Improving our understanding of plasma-surface interactions through in-situ measurements

LPP
Laboratoire de Physique des Plasmas

JP Booth

S.Zhang, G.A.Curley, A.Chatterjee, A Volynets, O.Guaitella (LPP)

D Lopaev, D. Voloshin, Y.Mankelevich (Moscow)

K.Mansfield, G.Ritchie (Oxford)

V Guerra (Lisbon)

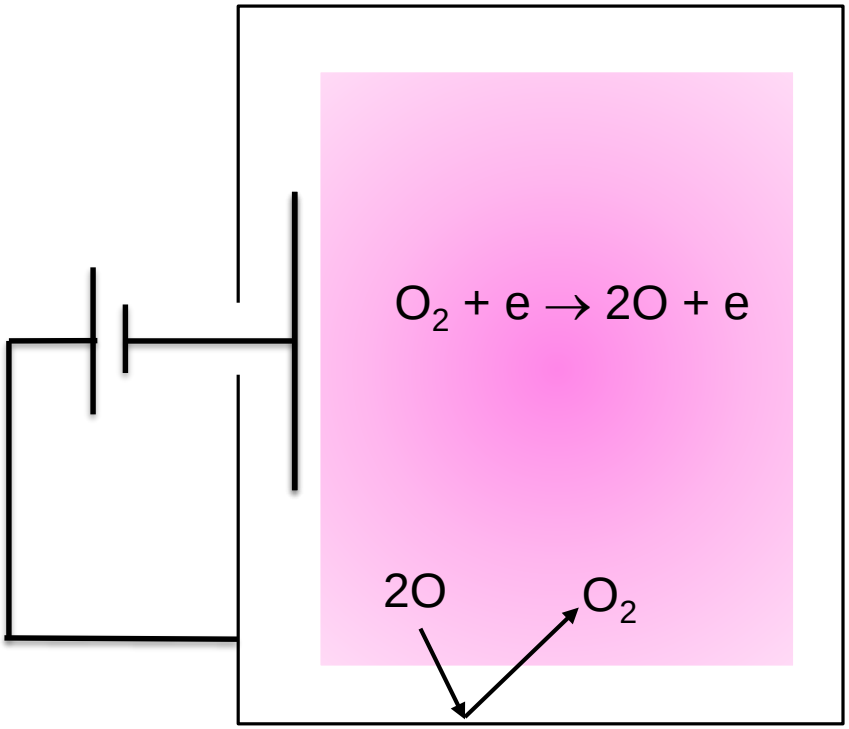
cnrs
dépasser les frontières

ÉCOLE POLYTECHNIQUE
UNIVERSITÉ PARIS-SACLAY

Dissociation equilibrium: O_2 plasma

In a low-pressure plasma process,

wall-catalysed recombination controls reactive species densities:



At steady state:

(Assuming gas-phase reactions of O are negligible)

Electron impact dissociation

$$O_2 \rightleftharpoons 2O$$

Surface catalysed recombination

$$2n_e k_{O_2}^{diss} n_{O_2} = k_O^{rec} n_O$$

Surface recombination probability, γ

$$2n_e k_{O_2}^{diss}\ n_{O_2} = k_O^{rec} n_O$$

At low pressure /fast diffusion:

Surface recombination probability,
γ (0↔1)

-typically assumed to be a constant

Mean kinetic velocity of atoms

$$k_O^{rec} \approx \frac{A}{V}\frac{\bar{v}\gamma}{4}$$

Surface to volume ratio of the chamber

What are the mechanisms of surface recombination?
First we need to measure it:

Measuring surface loss probability

If we extinguish the plasma:

$$\frac{dn_O}{dt} = -k_O^{loss} n_O \quad \Rightarrow \quad n_O(t) = n_O(0) e^{-k_O^{loss} t}$$

Or partially modulate the electron density:

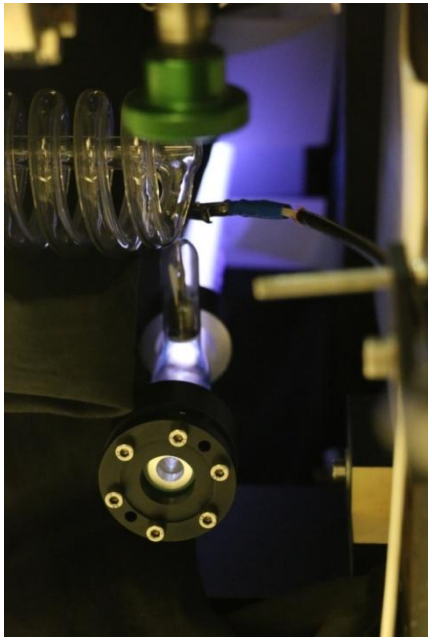
$$n_O(t) = n_O^1 + n_O^2 e^{-k_O^{loss} t}$$

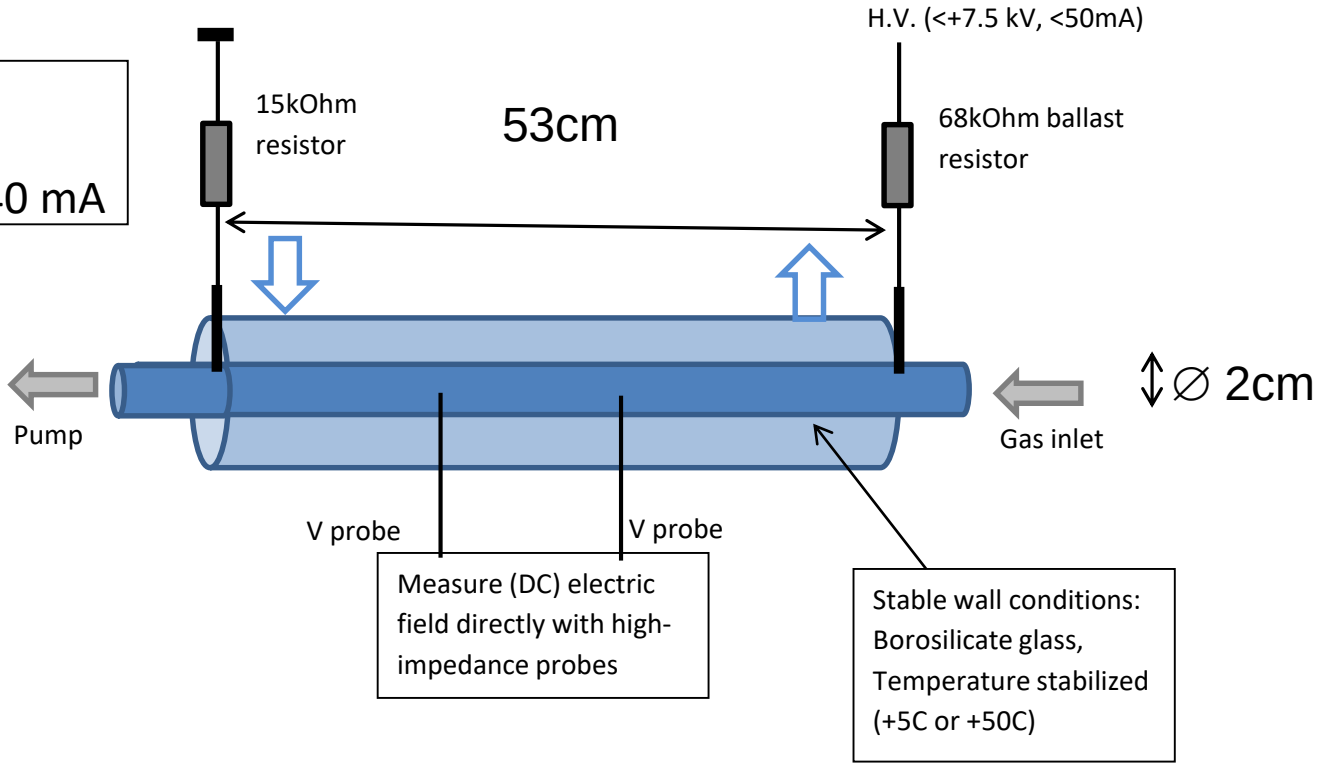
So what do we observe in practice?

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

Pressure: 0.2 – 10 Torr

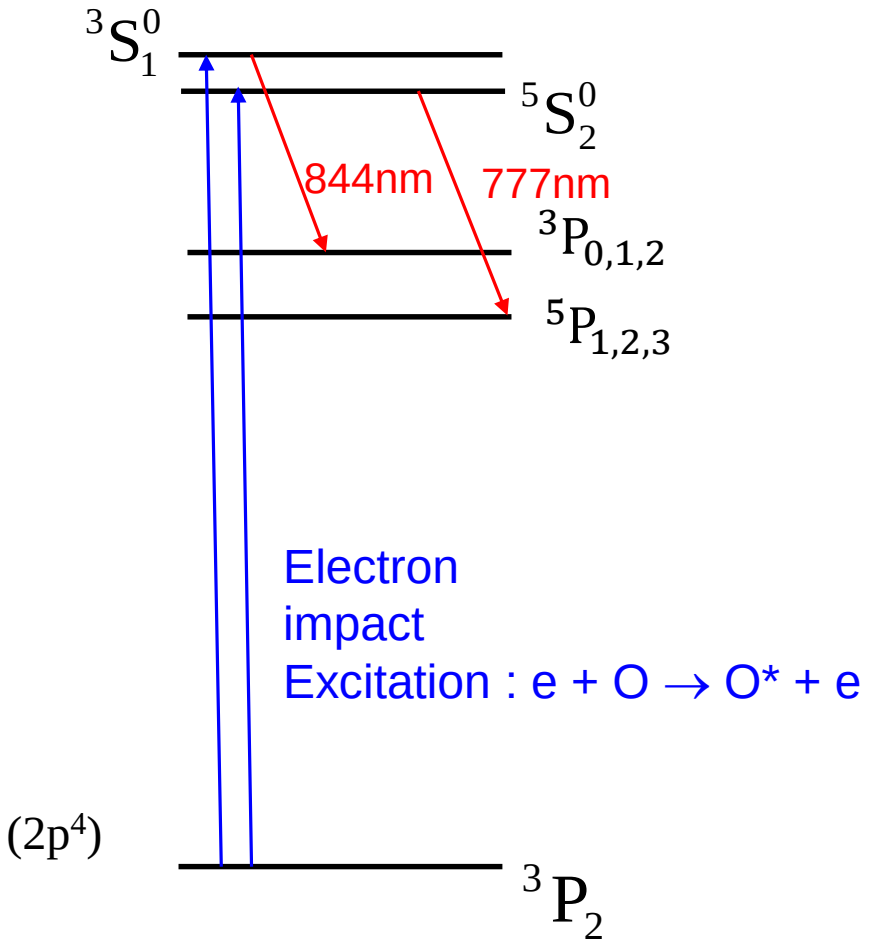
Discharge current: 10 - 40 mA





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

Measuring oxygen atom dynamics: Optical emission actinometry



Only possible when the plasma is running:

$$I_O^{844nm} = [O] n_e k_O^{exc}$$

Add 5% Ar (actinometer gas):

$$I_{Ar}^{750nm} = [Ar] n_e k_{Ar}^{exc}$$

Taking the ratio:

$$[O] \propto \frac{I_O^{844nm}}{I_{Ar}^{750nm}} \quad \text{or} \quad [O] \propto \frac{I_O^{777nm}}{I_{Ar}^{750nm}}$$

Oxygen mole-fraction

Absolute densities from actinometry:

-Measure reduced electric field, E/N

-calculate EEDF (Boltzmann equation)

-calculate excitation rates from excitation cross-sections

accuracy of the cross-sections?

Oxygen mole-fraction

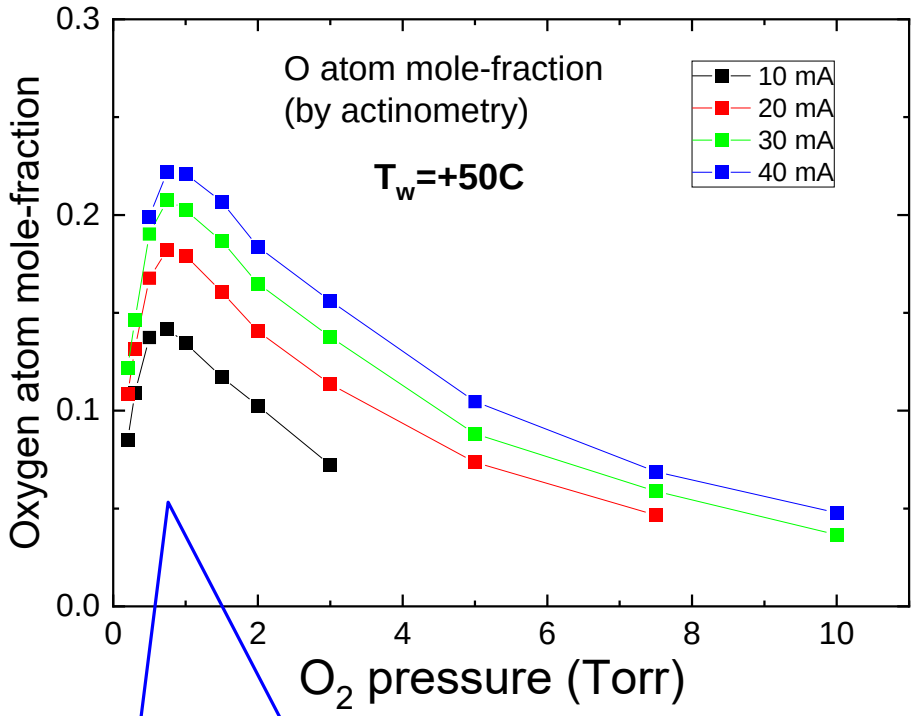
Absolute densities from actinometry:

-Measure reduced electric field, E/N

-calculate EEDF (Boltzmann equation)

-calculate excitation rates from excitation cross-sections

Up to ~25% of gas is O atoms!

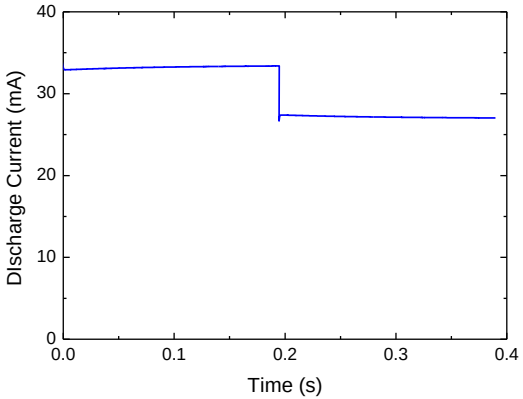


Surface temp

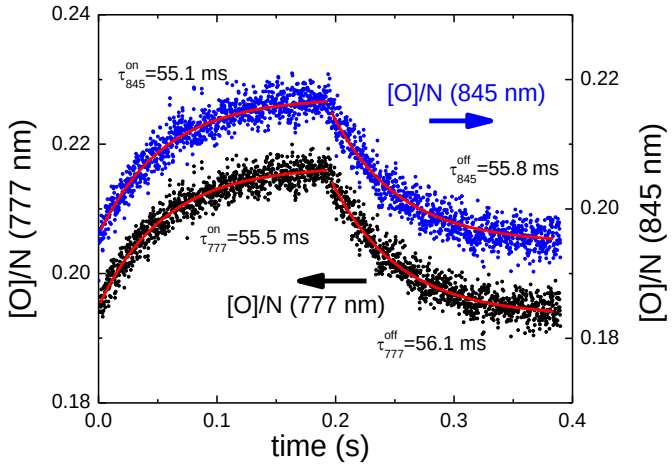
Why the maximum around 1 Torr (133 Pa) pressure?

