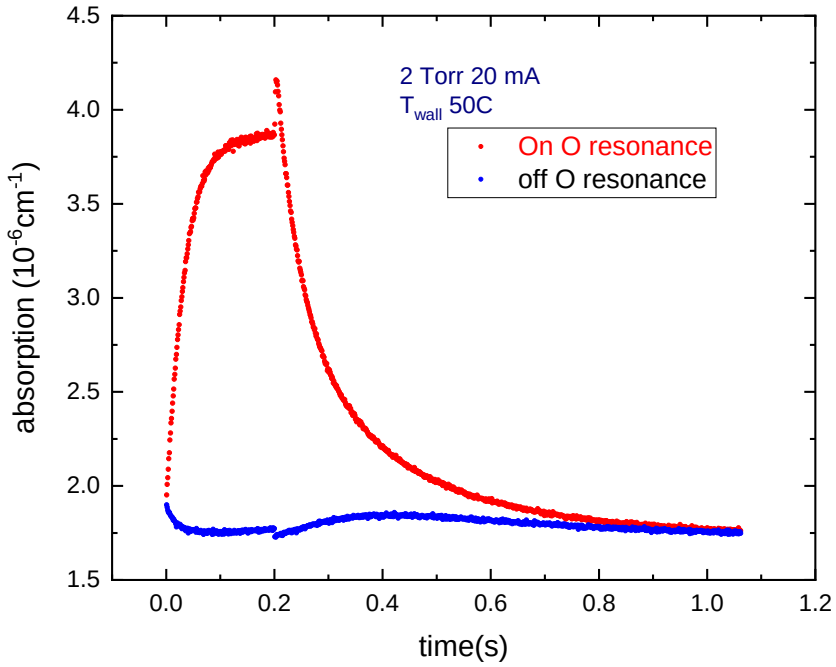
O atom decay: baseline :



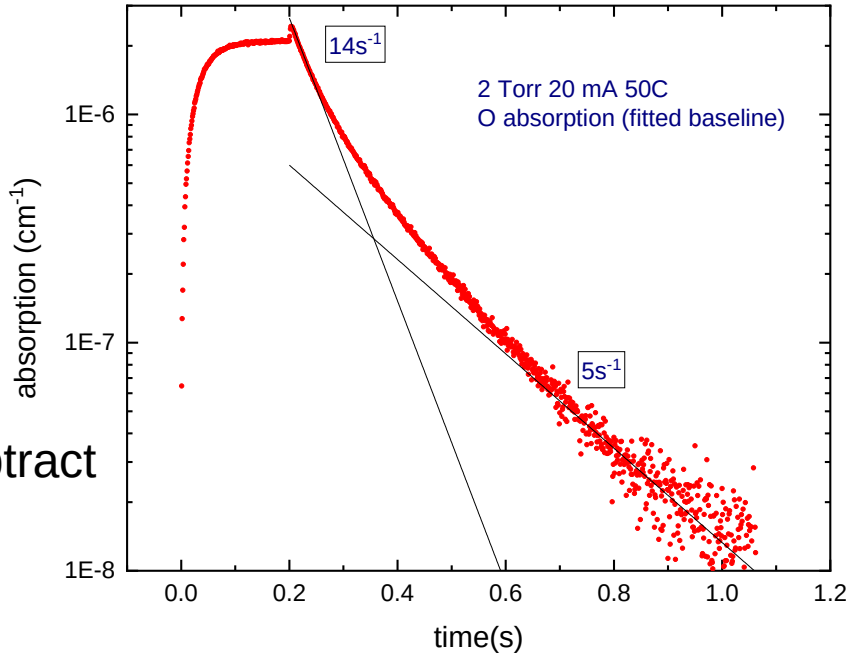
Subtract

Time-dependent baseline:
(Discussed later)

O atom decay:
with baseline subtraction:



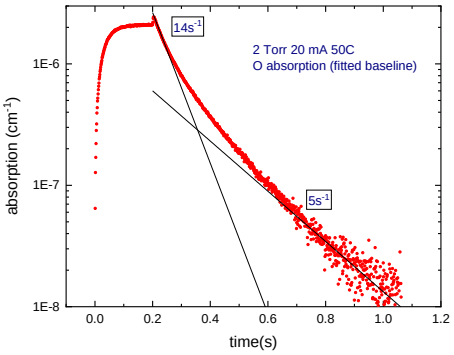
Subtract



Non-exponential decay: $14s^{-1} \Rightarrow 5s^{-1}$
(Cf Partial modulation : $40s^{-1}$)
-gas cools in 3ms

Possible explanations:

O atoms: Non-exponential decay in afterglow



Possible explanations:

A) Surface reactivity slows with time:

$-dO/dt = \alpha\,[O]^2 + \beta\,[O]$

Physisorbed O : Surface density $\propto$ flux

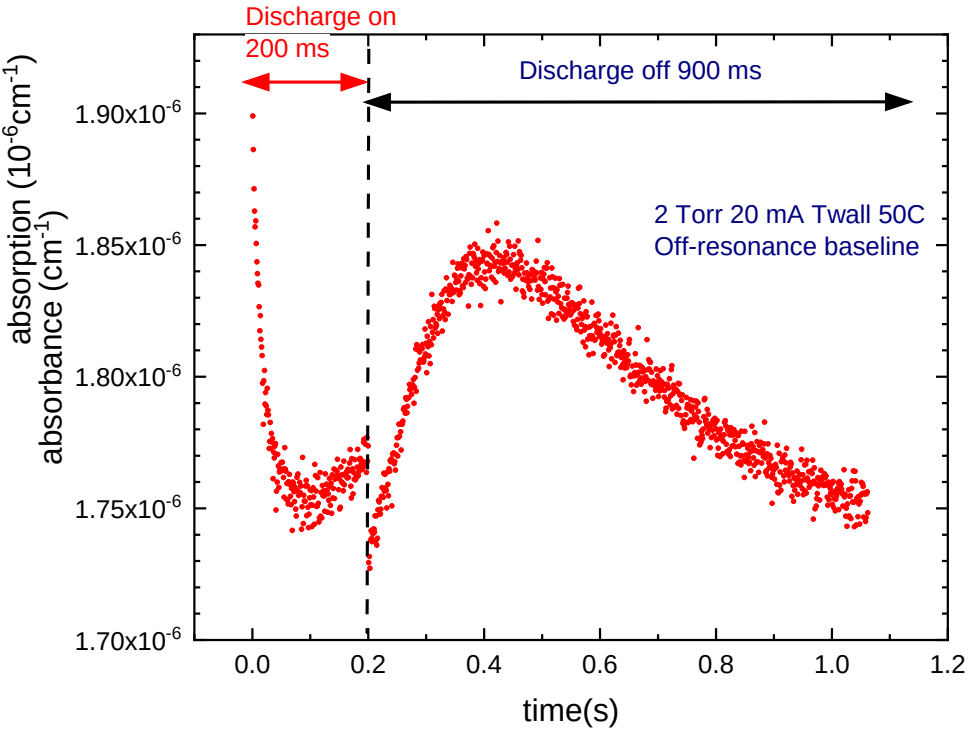
Chemisorbed O : Constant surface density