Oxygen atom loss kinetics: surface recombination

Modulate Current 15%



Actinometry : I_O/I_{Ar}



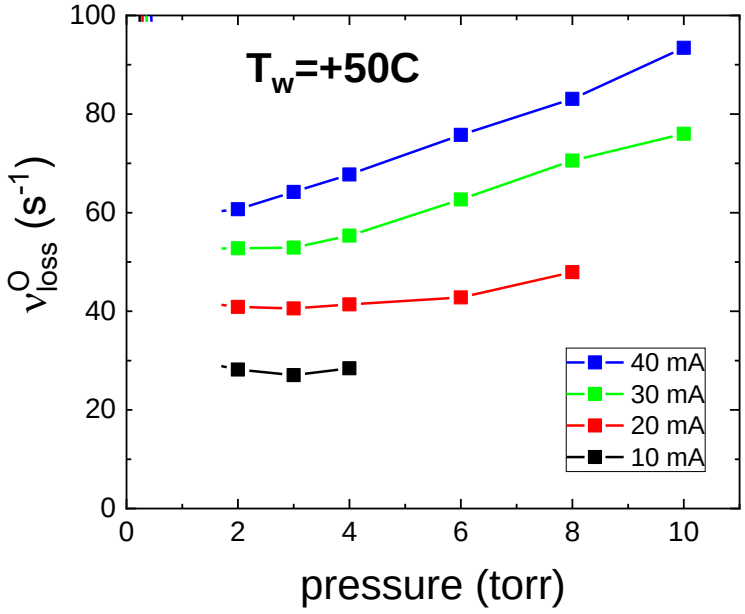
Step change in electron density
Reduced field/EEDF almost unchanged

Exponential decays / rise
-two emission lines

} all give similar loss frequencies, k_{loss}

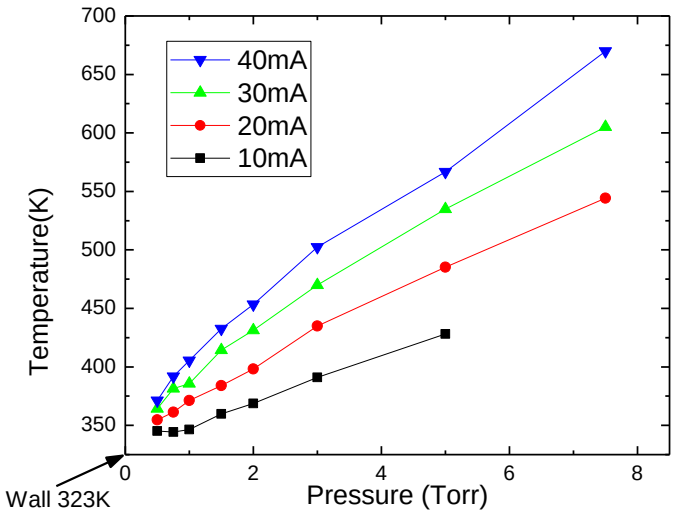
Booth et al., Plasma Sources Sci. Technol. 28 (2019) 055005

Loss frequency variation -pressure above 1 Torr



-Loss rate increases with pressure and current:

-Correlated with gas temperature:

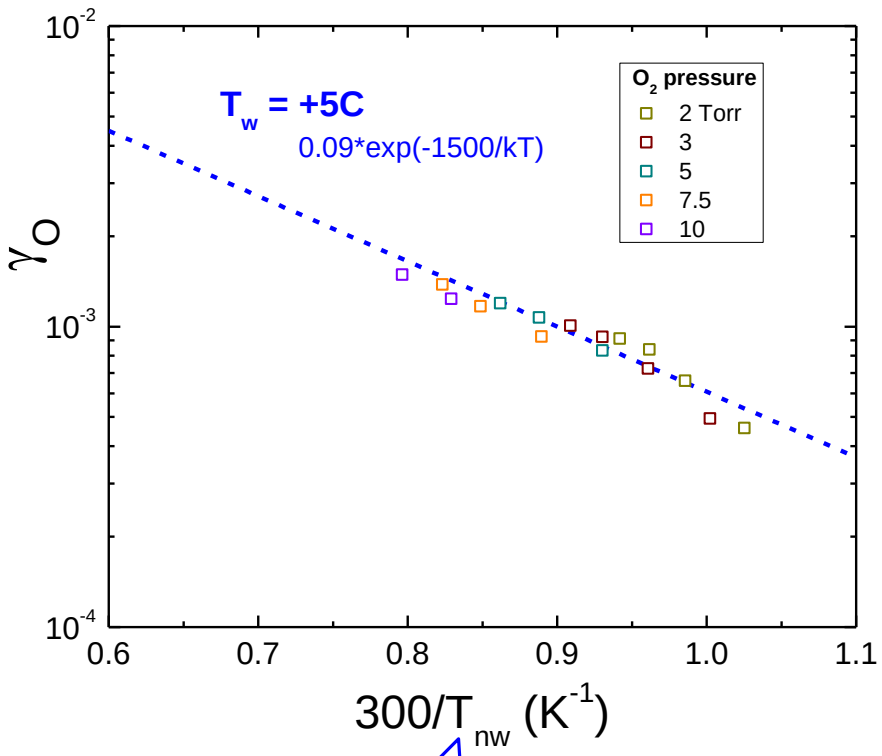


(From CRDS, or O_2 b emission)

Plot surface reaction probability as a function of gas temperature (Arrhenius plot):

O atom surface recombination: Eley-Rideal mechanism

Arrhenius plot vs temperature



GAS, not surface temperature

-Recombination activated by incident atom energy

-**Eley-Rideal** mechanism

$$O + O(s) \rightarrow O_2 \uparrow$$

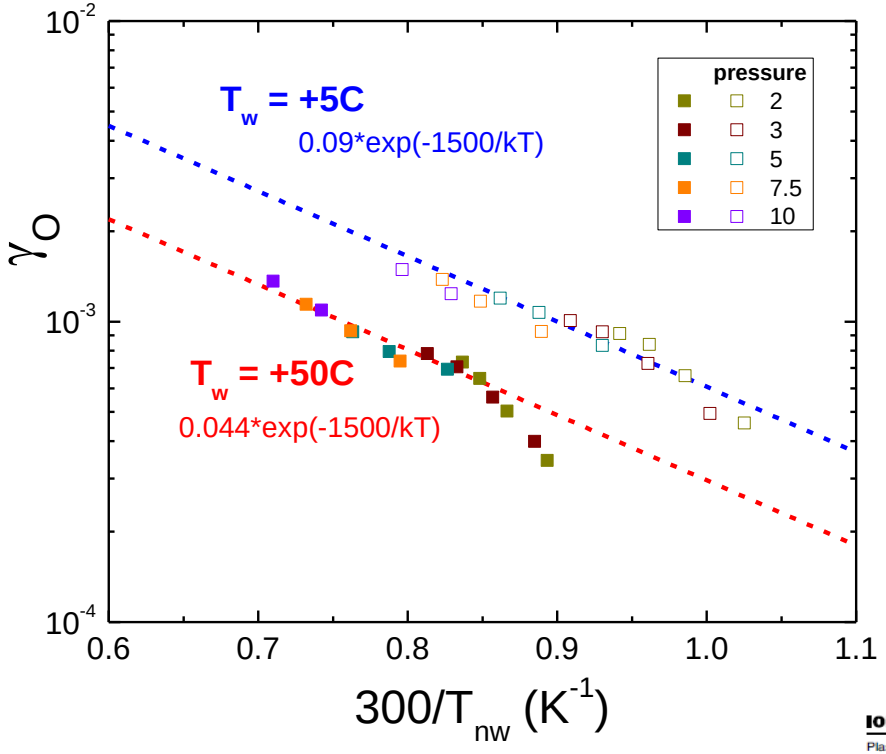
-activation energy= 0.13 eV

(in a Hinshelwood mechanism both atoms are thermalised on the surface, and therefore would not depend on gas temperature)

Effect of surface temperature?

O atom surface recombination: Effect of surface temperature

Arrhenius plot vs **gas** temperature



Same Activation Energy
-pre-exponential factor decreases with temperature

Increased surface temperature ⇒ reduces surface coverage ⇒ Reduces recombination probability

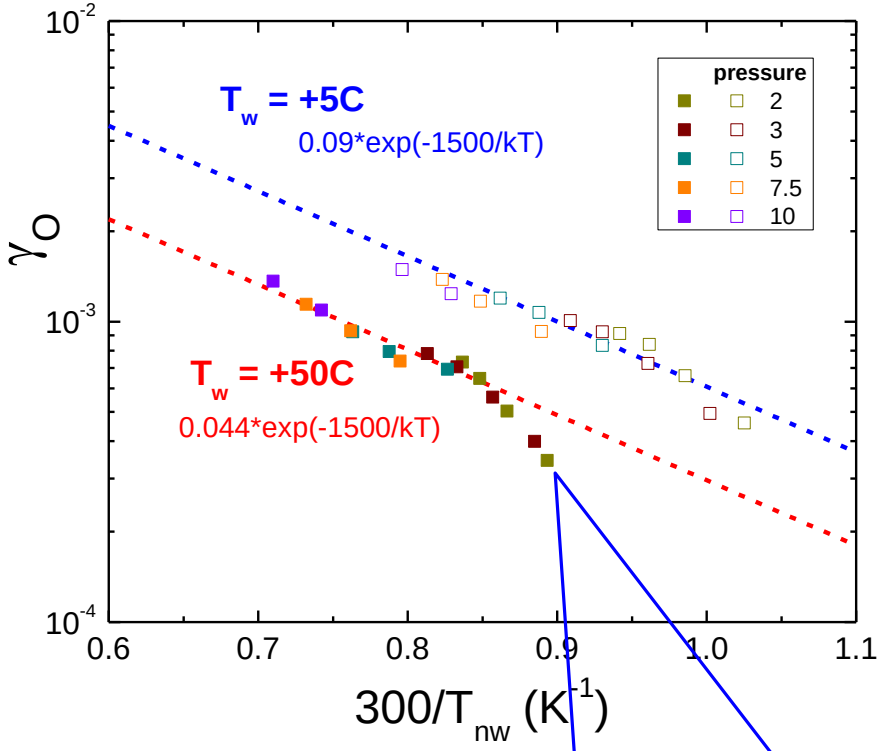
IOP Publishing
Plasma Sources Science and Technology
Plasma Sources Sci. Technol. **28** (2019) 055005 (20pp)
https://doi.org/10.1088/1361-6595/ab13e8

Oxygen (^{3}P) atom recombination on a Pyrex surface in an O_2 plasma

J P Booth[1], O Guaitella[1], A Chatterjee[1], C Drag[1], V Guerra[2], D Lopaev[3], S Zyryanov[3], T Rakhimova[3], D Voloshin[3] and Yu Mankelevich[3]

O atom surface recombination: Effect of surface temperature

Arrhenius plot vs **gas** temperature



Same Activation Energy
-pre-exponential factor decreases with temperature

Increased surface temperature ⇒ reduces surface coverage ⇒ Reduces recombination probability

-but the story is a bit more complicated
-also depends on incident O flux..

Viegas et al, PSST 2024
Mesoscopic model

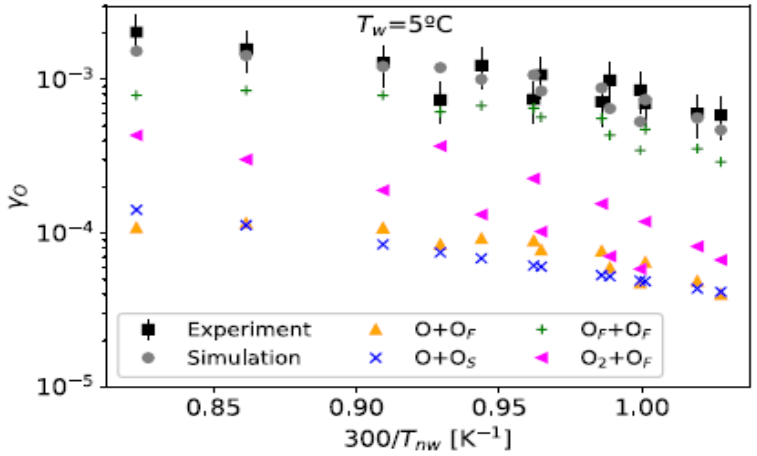
Nbr.	Reaction	Rate ($\text{site}^{-1}\cdot\text{s}^{-1}$)
R1	$O(g) + Fv \rightarrow O_F$	$r_1 = \frac{P_1^0}{[F]+[S]}\phi_O$
R2	$O_F \rightarrow O(g) + Fv$	$r_2 = \nu_d \cdot \exp\left(-\frac{E_d^O}{RT_w}\right)$
R3	$O(g) + Sv \rightarrow O_S$	$r_3 = \frac{P_3^0}{[F]+[S]}\phi_O$
R4	$O(g) + O_S \rightarrow O_2(g) + Sv$	$r_4 = r_3 \times P_{ER}^S, P_{ER}^S = P_4^0 \cdot \exp\left(-\frac{E_{ER}^S}{RT_{nw}}\right)$
R5	$O(g) + O_F \rightarrow O_2(g) + Fv$	$r_5 = r_1 \times P_{ER}^F, P_{ER}^F = P_5^0 \cdot \exp\left(-\frac{E_{ER}^F}{RT_{nw}}\right)$
R6	$O_F + Sv \rightarrow Fv + O_S$	$r_6 = \frac{3}{4} \times \tau_D^{-1}, \tau_D^{-1} = \nu_D \cdot \exp\left(-\frac{E_D}{RT_w}\right)\frac{[F]}{[F]+[S]}$
R7	$O_F + O_S \rightarrow O_2(g) + Fv + Sv$	$r_7 = P_{LH}^S \times \tau_D^{-1}, P_{LH}^S = P_7^0 \cdot \exp\left(-\frac{E_{LH}^S}{RT_w}\right)$
R8	$O_F + O_F \rightarrow O_2(g) + Fv + Fv$	$r_8 = 2 \times P_{LH}^F \times \tau_D^{-1}, P_{LH}^F = P_8^0 \cdot \exp\left(-\frac{E_{LH}^F}{RT_w}\right)$
R9	$O_2(g) + Fv \rightarrow O_{2,F}$	$r_9 = \frac{P_9^0}{[F]+[S]}\phi_{O_2}$
R10	$O_{2,F} \rightarrow O_2(g) + Fv$	$r_{10} = \nu_d \cdot \exp\left(-\frac{E_d^{O_2}}{RT_w}\right)$
R11	$O_2(g) + O_F \rightarrow O_3(g) + Fv$	$r_{11} = r_9 \times P_{ER}^{O_2+O_F}, P_{ER}^{O_2+O_F} = P_{11}^0 \cdot \exp\left(-\frac{E_{ER}^{O_2+O_F}}{RT_{nw}}\right)$
R12	$O_2(g) + O_{2,F} \rightarrow O_2(g) + O_2(g) + Fv$	$r_{12} = r_9 \times P_{ER}^{O_2+O_{2,F}}, P_{ER}^{O_2+O_{2,F}} = P_{12}^0 \cdot \exp\left(-\frac{E_{ER}^{O_2+O_{2,F}}}{RT_{nw}}\right)$
R13	$O(g) + O_{2,F} \rightarrow O_3(g) + Fv$	$r_{13} = r_1 \times P_{ER}^{O+O_{2,F}}, P_{ER}^{O+O_{2,F}} = P_{13}^0 \cdot \exp\left(-\frac{E_{ER}^{O+O_{2,F}}}{RT_{nw}}\right)$
R14	$O_F + O_{2,F} \rightarrow O_3(g) + Fv + Fv$	$r_{14} = P_{LH}^F/\tau_D, P_{LH}^{O_F+O_{2,F}} = P_{14}^0 \cdot \exp\left(-\frac{E_{LH}^{O_F+O_{2,F}}}{RT_w}\right)$
R15	$O_{2,F} + O_F \rightarrow O_3(g) + Fv + Fv$	$r_{15} = P_{LH}^F/\tau_D, P_{LH}^{O_{2,F}+O_F} = P_{15}^0 \cdot \exp\left(-\frac{E_{LH}^{O_{2,F}+O_F}}{RT_w}\right)$

Includes:

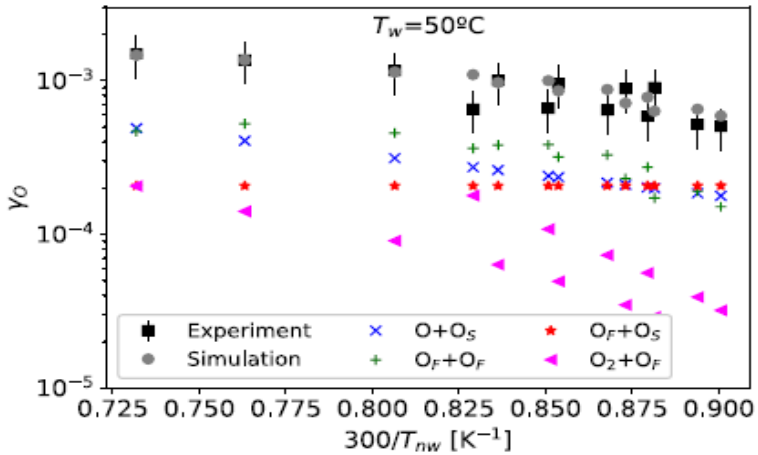
Eley-Rideal and Langmuir-Hinshelwood mechanisms

O_2 ER and LH mechanisms to form O_3

Viegas 2024



(b)



(d)

Cold surface (5 °C):

-LH reaction between physisorbed atoms dominates

(because assumed that ER with physisorbed O is unlikely)

-also $O_F + O_2 \rightarrow O_3$

Surface Ozone production

Hot surface (50 °C):

-ER with chemisorbed O

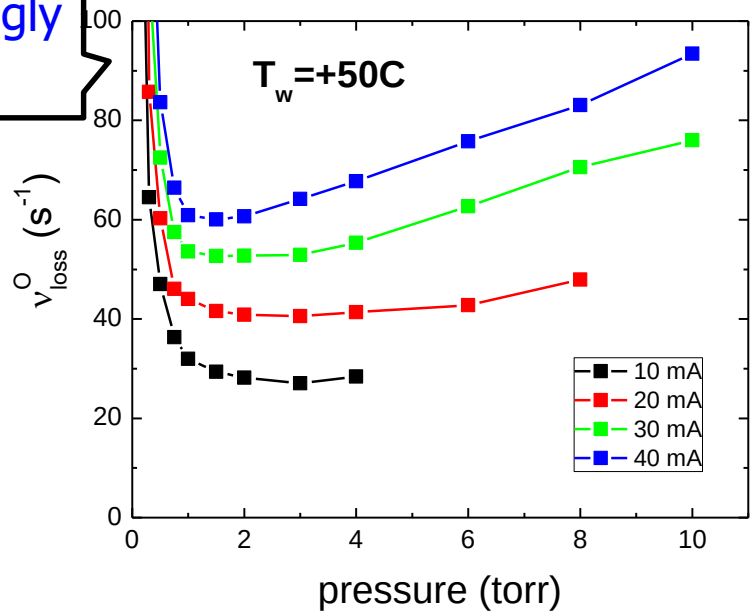
-LH reaction between physisorbed atoms

-LH reaction between physi/chem atoms

But concludes that it is difficult to distinguish experimentally between ER and LH mechanism with high mobility

What happens below 1 Torr?