B) Continuing production of O:

$O_3 + O_2a \rightarrow 2O_2 + O$

Or both? $\Rightarrow$Modelling

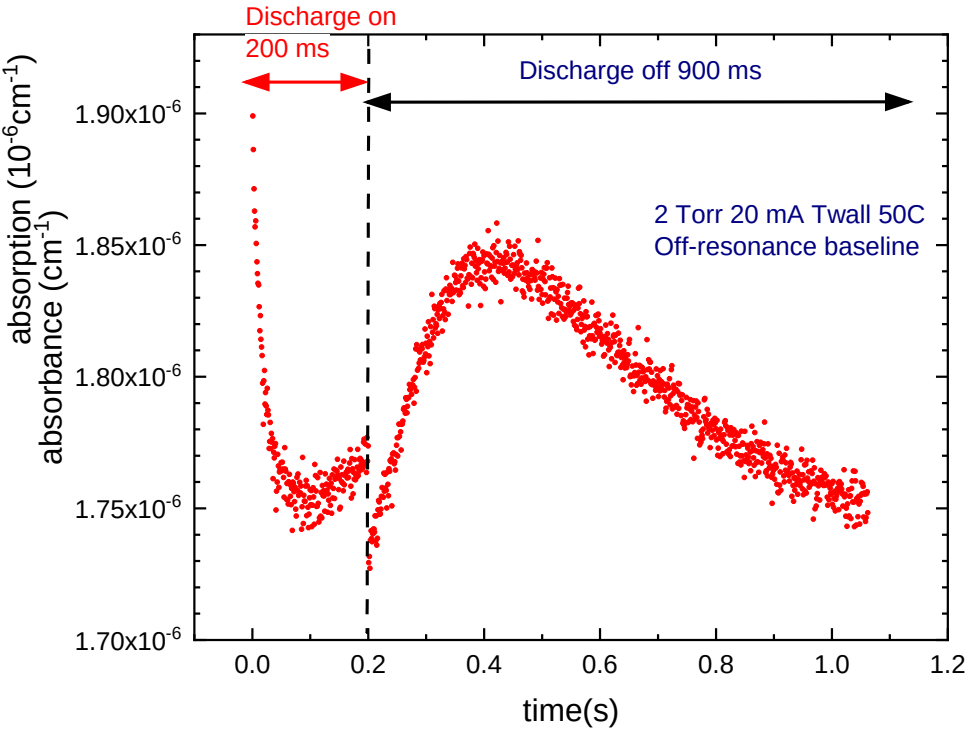
Origin of time-dependent baseline?



Complex time-behaviour

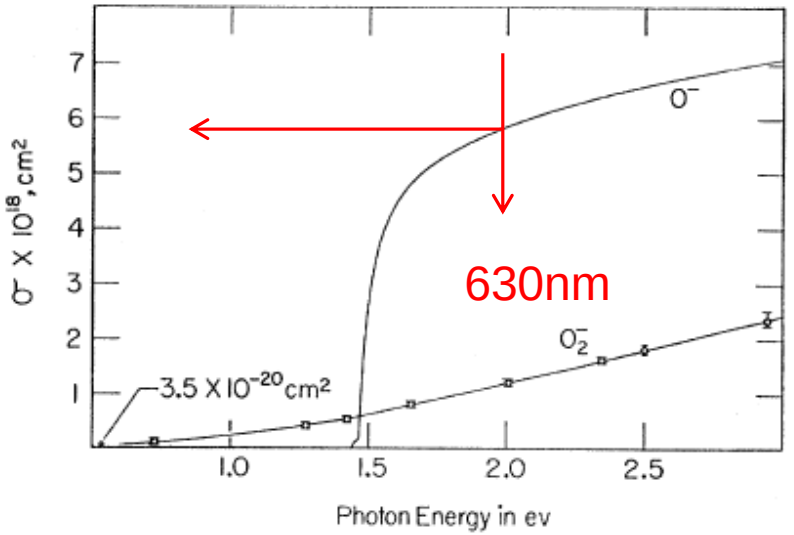
What else absorbs in this spectral region?

Origin of time-dependent baseline?



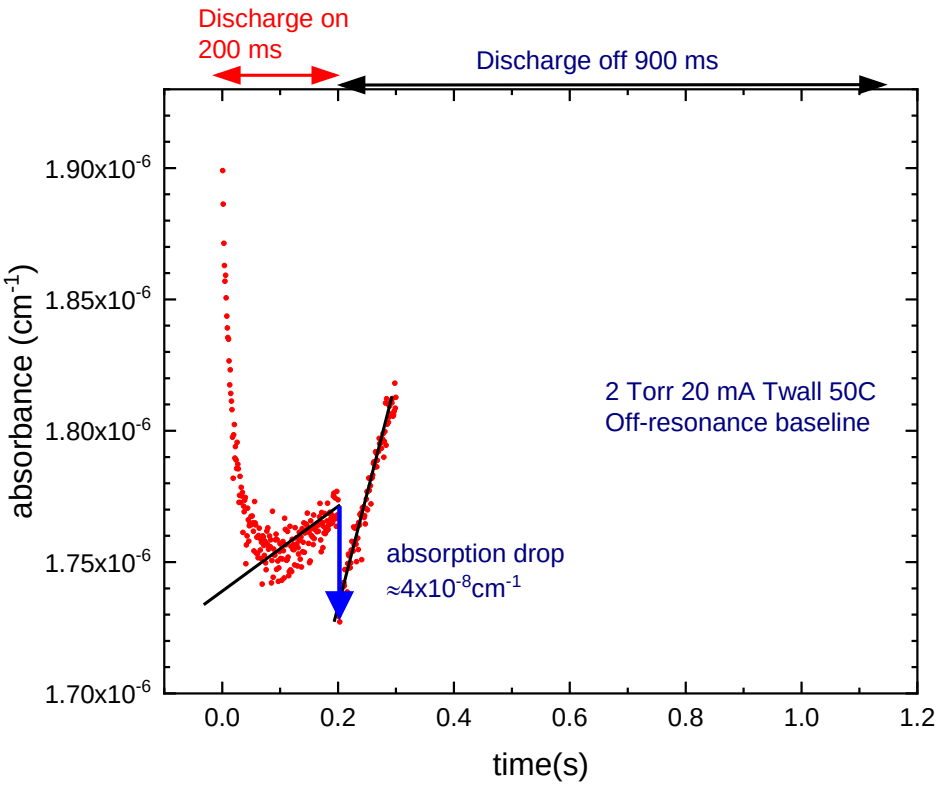
Complex time-behaviour
What else absorbs in this spectral region?