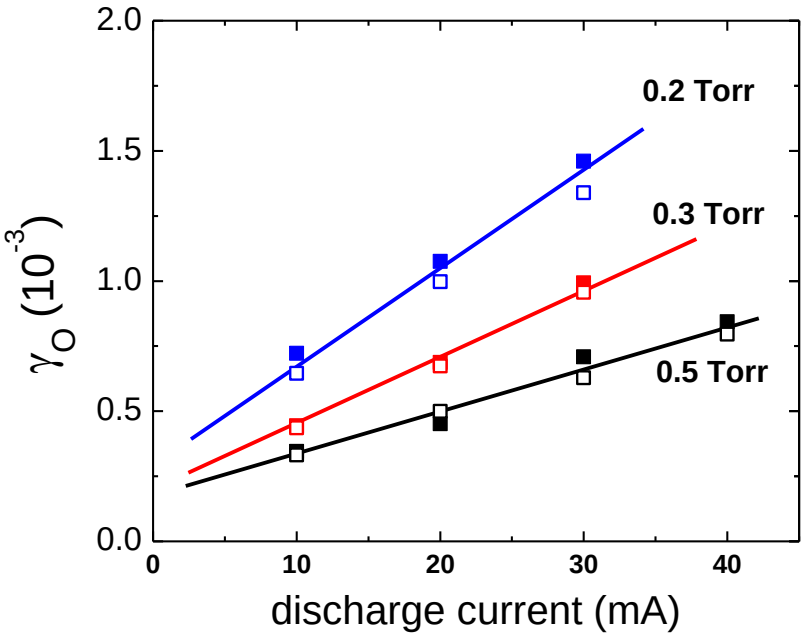
-Loss rate increases strongly at low pressure



At lower pressures, ion energy is higher:

Plot loss rate vs. current for each pressure:

Effect of ion flux on O recombination



Surface recombination $\gamma \propto$ ion flux

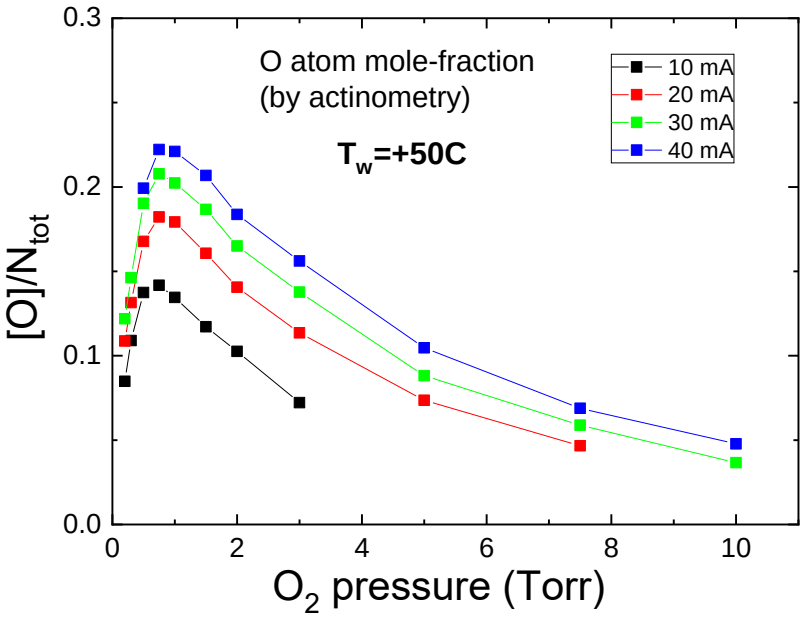
Energetic Ion bombardment at low pressure

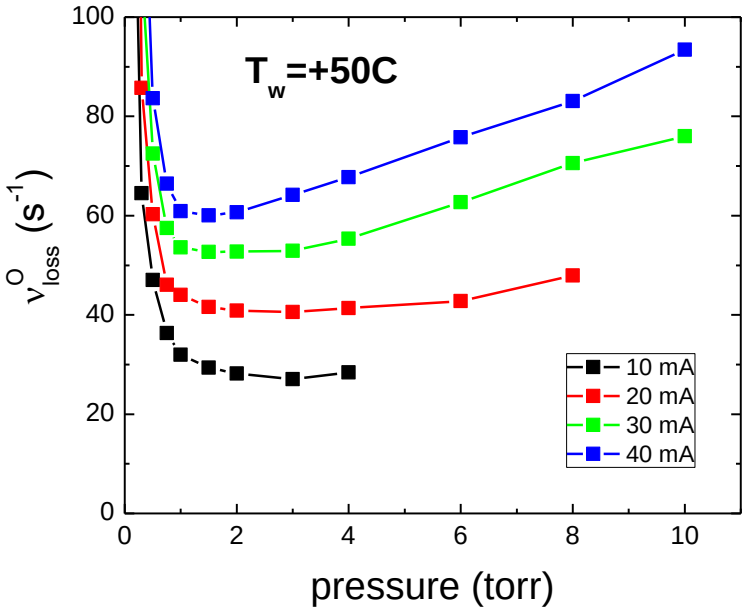
$\Rightarrow$ Creation of reactive sites/surface cleaning?
$\Rightarrow$ Product desorption?

NB note that this is done by actinometry, for which 5% Ar is added…..

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

Oxygen mole-fraction & surface recombination





Maximum in O atom mole fraction corresponds to minimum in recombination rate

What happens in the afterglow (full current modulation)?

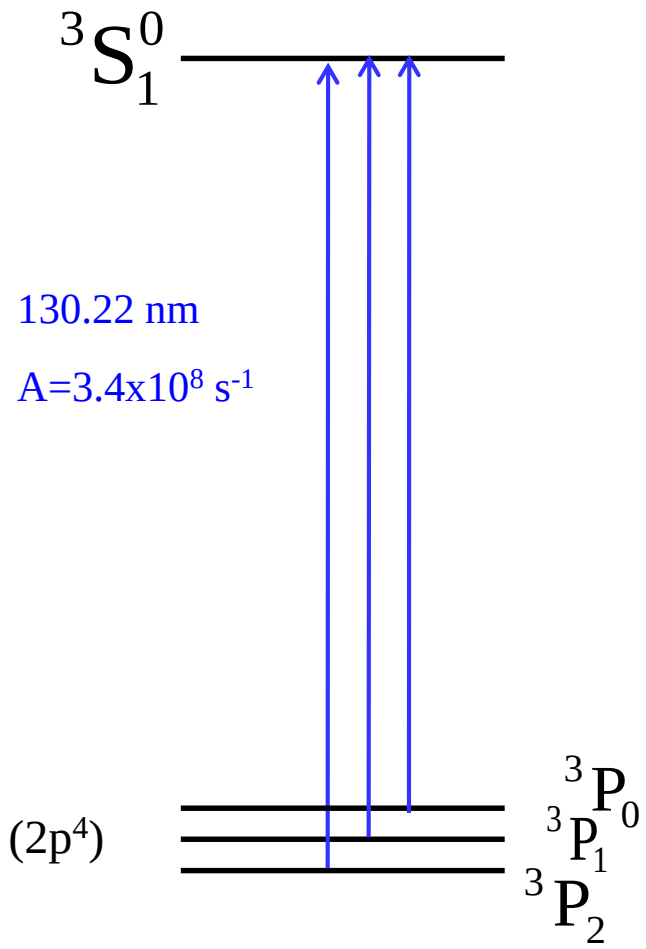
Optical emission actinometry not possible in afterglow (no electrons)

⇒ **Need to use active spectroscopy:**

- TALIF at 226nm, with calibration against Xe
  - Highly non-linear → very noisy
  - Absolute calibration : complex and imprecise
  - Photolysis issues: $O_2(v) + hv \rightarrow 2O$

- Absorption spectroscopy?

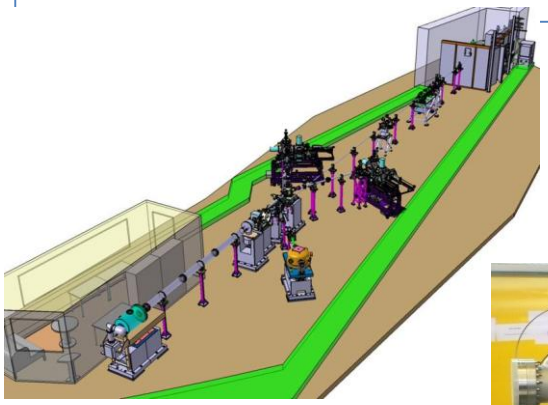
O atom resonance transitions



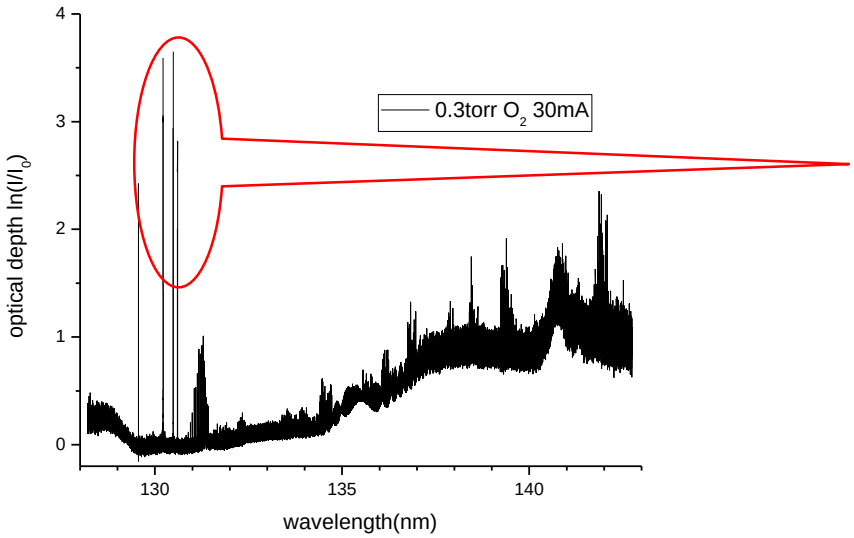
1) Classical Resonance absorption
using an atomic lamp:
-calculate line profile convolution
-requires assumptions !
-noisy, small dynamic range

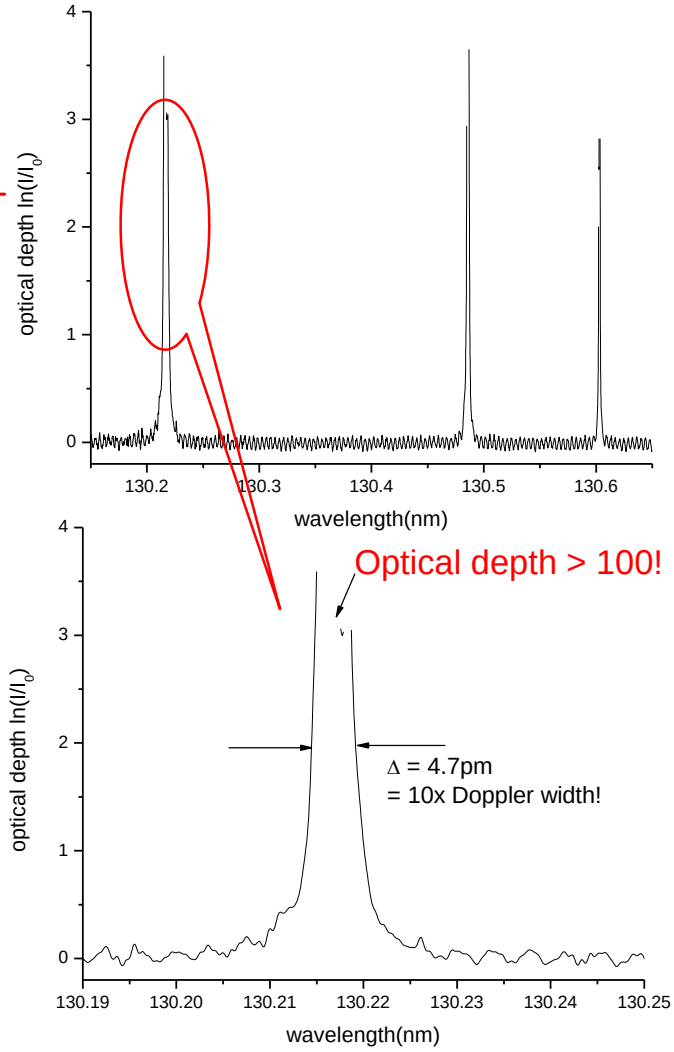
2) **Doppler-resolved measurements**?:

⇒ FT spectrometer at **Synchrotron Soleil**
10^6 resolution!



O atom resonance absorption FTS at Synchrotron Soleil

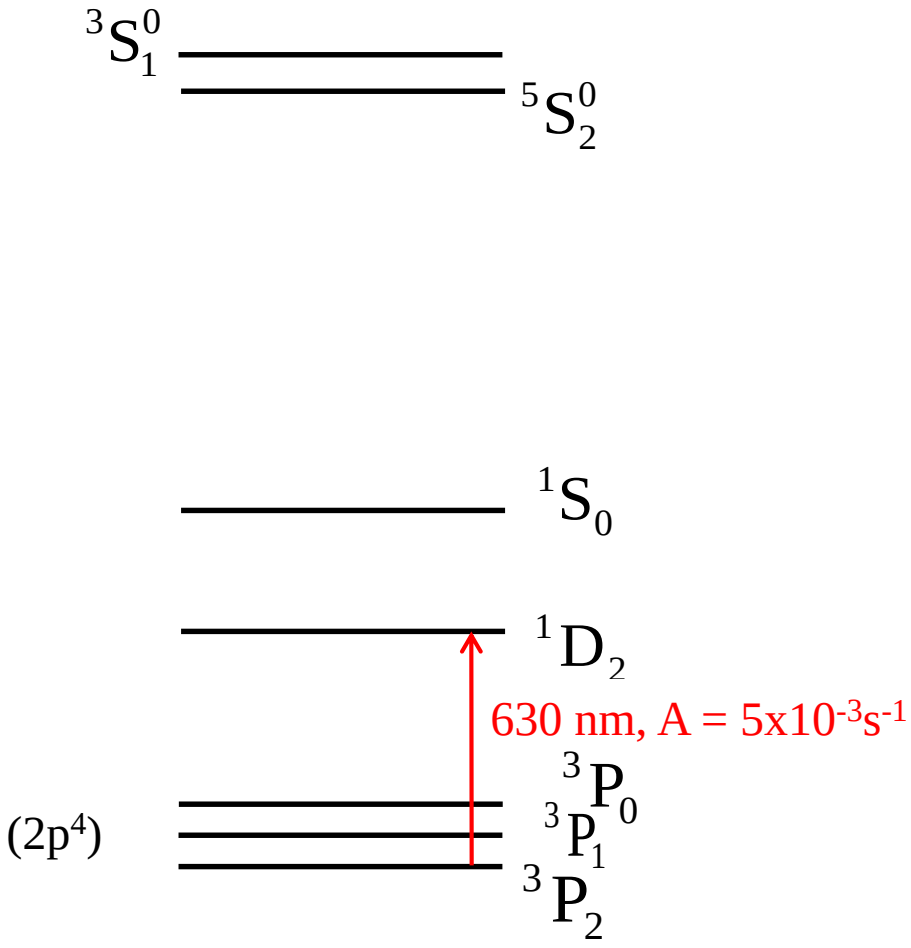




Totally saturated lines - impossible to interpret! (also FT not time-resolved..)

Can we use a weaker absorption line?

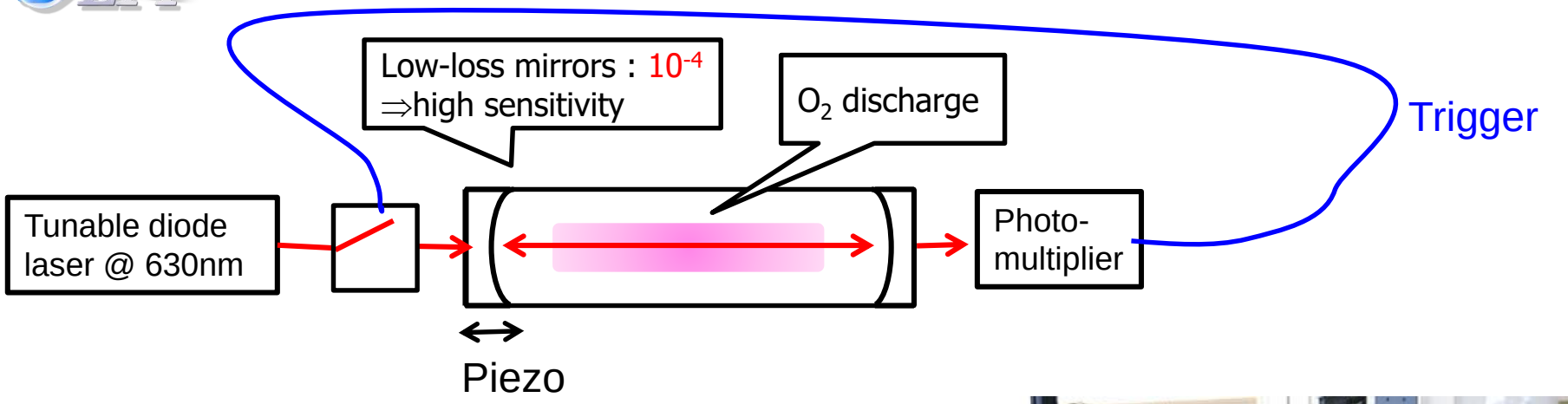
Oxygen atom transitions

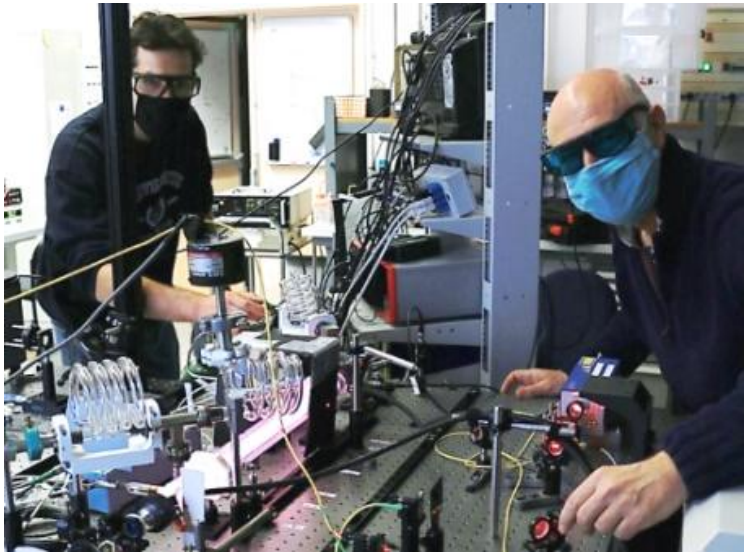


Spin-forbidden:
10^9x smaller cross-section!
Single pass absorption $\approx 10^{-4}$

$\Rightarrow$Multipass techniques necessary

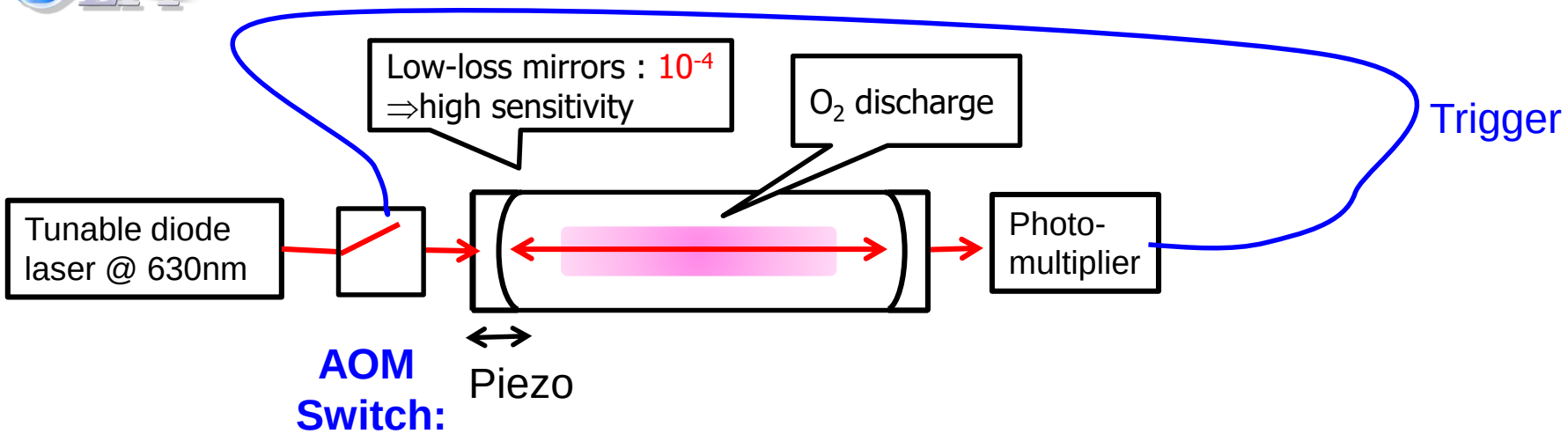
Cavity ringdown spectroscopy with a monomode diode laser





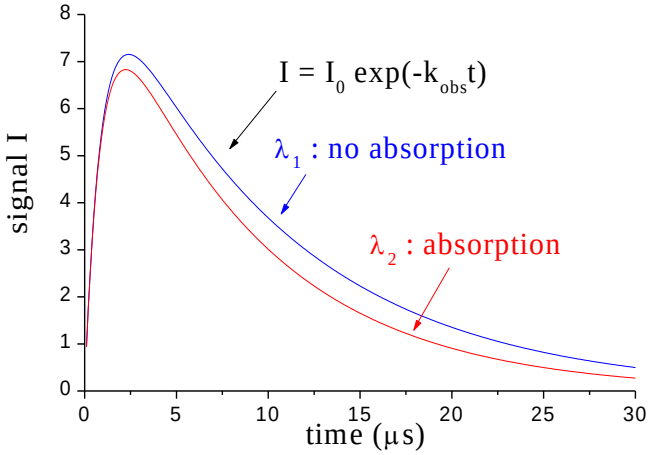
Booth et al.Plasma Sources Sci.Technol. 32 (2023) 095016

Cavity ringdown spectroscopy with a monomode diode laser



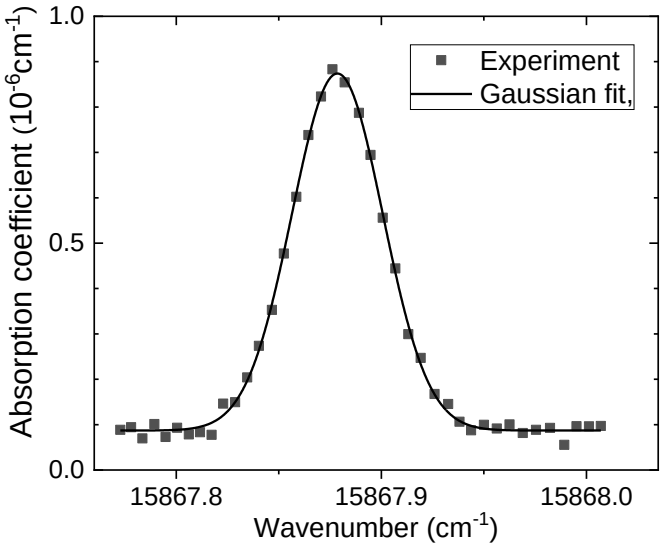
Stop laser when longitudinal mode is matched
⇒intensity passes a threshold

-measure exponential decay rate
⇒ Determine linear absorption coefficient

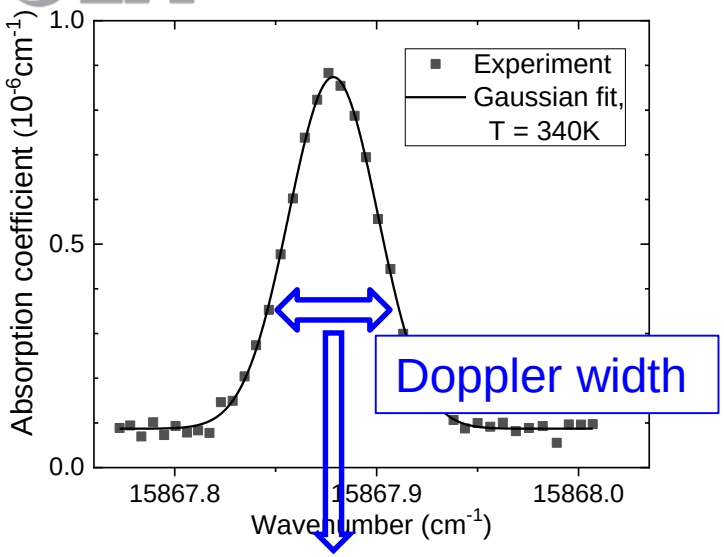


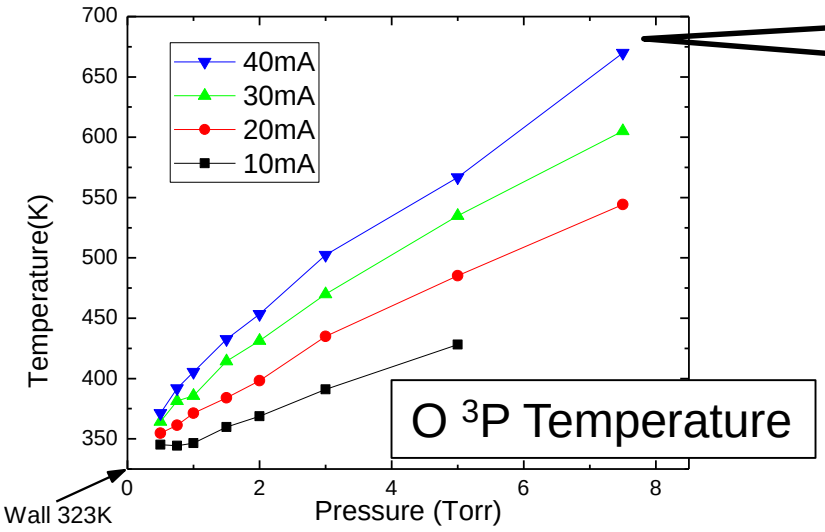
Booth et al.Plasma Sources Sci.Technol. 32 (2023) 095016

CRDS in an O_2 DC positive column



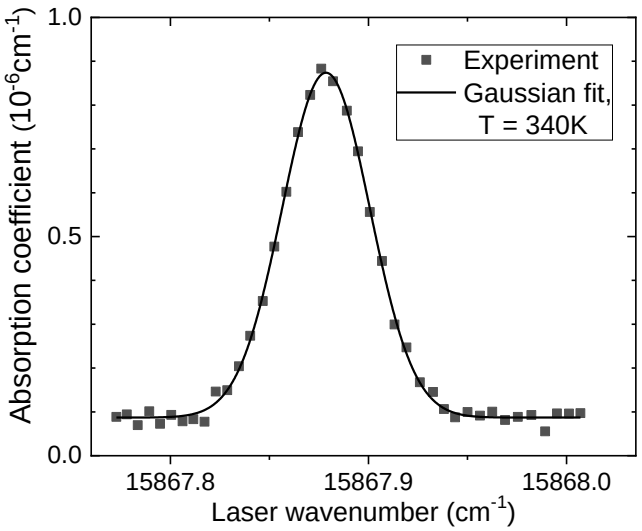
Gas temperature from CRDS



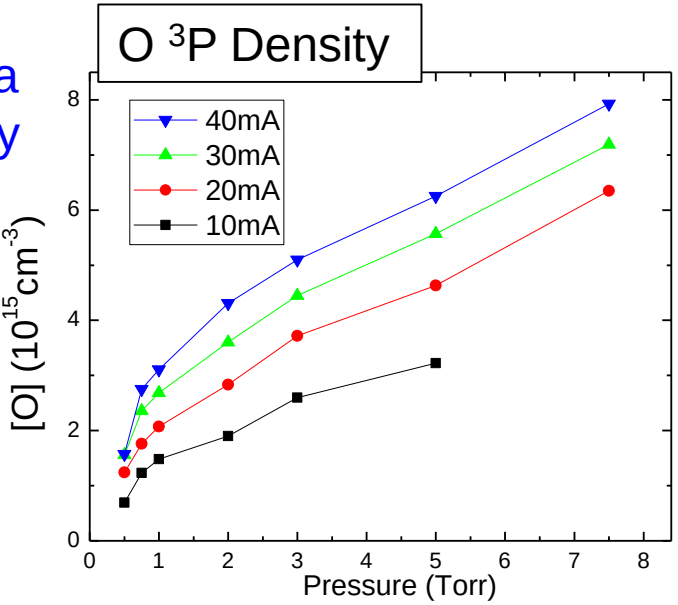


up to 700K

O atom number density



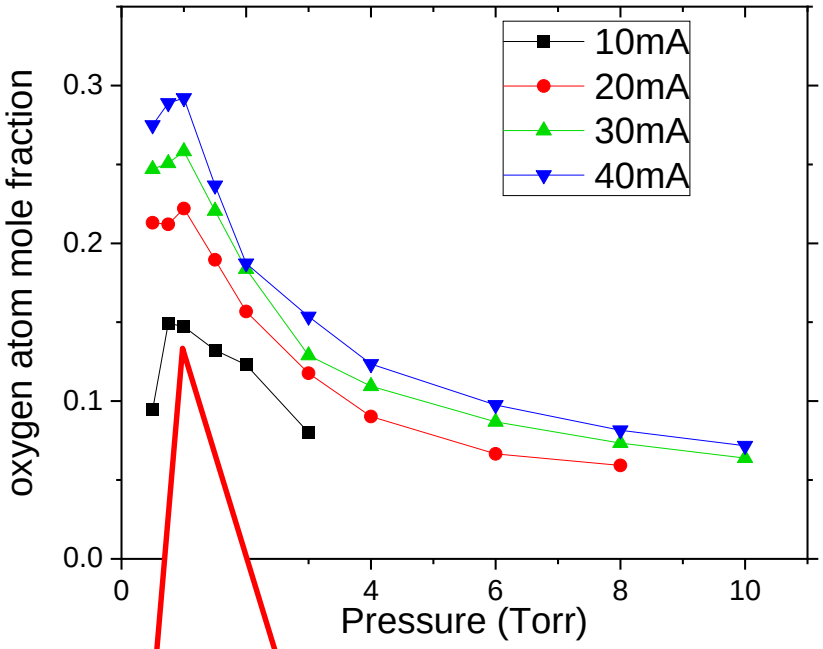
Integrated area
$\propto$ O $^3P_2$ density