O^- photo-detachment continuum



$\sigma = 5.8\text{x}10^{-18}\text{cm}^2$ @ 630nm

O^- negative ions



O^- :

produced by dissociative attachment:

$O_2 + e \rightarrow O^- + O$

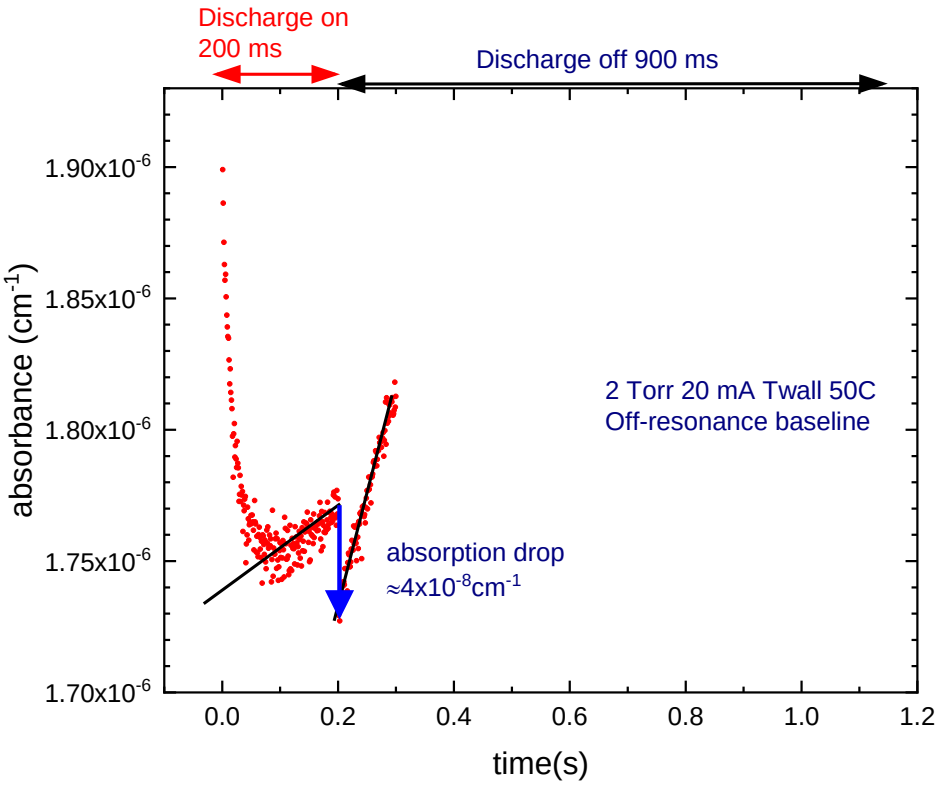
Destroyed in ~1 μs in afterglow:

$O^- + O \rightarrow O_2 + e$

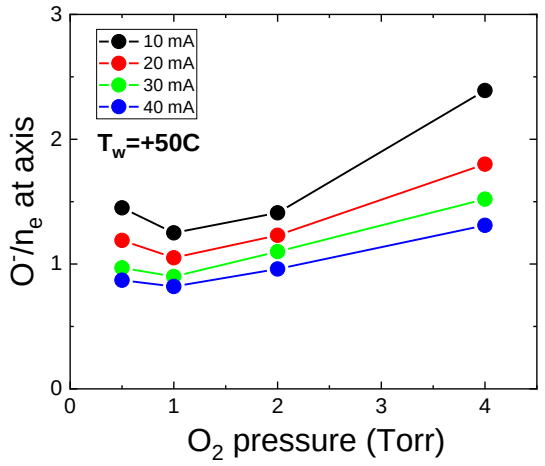
and:

$O^- + O_2\ ^1\Delta_g \rightarrow O_3 + e$

O^- negative ions

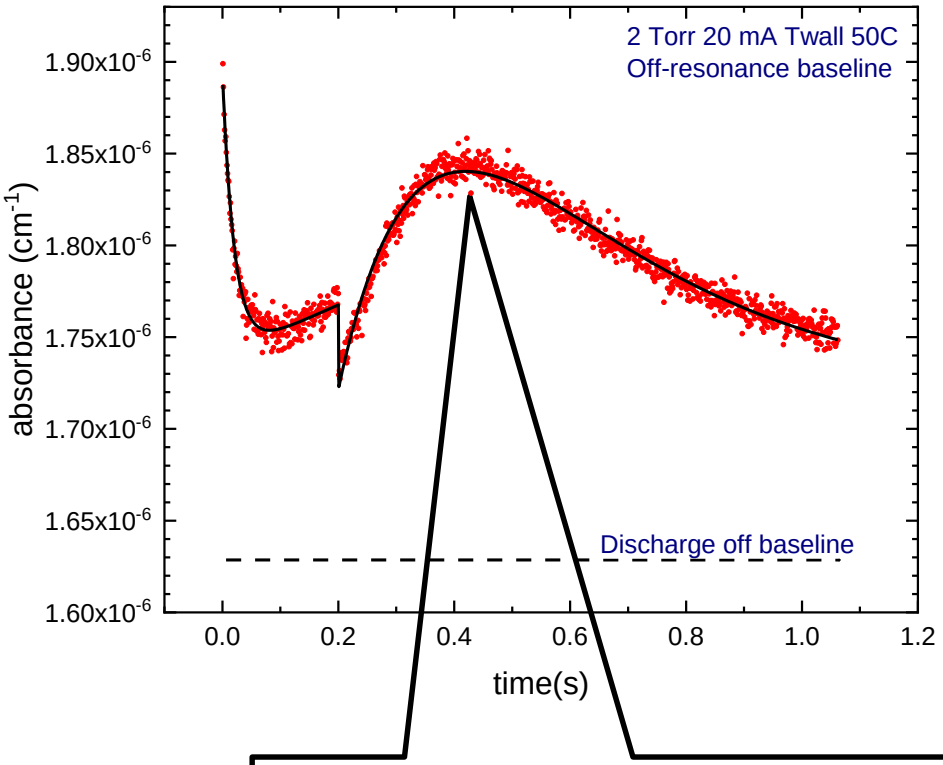


Electronegativity:



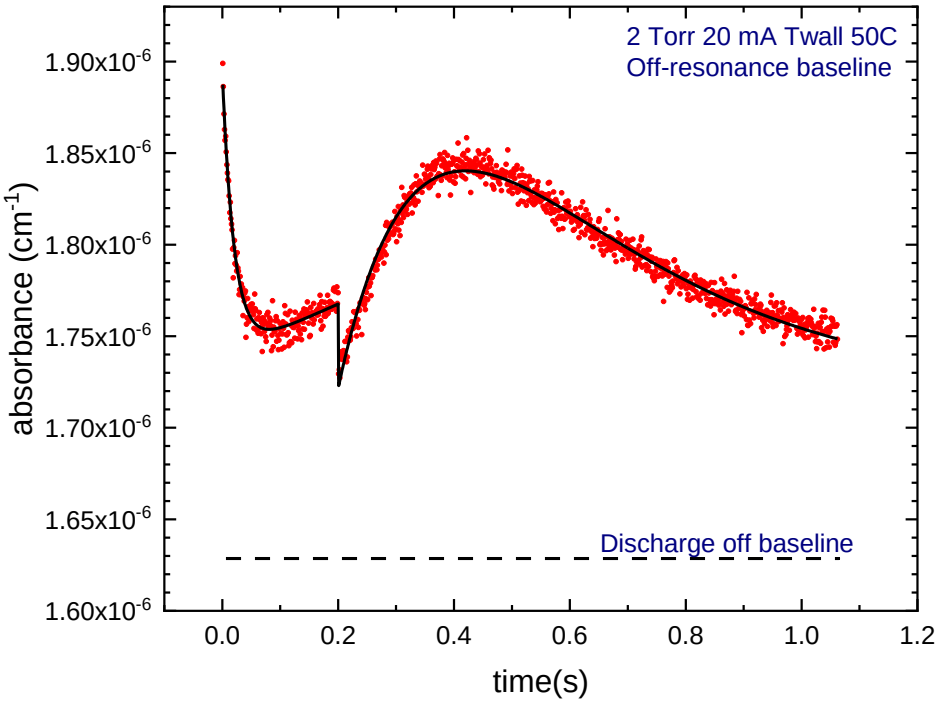
Neutral chemistry affects plasma density, conductivity etc

Later afterglow: What else absorbs?