(add density of $^3P_1$ and $^3P_0$
assuming equilibrium with T_{trans})

Combine [O] and temperature measurements $\Rightarrow$

O atom mole fraction (pure O_2)



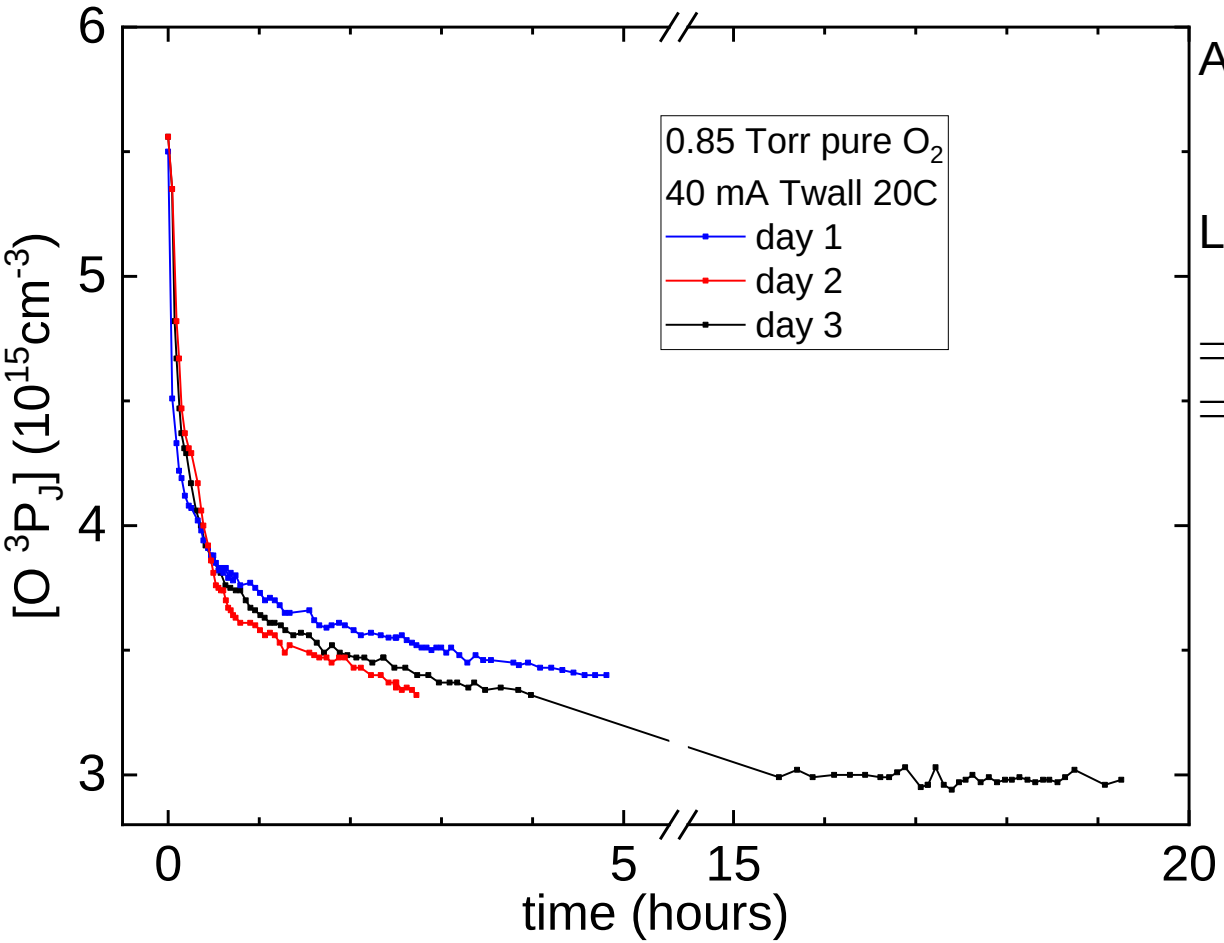
maximum at ~1 Torr.
Some differences with actinometry (actinometry limitations?)

BUT: significant problems with reproducibility!

⇒Investigate long-term stability of O density

Automate scanning + fitting of Gaussian peak

Day 3



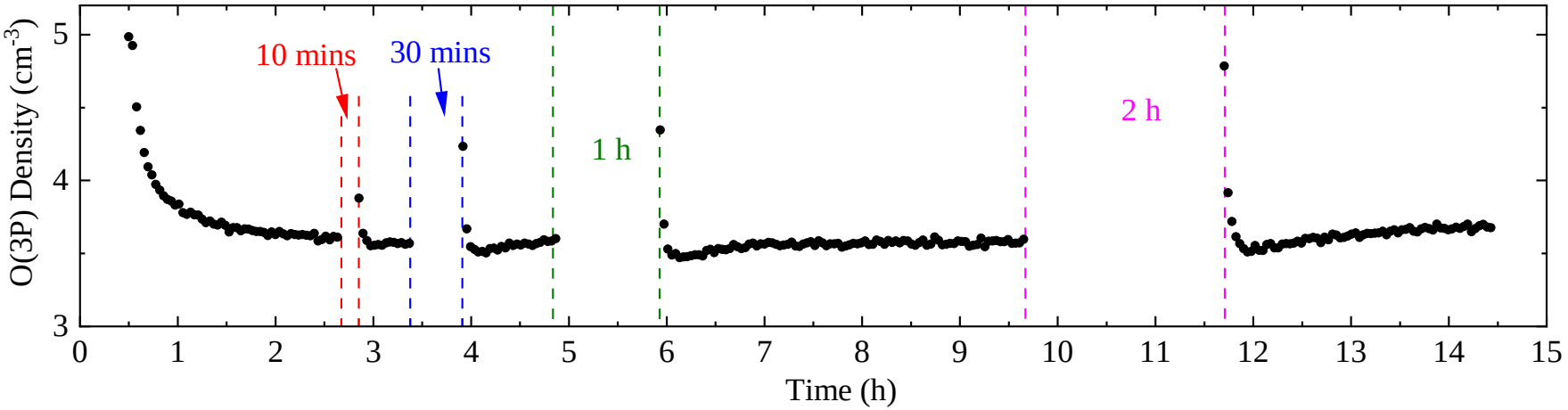
Again similar behaviour.

Leave running all night:

⇒ Finally stabilised.

⇒ 45% lower than initial value!

Effect of stopping discharge

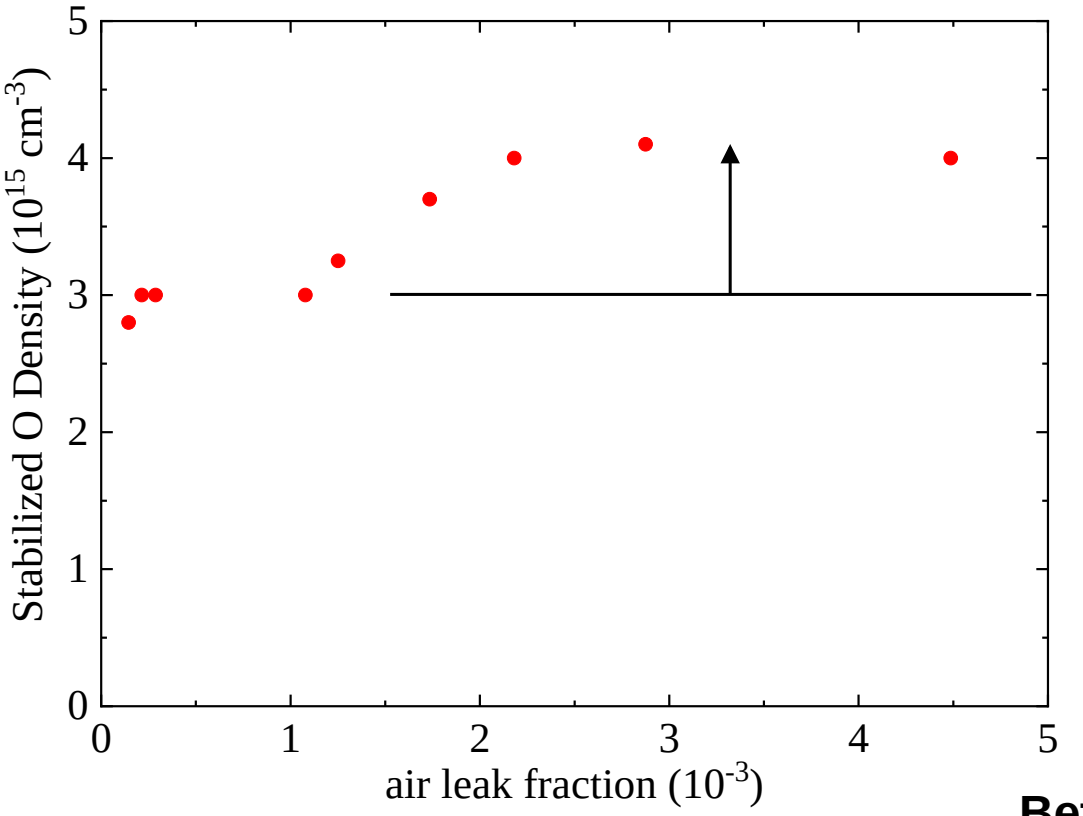


Initial density recovers with a 1-exp time of about 1 hour

Why does [O] drift?

- CRDS : absolute measurement without calibration
  - **not a measurement artefact**
- Active stabilisation of
  - Gas pressure
  - discharge current
  - wall temperature
- $\Rightarrow$ **O atom surface recombination drifts**
  - $H_20 \rightarrow$ block recombination sites by -OH?
  - Plasma strips OH $\Rightarrow$ more recombination sites?
- Variation between tubes?
  - Effect of base pressure/air leak?

Variations between tubes: Effect of a small air leak?



Reduce leak to minimum, then test effect of a small leak via a needle valve

- $2x10^{-3}$ air leak increases the O density by about 35%
- Similar effect when pure N_2 added

Better vacuum ⇒ less O !

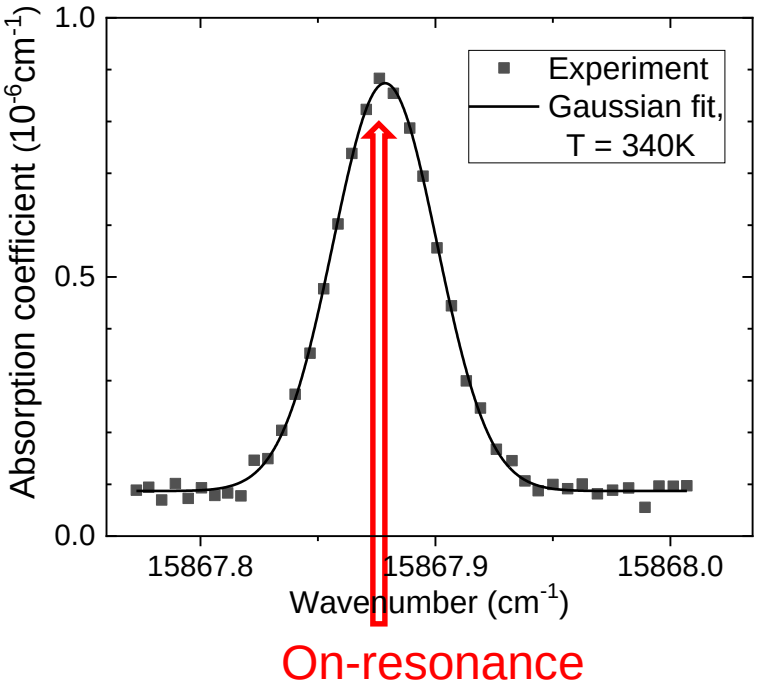
Poor reproducibility likely came from:
-different stabilisation time
-different leak rates,

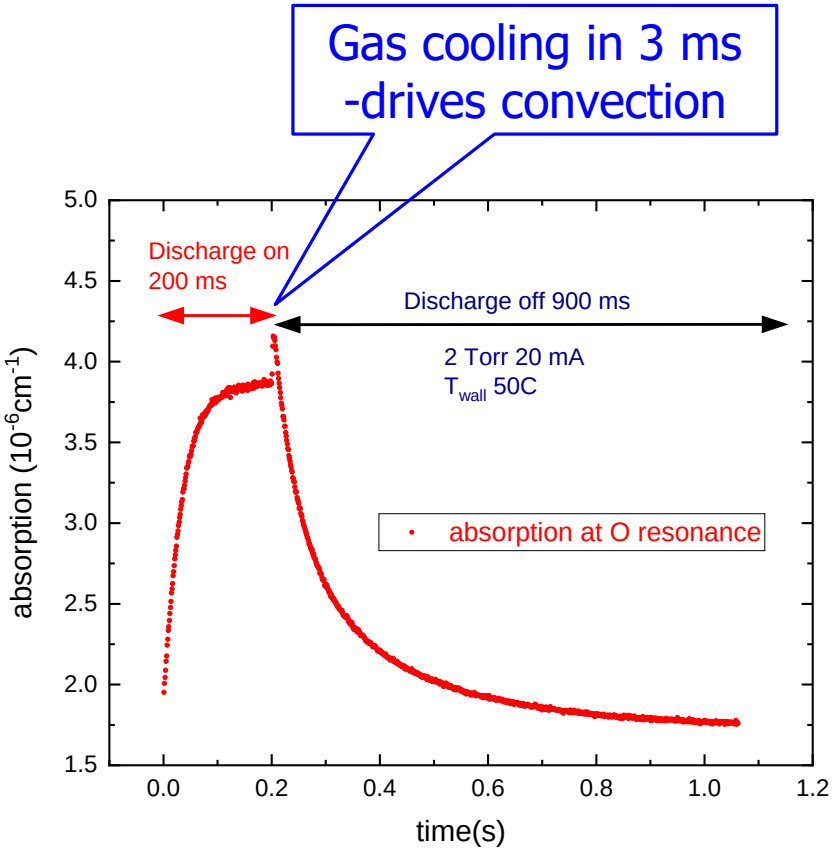
O decay in the afterglow of fully-modulated discharge: CRDS

Laboratoire de Physique des Plasmas

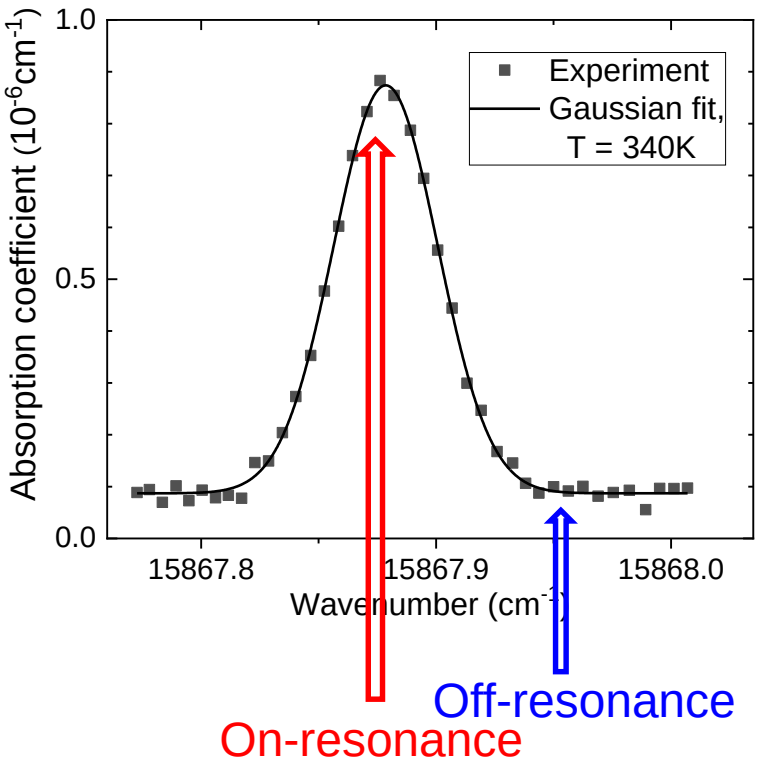
Time-resolved CRDS with 100% modulation

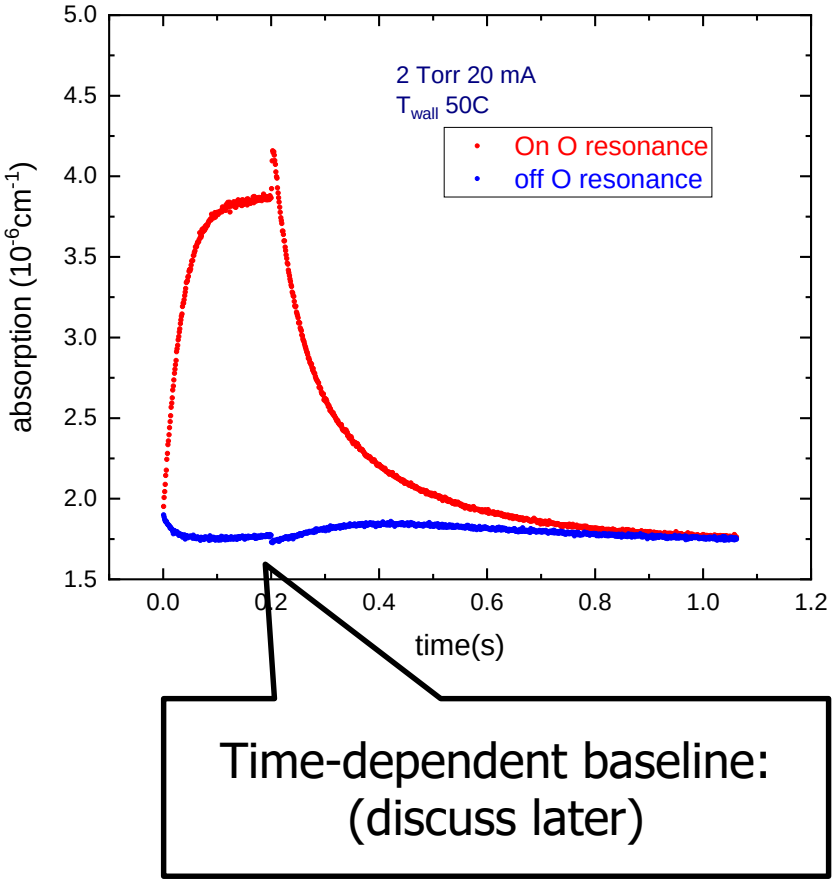
O atom kinetics are slow enough for time-resolved CRDS (~10 μs)





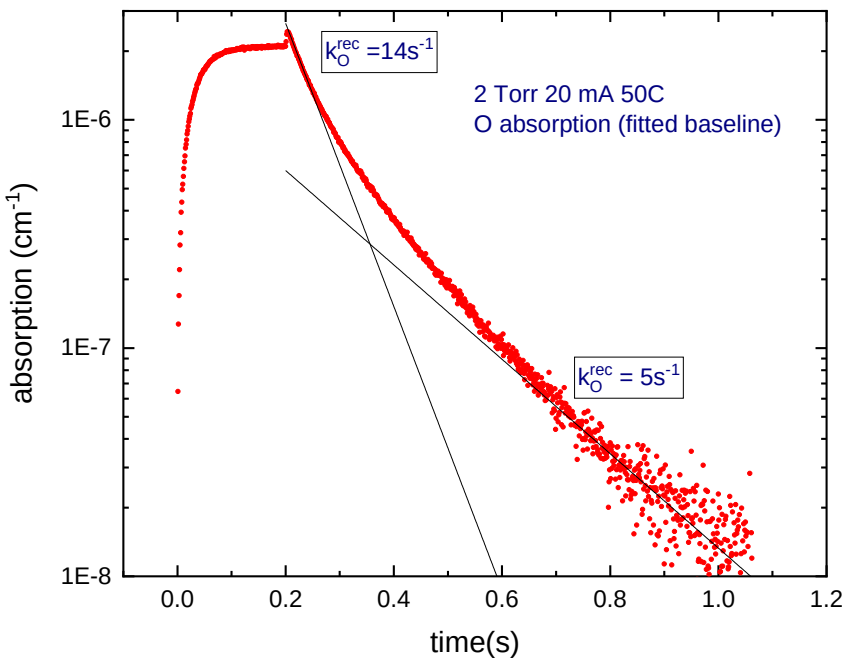
Time-resolved CRDS with 100% modulation





Time-dependent baseline:
(discuss later)

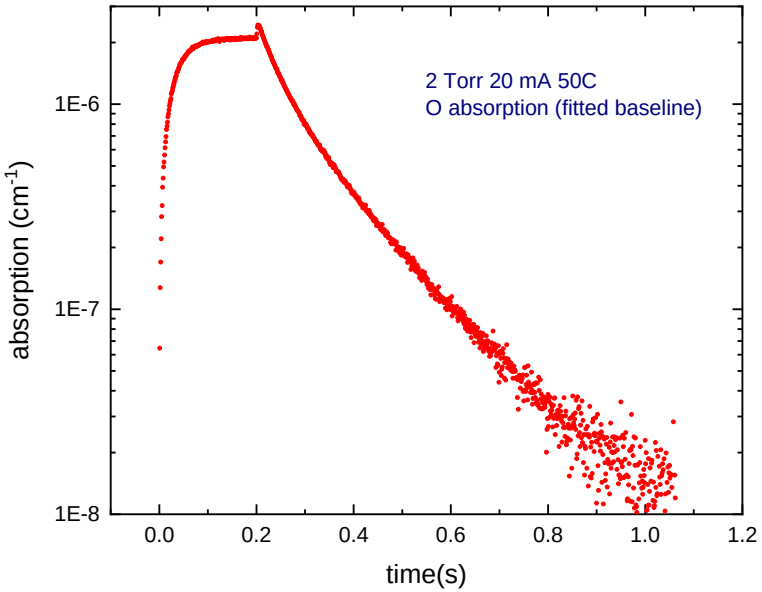
O atom decay:
with baseline subtraction:



-Non-exponential decay-

Surface reactivity slows with time

O atoms: Non-exponential decay in afterglow

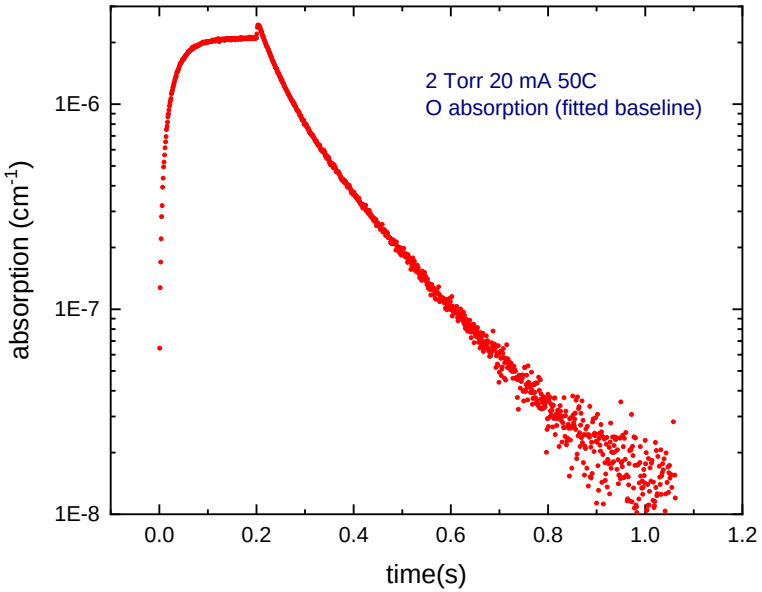


$$\frac{d[O]}{dt} = -a[O]$$

$$\Rightarrow \quad \frac{d[O]}{dt} = -(a[O] + b[O]^2)$$

Quadratic term:
Important when [O] is high,
i.e. at start of afterglow

O atoms: Non-exponential decay in afterglow



$$\frac{d[O]}{dt} = -a[O]$$

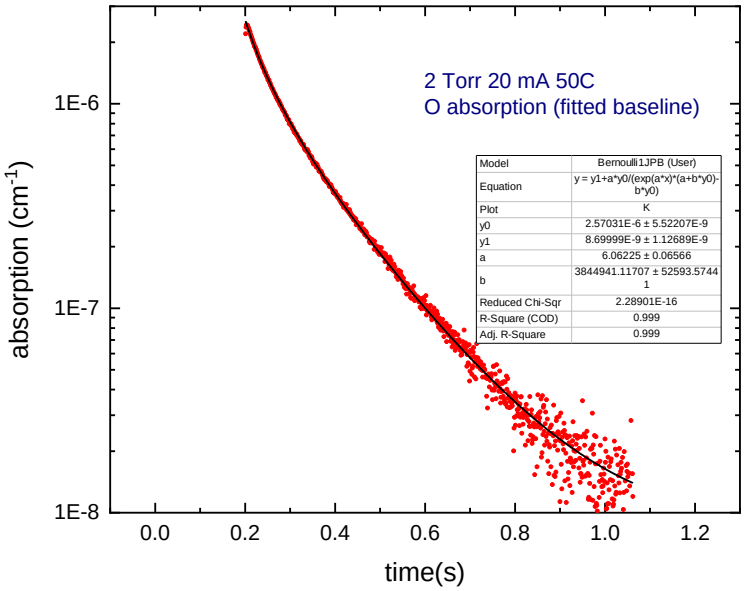
$$\Rightarrow \quad \frac{d[O]}{dt} = -(a[O] + b[O]^2)$$

Bernouilli Equation,

-has the solution:

$$O_t = \frac{aO_o}{(e^{at}(a+bO_0)-bO_0)}$$

O atoms: Non-exponential decay in afterglow



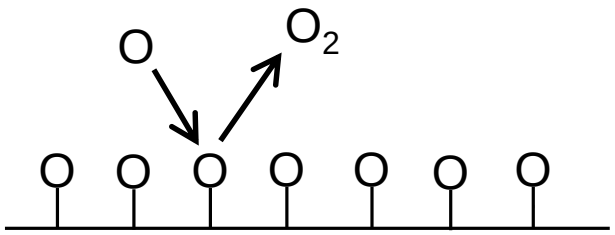
Fit the curves to obtain a and b parameters:

$$\frac{d[O]}{dt} = -(a[O] + b[O]^2)$$

Physical meaning of a and b terms?

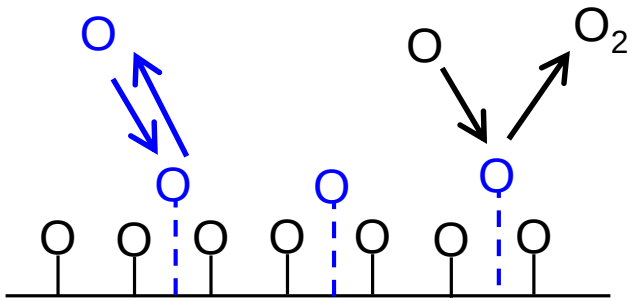
Surface reaction mechanisms

Strongly-bound (chemisorbed) O :



+

Quadratic term b:
Weakly-bound (Physisorbed) O :



No spontaneous desorption;
Saturated surface

Constant O recombination probability

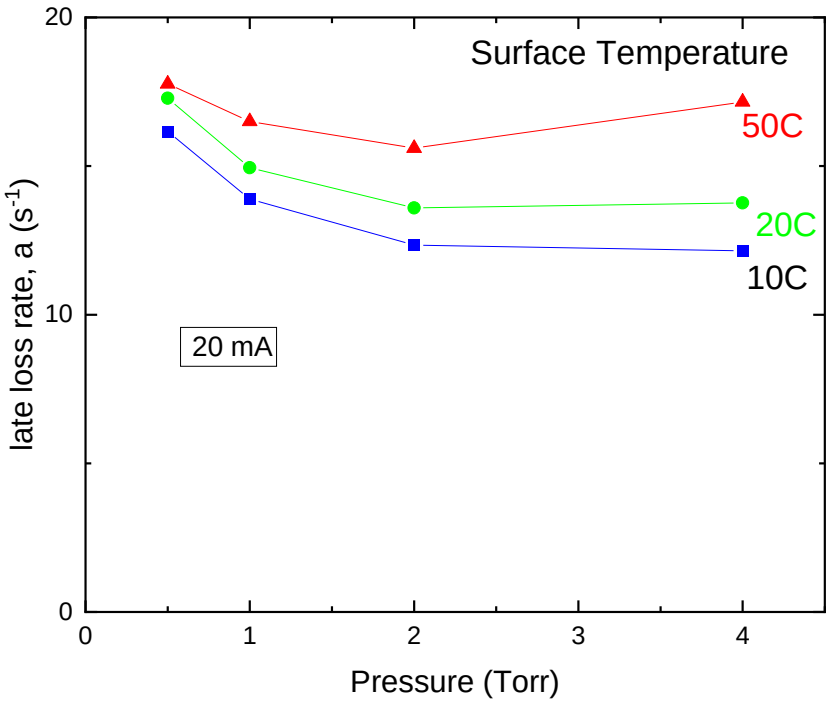
Absorption/desorption equilibrium
O recombination probability
$\propto$ Surface density $\propto$ Incident O flux

$$\frac{d[O]}{dt} = -a[O]$$

$$\frac{d[O]}{dt} = -b[O]^2$$

$$\Rightarrow \frac{d[O]}{dt} = -(a[O] + b[O]^2)$$

Fitting 2-term decay: linear component, a



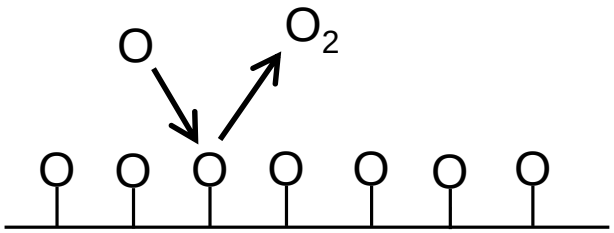
Late decay rate (a):

-*increases with surface temperature*

→fits Eley-Rideal model with activation energy for reaction

-*slight decrease with pressure:*

O_2 blocks reaction sites?