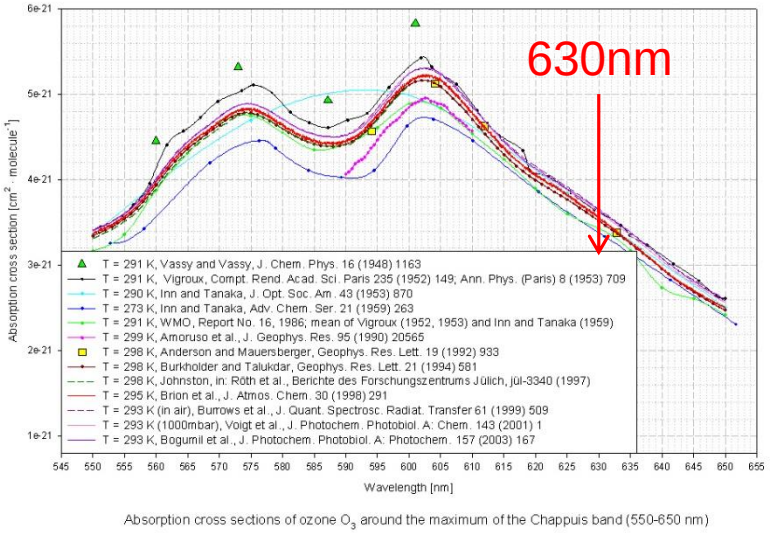


Slow increase then decay in absorption :
Negative ions are gone!

Afterglow – no O^- what else absorbs?



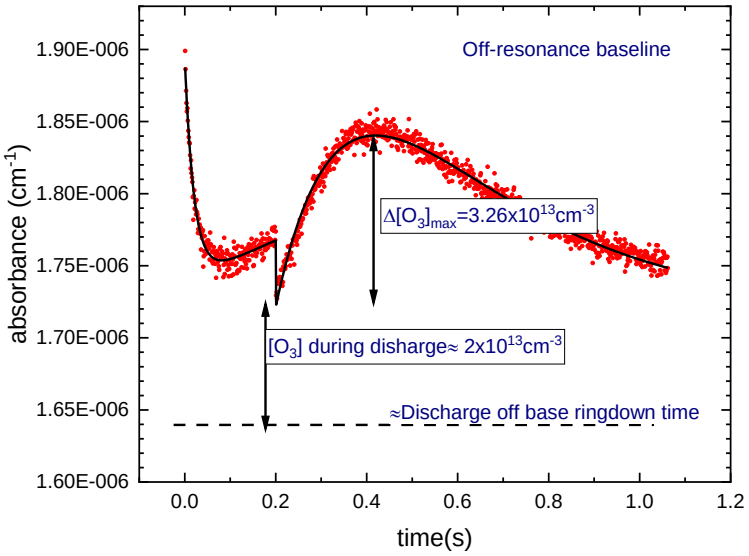
Ozone:
Chappuis bands:



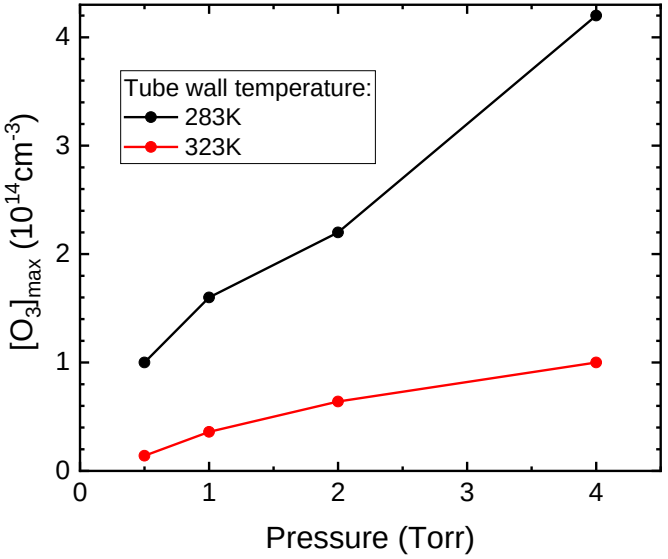
Absorption cross sections of ozone O_3 around the maximum of the Chappuis band (550-650 nm)

$\sigma = 3.6 \times 10^{-21} cm^2$ @ 630nm

Ozone



Peak O_3 density:

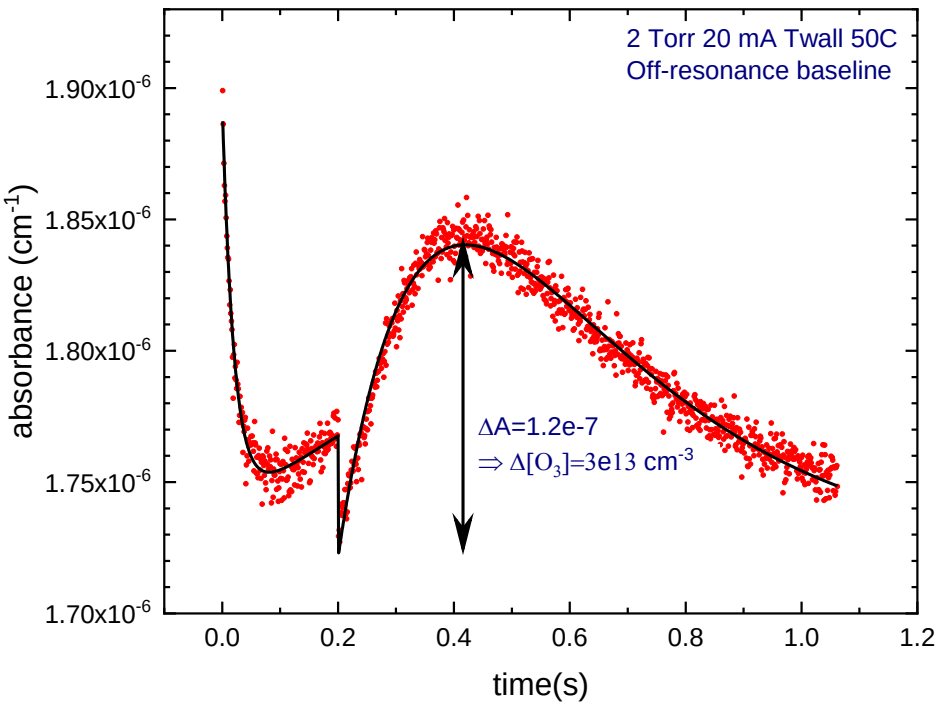


More O_3 at high pressure
and low temperature:

$O + O_2 + M \rightarrow O_3 + M$ (and at surfaces)

$k=2.15 \cdot 10^{-34} \cdot \exp(345/T)$

Ozone destruction



Destroyed by:

$O_3 + e \rightarrow O_2 + O + e$
$O_3 + M \rightarrow O_2 + O + M$
(Thermal decomposition)

} Fast in Discharge

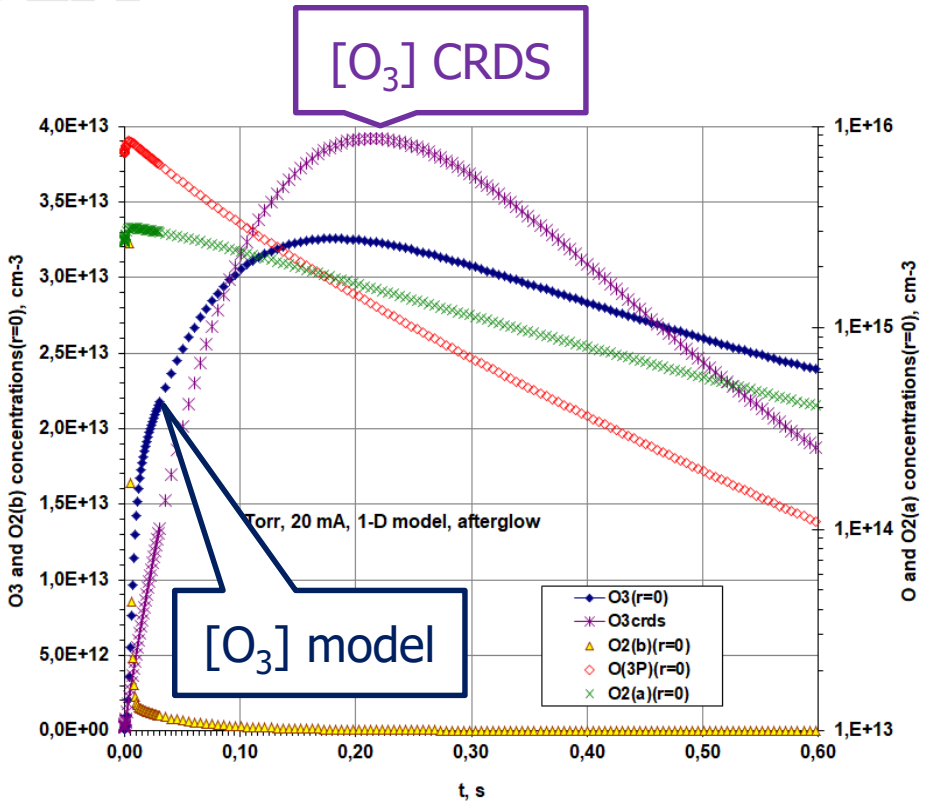
$O_3 + O \rightarrow 2O_2$
$O_3 + O_2a \rightarrow 2O_2 + O$
$O_3 + \text{surface} \rightarrow O_2 + O$

} in afterglow (slower)

+ gas flow….

⇒ Time-dependent modelling-

Time-dependent modelling of afterglow dynamics



O_3 Peak value reasonably good, but:

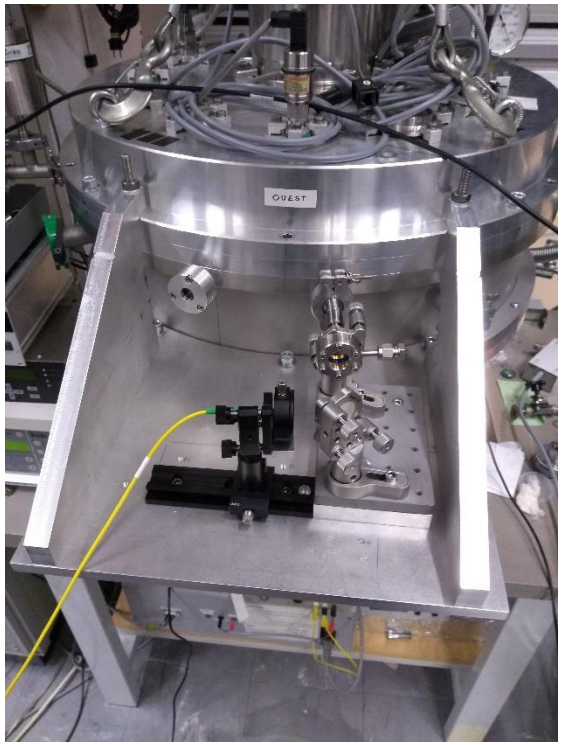
-Initial rise much too fast

-Decay too slow

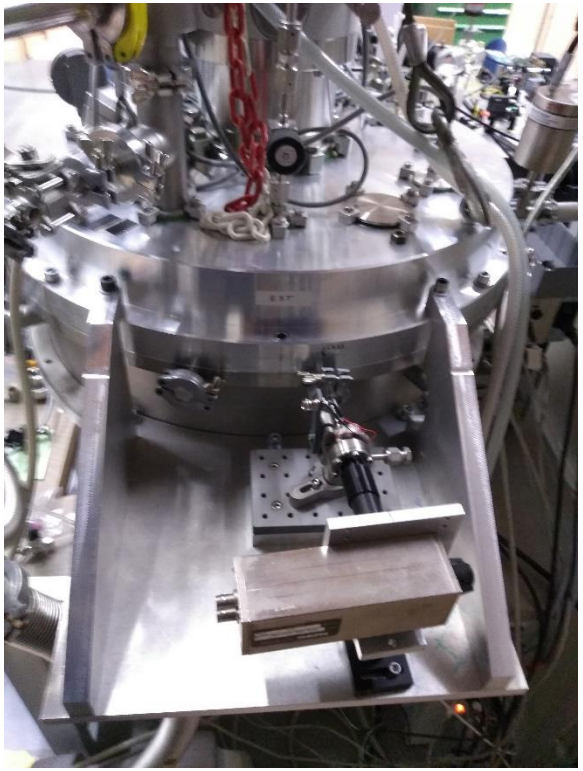
$\Rightarrow$ Work in progress…

CRDS in a symmetric 50cm diameter RF CCP

Setup transferred from DC discharge to RF CCP:

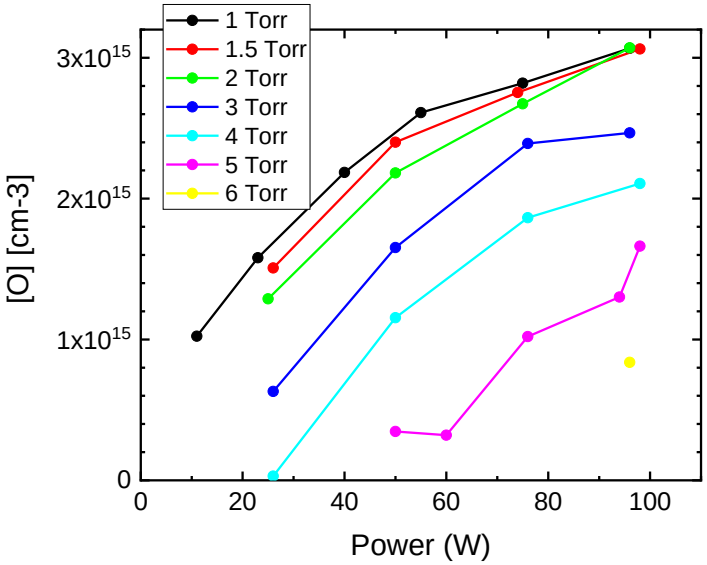


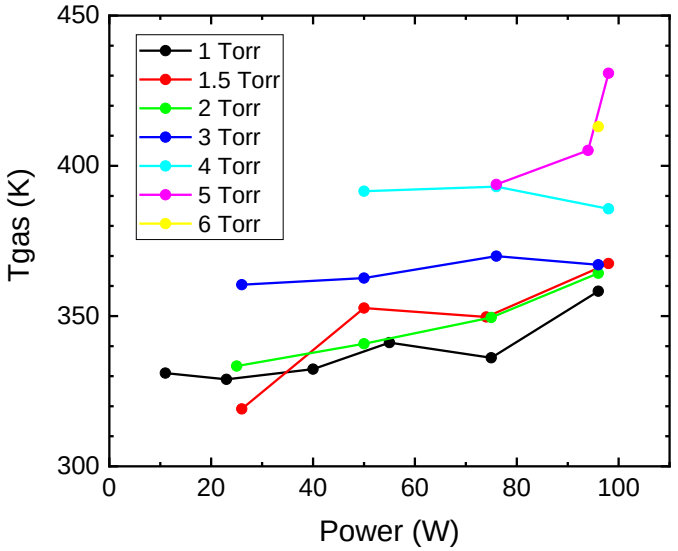
Laser arrives by fibre optic



Output mirror
and photomultiplier

[O] and Tgas
13.56 MHz



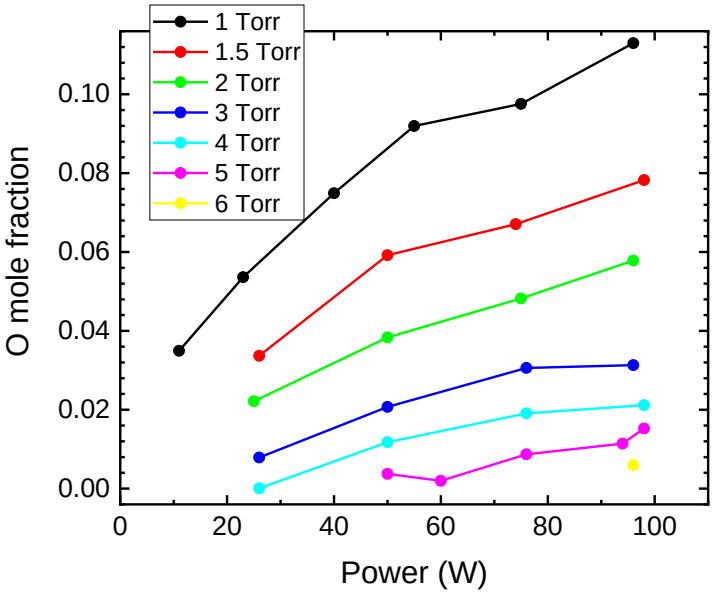


Increasing pressure does not produce more O atoms:

- very few high energy electrons at high pressure

Modest increase in gas temperature with pressure at these low powers

O Mole-fraction



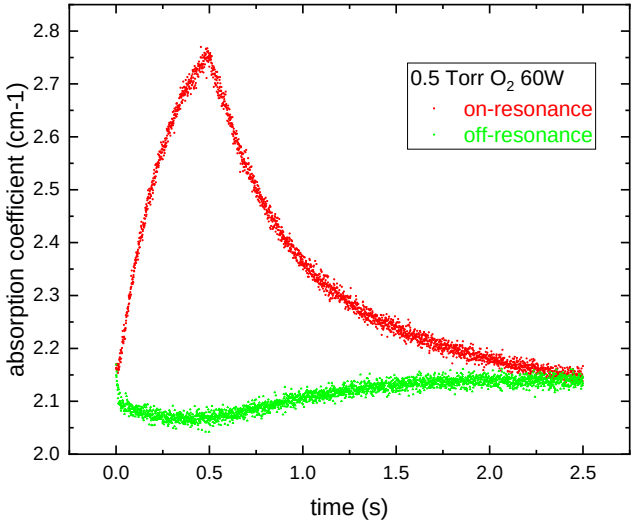
At 1 Torr, quite significant dissociation even at very low power densities ($50mW/cm^2$)

Dissociation fraction drops significantly with pressure

What is O surface recombination coefficient?

Expect about:
-10% on bare metal,
-10^{-3} on glass

Loss frequency
13.56 MHz 100W



Very low O loss rate:

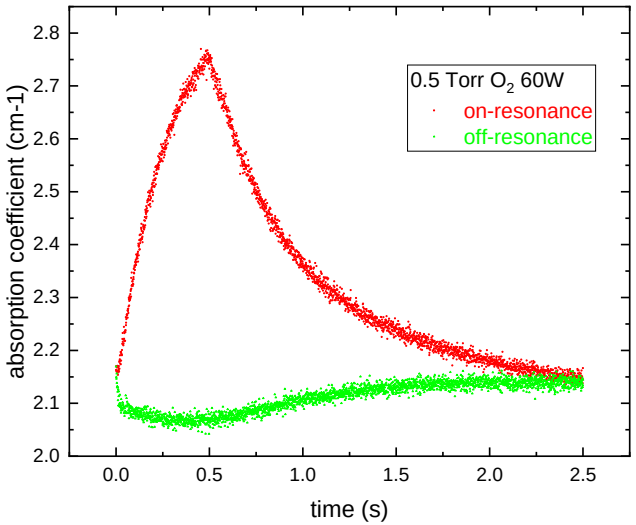
$k = 2\ s^{-1}$

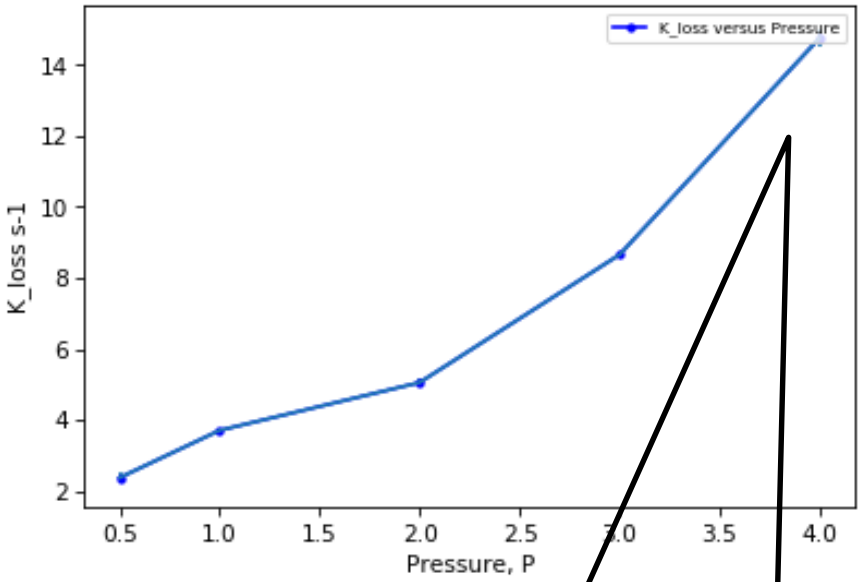
$\gamma \sim 10^{-4}$!!