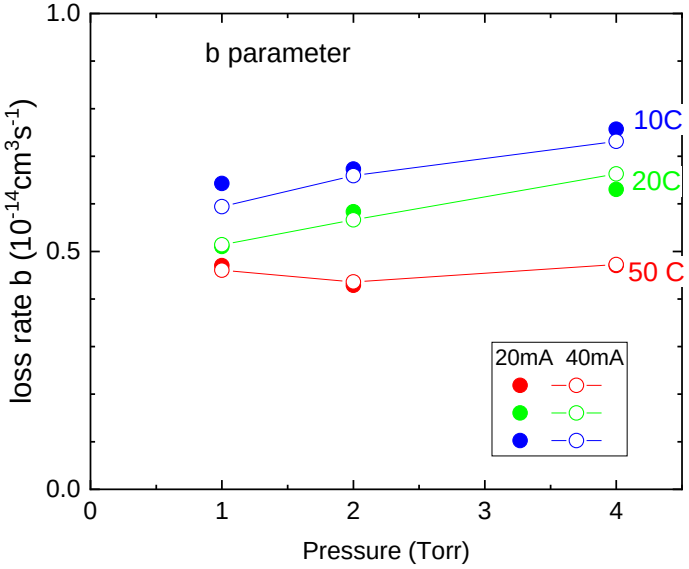


Note : the a parameter changes with air leak, tube conditioning time

→ Consistent with blocking of chemisorption sites

→ Origin of drift in [O]

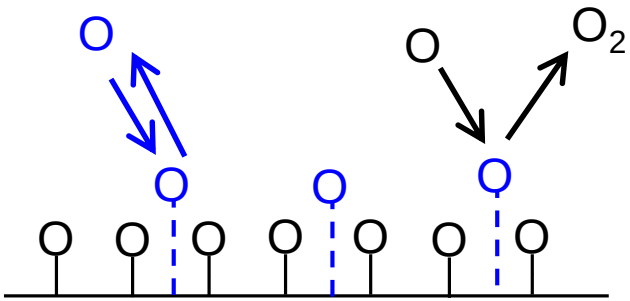
Fitting 2-term decay quadratic component, b



Quadratic (b) parameter:

-*decreases at high temperature*

→agrees with physisorbed atom model (surface coverage of weakly-bonded O decreases)

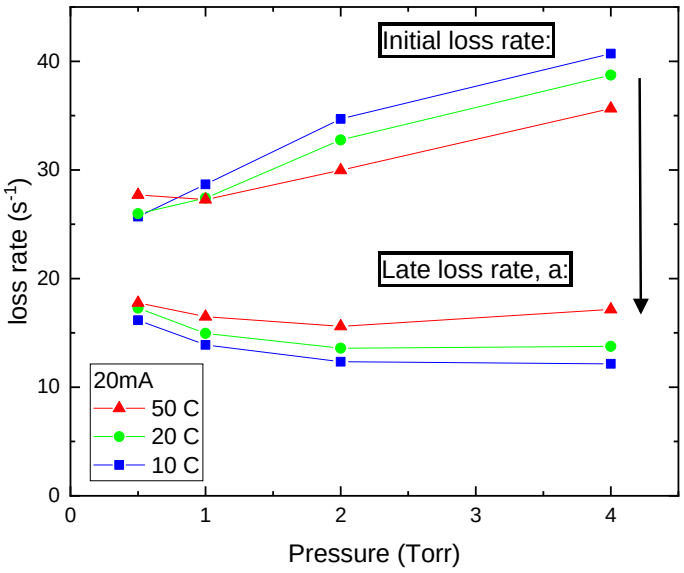


Note:

→ b parameter does not correlate with air leaks, drift etc

→ Weakly bonded sites NOT affected by site blocking

Initial and final decay rates



Initial decay rate:

$k_{init} = a + b[O]_0$

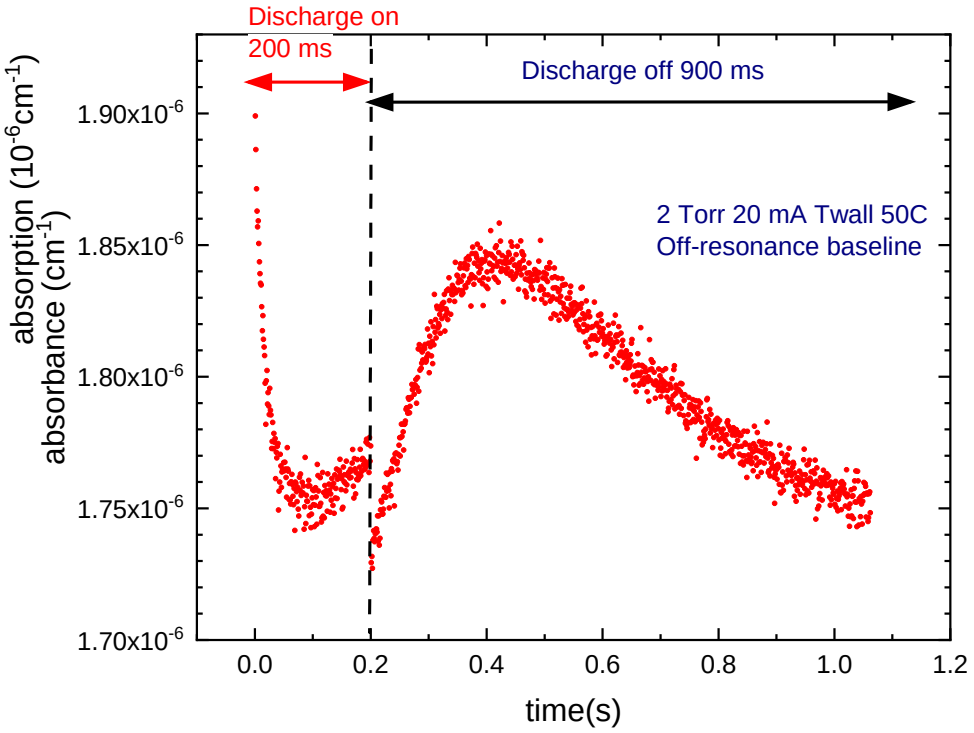
This is the effective rate in the active plasma

(≈ rate measured by partial modulation)

Much faster than final rate (a) :

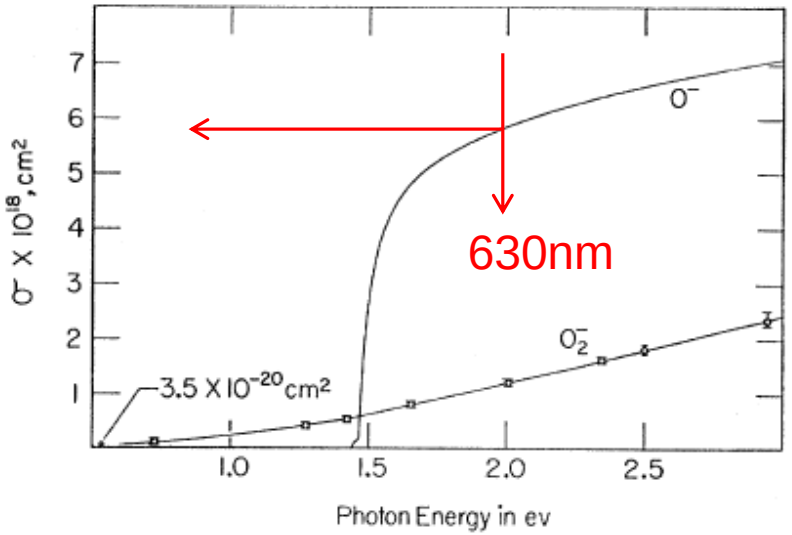
Fitting single exponential to late afterglow data can lead to significant errors!

Origin of time-dependent baseline?



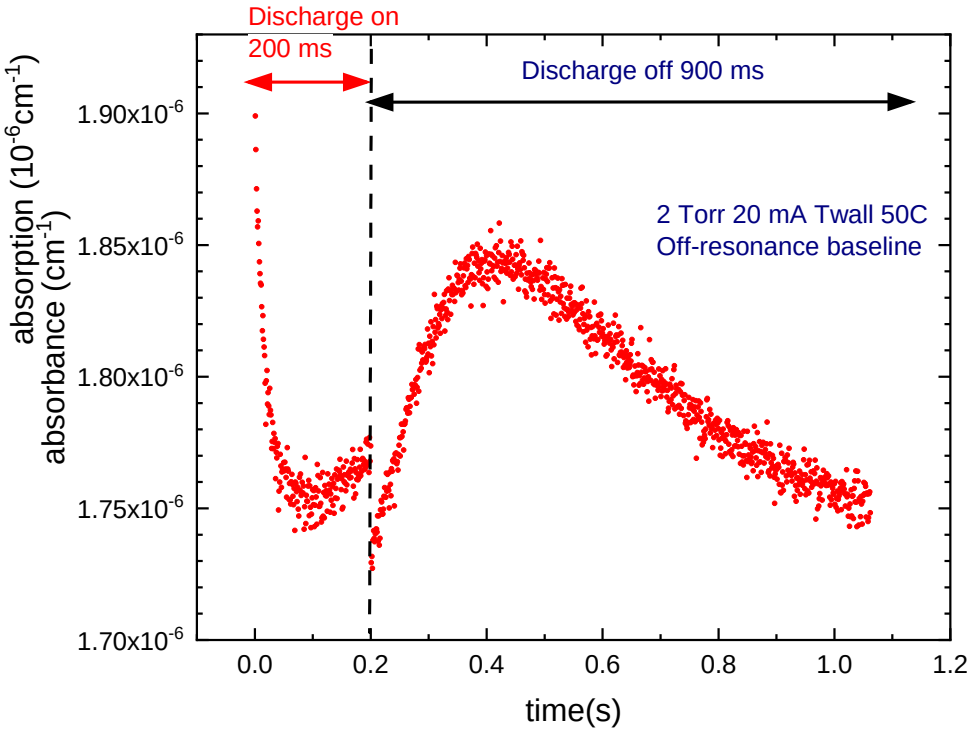
Complex time-behaviour
What else absorbs in this spectral region?

O^- photo-detachment continuum

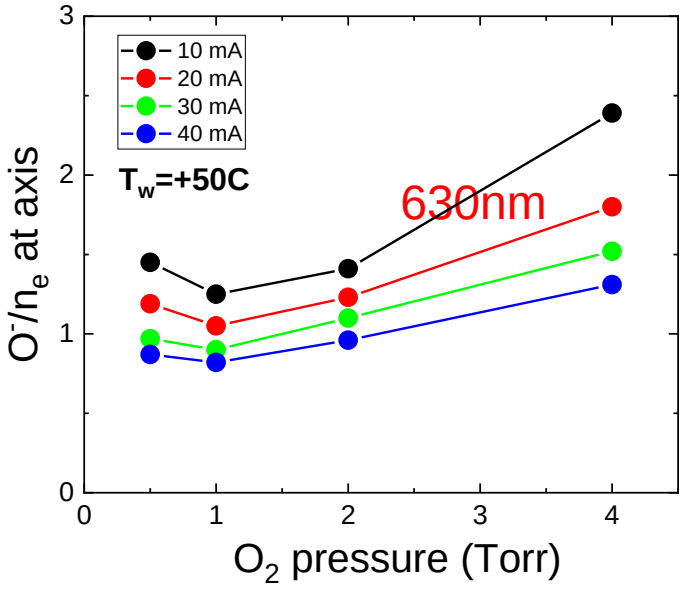


$\sigma = 5.8\text{x}10^{-18}\text{cm}^2$ @ 630nm

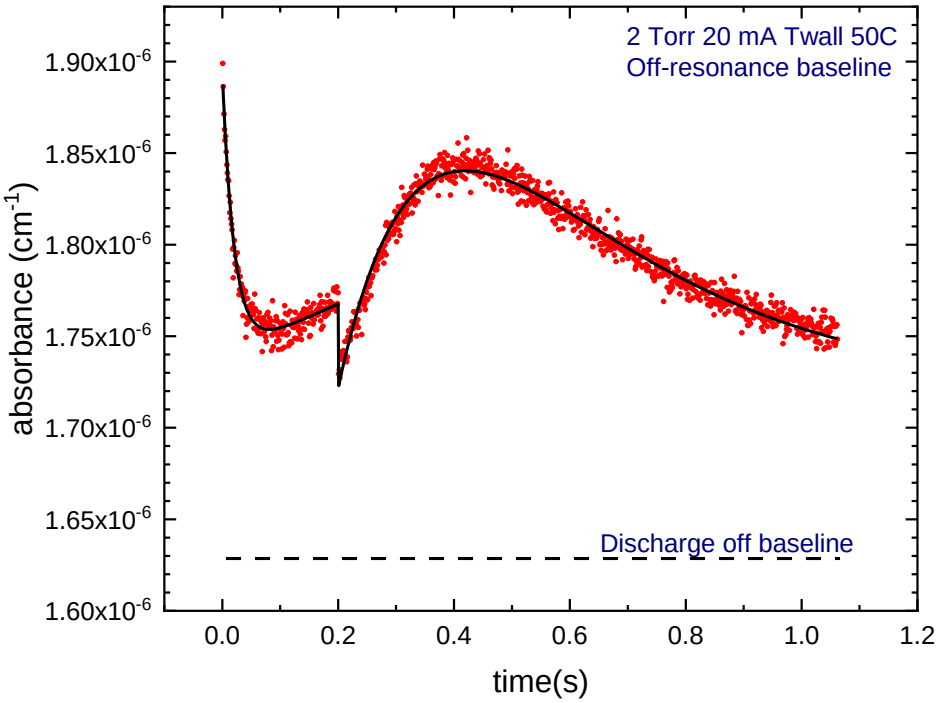
Origin of time-dependent baseline?



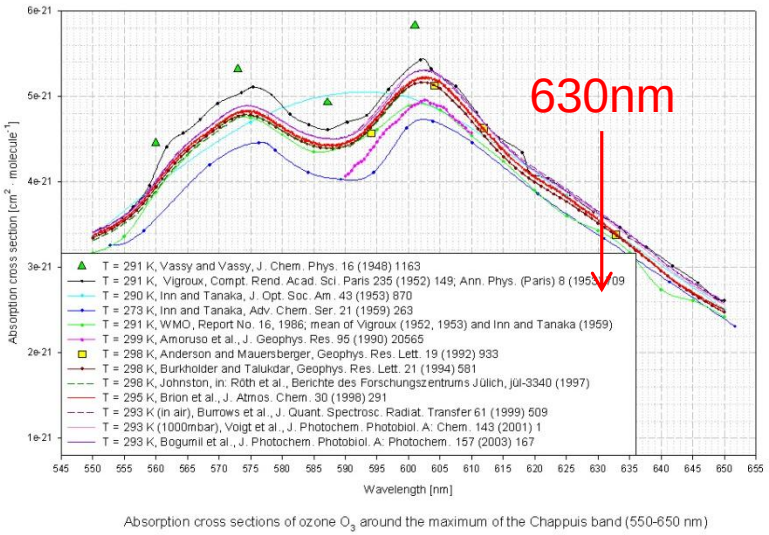
Determine negative ion density directly:



Late afterglow



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

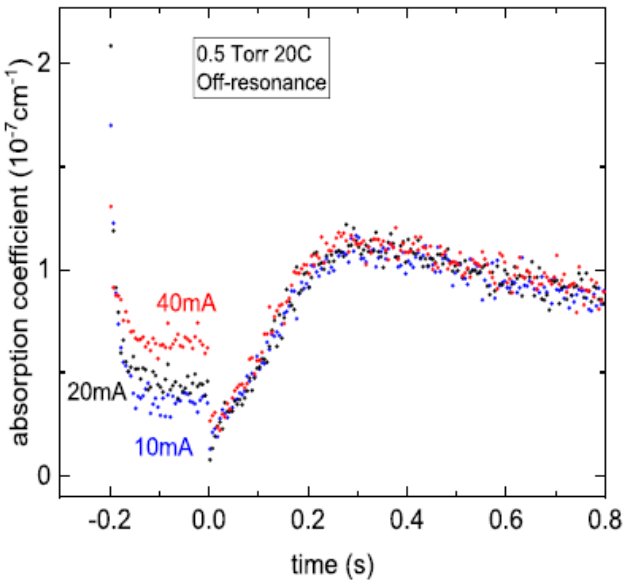
Ozone builds up in the afterglow:

$O + O_2 \rightarrow O_{3(v)}$

$O_{3(v)} + M \rightarrow O_3 + M$?