How can this be so low on bare Al metal?

Variation with pressure ?

Loss frequency
13.56 MHz 100W

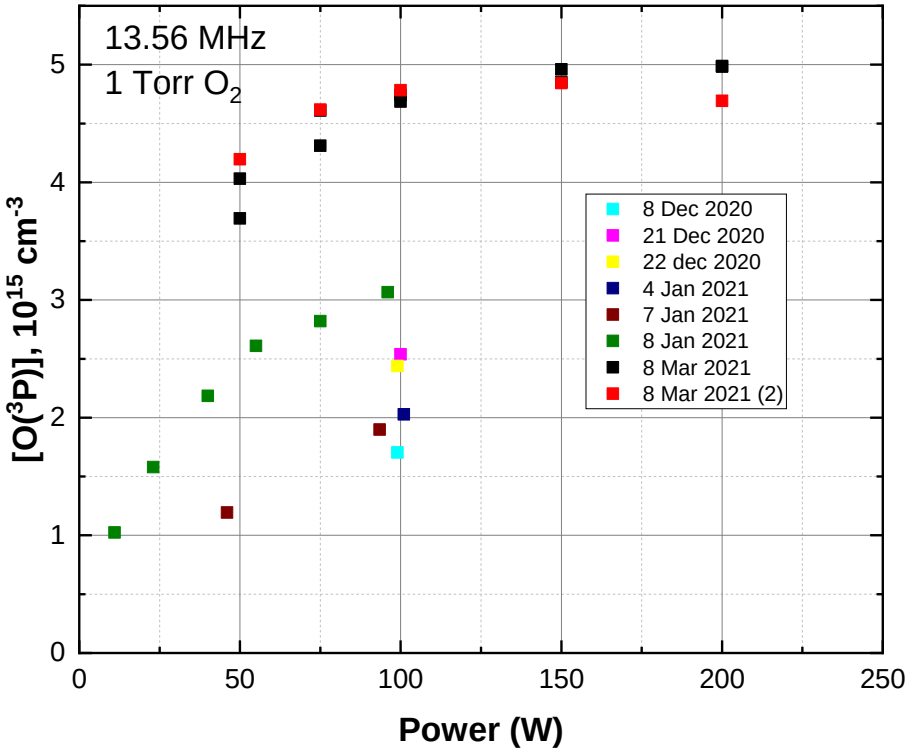




At higher pressures ozone formation kicks in:

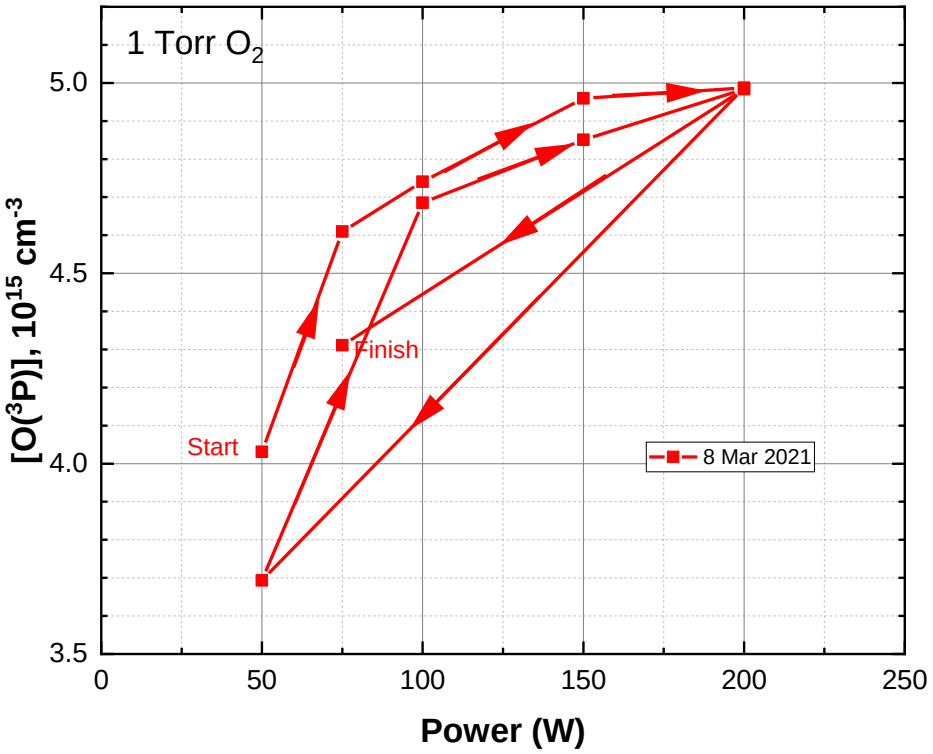
$$O + O_2 + M \rightarrow O_3 + M$$

O density by CRDS
13.56 MHz: reproducibility



Poor reproducibility
Does chamber history matter?
Does measurement order matter?

O density by CRDS @ 13.56 MHz: effect of order of measurement

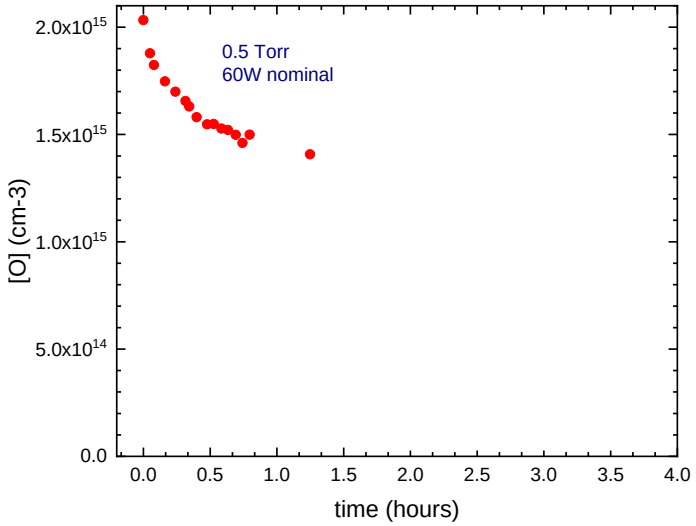


[O] seems to be continually decreasing with time

Effects mush stronger at lower pressure (0.5 Torr)

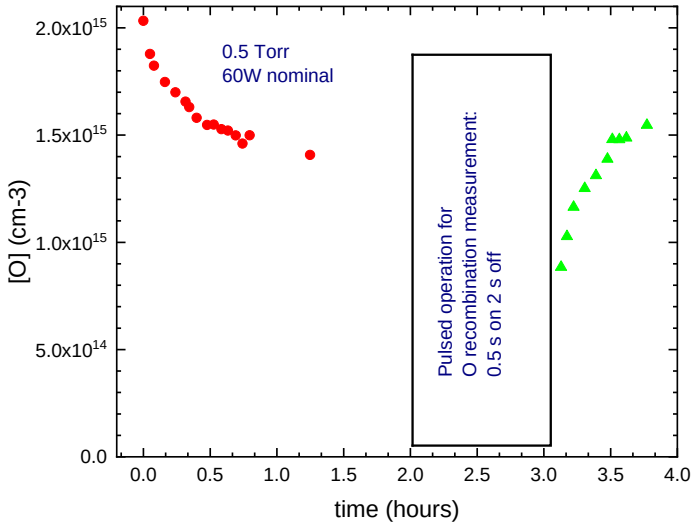
2 Torr results more reproducible

Chamber history effects on O density: most marked at 0.5 Torr



After weekend:
[O] initially high, returns to steady state value in about 30 minutes

Chamber history effects on O density 0.5 Torr



After weekend:
[O] initially high, returns to steady state value in about 30 minutes

Pulsed mode :
-suppresses O density in subsequent cw operation!

-Returns to steady state in about 30 minutes

We repeated this, and got very similar results

Are the measurements of O lifetime from pulsed measurements even valid??

Chamber Drift : discussion

O recombination coefficient ~10^{-4}
-much lower than values observed in low-pressure systems (10's %)

O recombination at surfaces increased by:
-low pressure
-high RF power
-plasma pulsing

What is special about pulsed mode?
-over-voltage at breakdown? Not significant

-ratio Γ_{ion}/Γ_O higher? $\rightarrow$ less oxidised, more metallic surface?

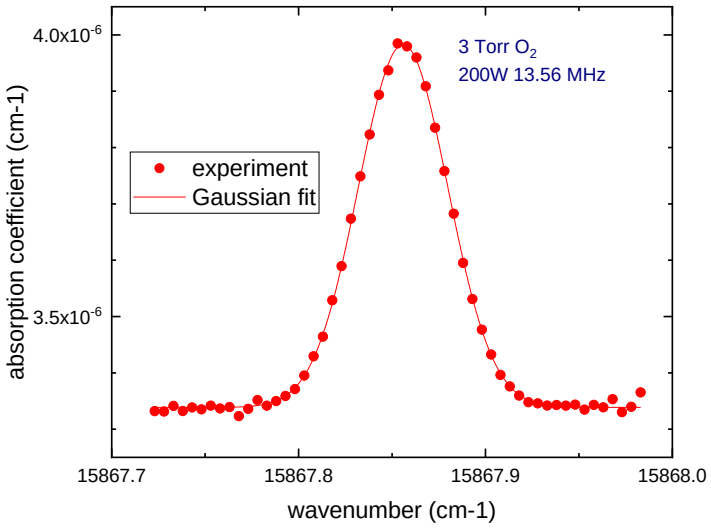
-ratio Γ_{O2+}/Γ_{O+} higher?

Passivation/oxidation of Al (Al_2O_3?) at high O/ low ion energy and flux

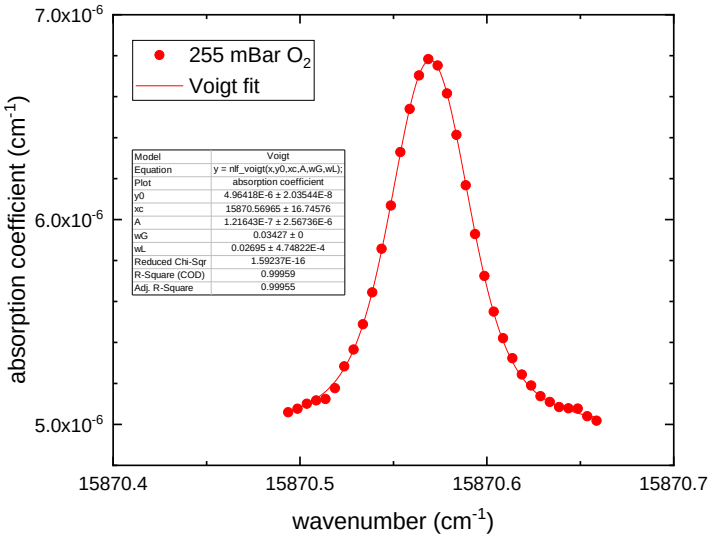
CRDS stability check : O_2 molecules

O_2 b←X (2,0) P9 transition adjacent (+2.7cm^{-1}) to O $^1D_2$ ←$^3P_2$:

O atoms in 3 Torr plasma:



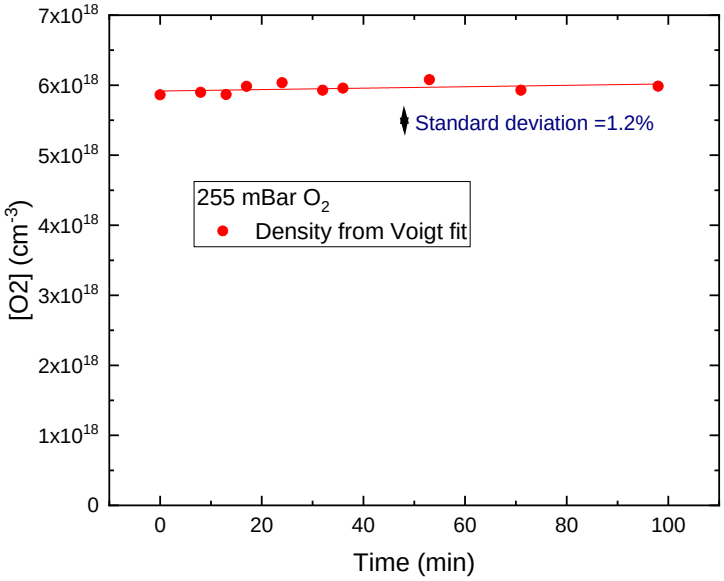
O_2 255 mBar (no plasma)



Need to include pressure broadening in line shape

Monitor O_2 CRDS signal over 100 minutes:

CRDS stability check : O_2 molecules



Signal stable to ± 1.2%

-O_2 signal about 2.5 times bigger than for O

⇒drift is not due to problems with CRDS

Future : check O_2 X depletion in O_2 discharge (time resolved)

→ use (0,0) transition at 763nm
(100x stronger)

Conclusions

Cavity ringdown spectroscopy provides reliable direct absolute measurements :

- O $^3P_2$ density @ 630nm
- Gas translational temperature
- O^- & O_3 density also, from continuum baseline

- Time-resolved measurements are possible
  for timescales longer than ringdown time (10's μs)

O_2 X density can be measured by the b-X transition ((0,0) around 763nm)
-Time-resolved measurements in pulsed plasmas (O_2 X depletion) can be used to probe other species (O ^3P, O_2a)

O surface recombination strongly influenced by ion bombardment:
$\gamma \sim 10^{-3}$ on glass and Aluminium without energetic ions
much higher at low pressure/ high ion/neutral flux ratio