Not so simple:

Ozone generation at low pressure



Ozone creation independent of
Discharge current/ O density

Density 3x that predicted by O + O_2 +M rate

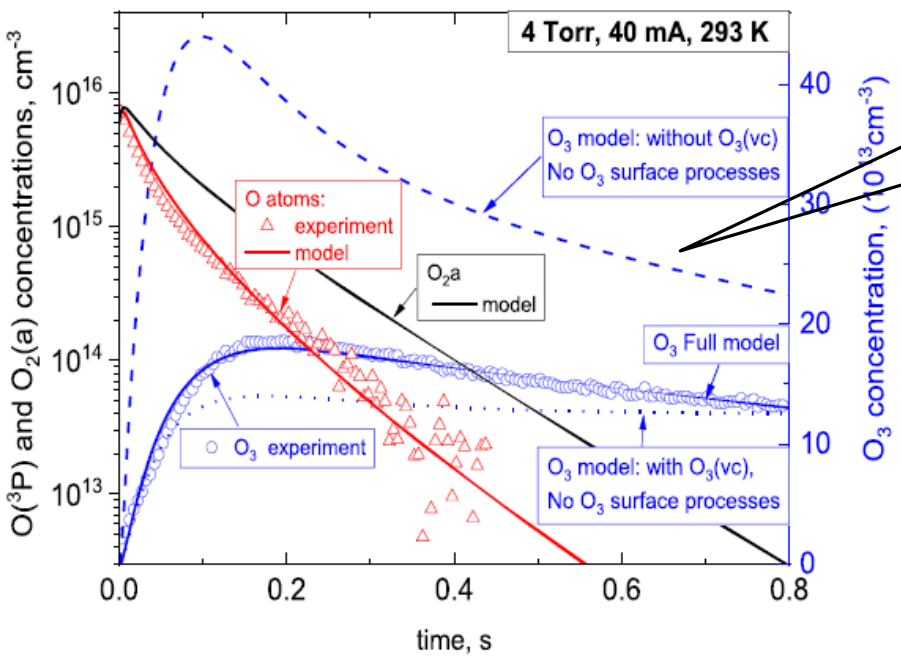
⇒Surface production mechanism:

$$O_{surface} + O_2 \rightarrow O_3 \uparrow$$

Agrees with Viegas 2024 model, but :

peak O_3 density only represents about 1% of steady-state O density (minor loss path)

Ozone in the afterglow at high pressure



O_3 production significantly smaller than predicted

$O + O_2 \rightarrow O_{3(v)}$

$O_{3(v)} + M \rightarrow O_3 + M$

But also: $O_{3(v)} + O \rightarrow 2O_2$

$O_{3(v)} + O_2\ ^1\Delta_g \rightarrow 2O_2 + O$

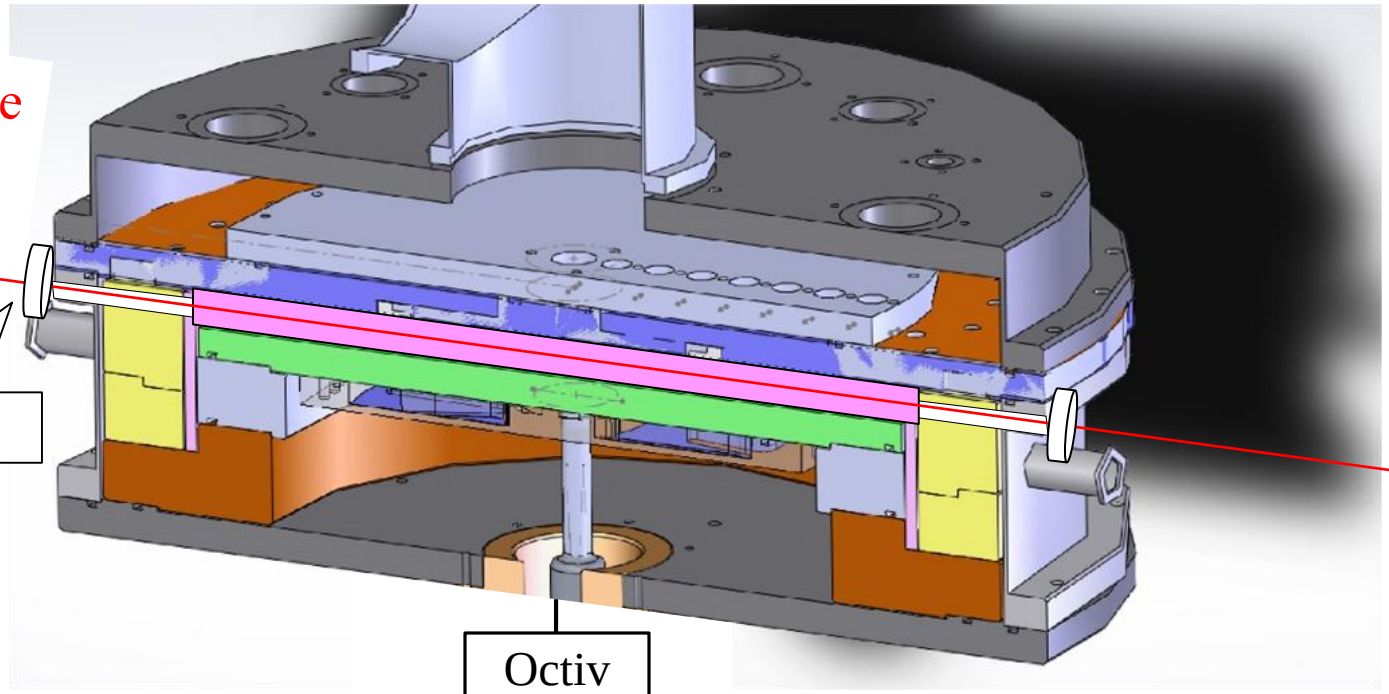
Vibrationally-resolved O_3 reaction/VT model:
Booth et al. PSST **32** (2023) 095016

What about RF reactors?

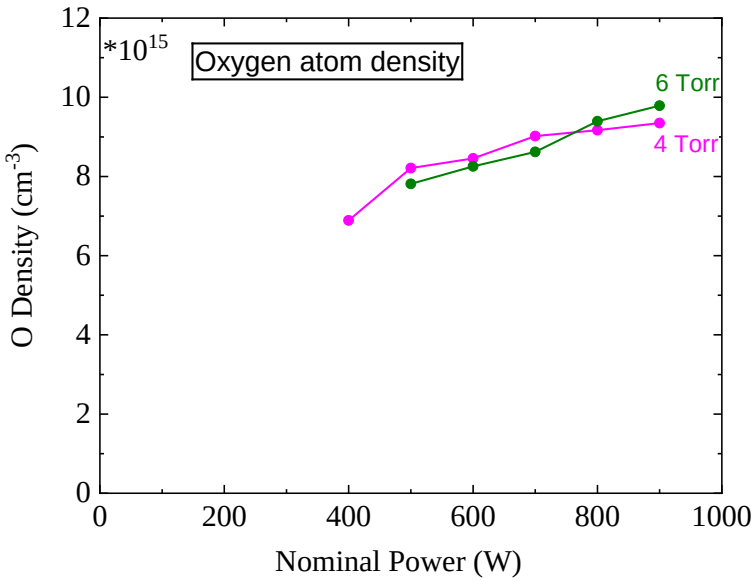
1) RF CCP at intermediate pressures (0.5-6 Torr), (oxidised) Al surfaces

2) RF ICP 5-100mTorr, Al_2O_3 surfaces

Oxygen recombination in an RF-CCP at intermediate (1-6 Torr) pressure



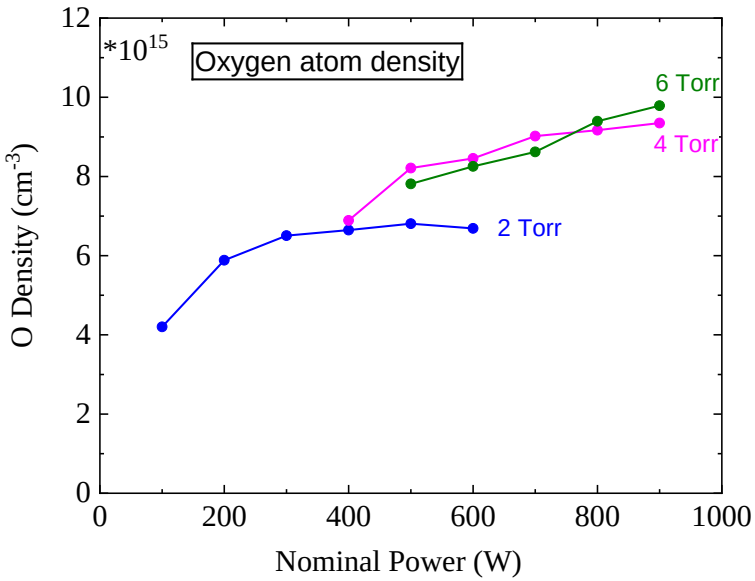
O Density vs power and pressure



6 Torr: Slow increase with power

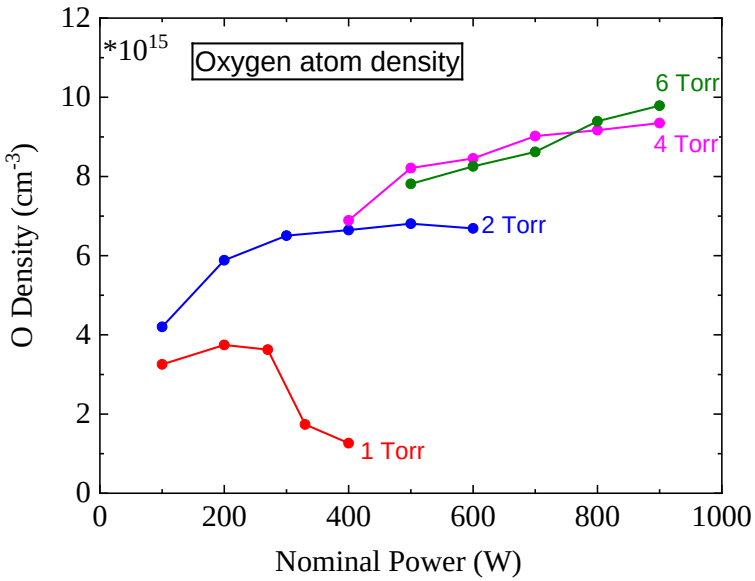
4 Torr .....

O Density vs power and pressure



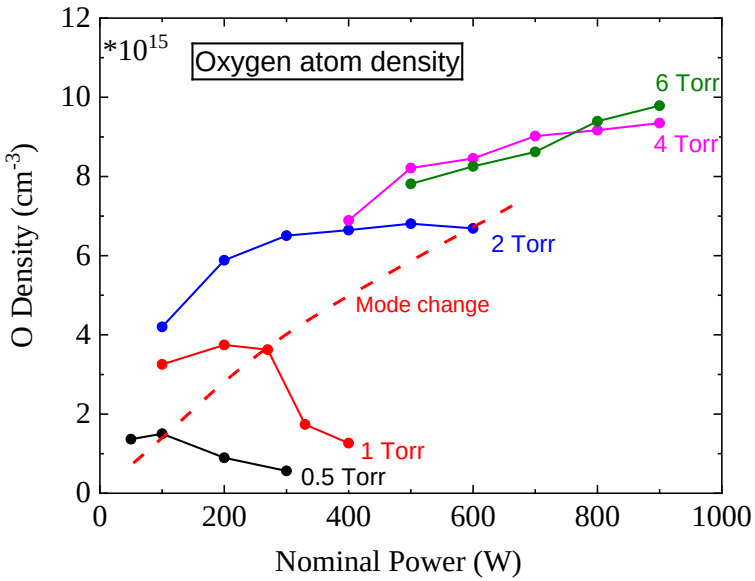
4-6 Torr: Increases with power
2 Torr - saturates

O Density vs power and pressure



4-6 Torr: Increases with power
2 Torr – saturates
1 Torr – passes maximum

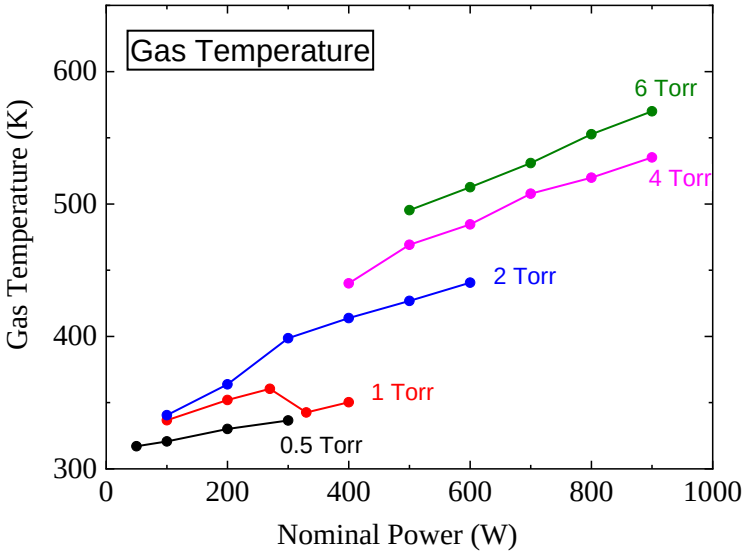
O Density vs power and pressure



4-6 Torr- Increases with power
2 Torr – saturates
1 Torr – passes maximum
0.5 Torr -……

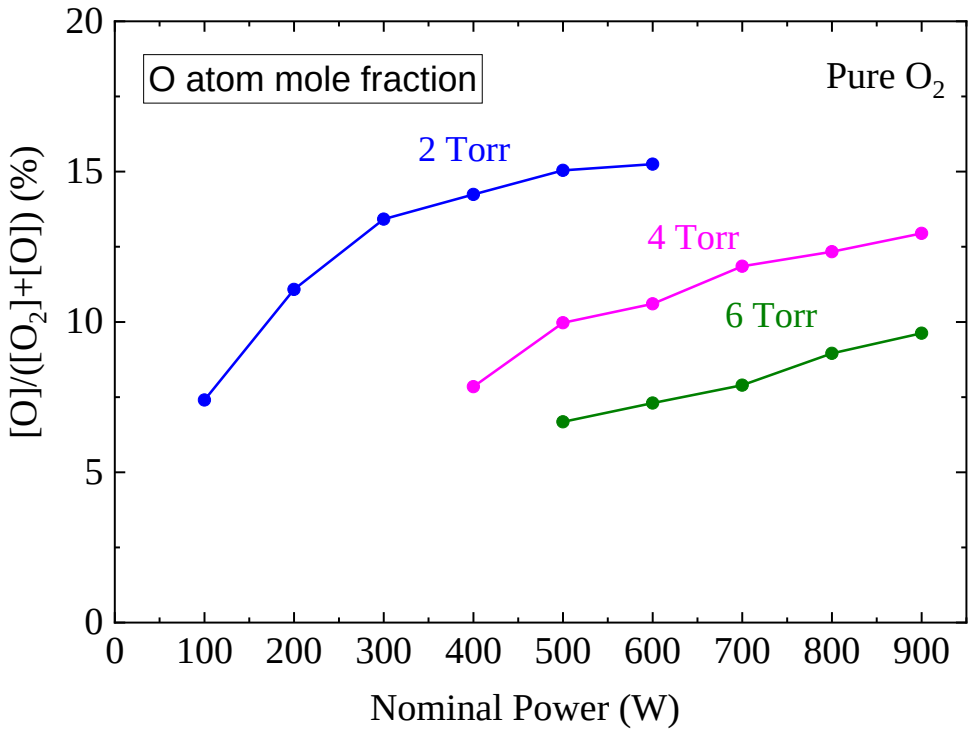
Apparent mode change:
Occurs at higher power for higher pressure
-Decreased production?
-Increased surface loss?

Gas Temperature



Increases with power and pressure

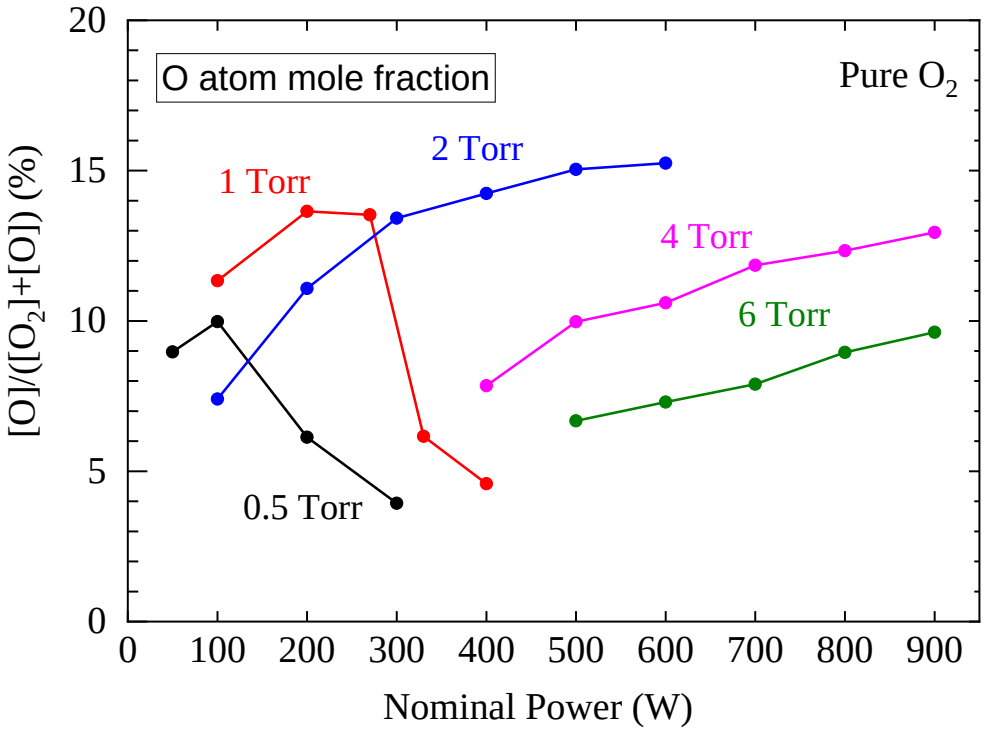
Oxygen atom mole fraction



Up to 15% even for low power density (0.1 -0.4 W/cm^2)

Saturates above 2 Torr
-more power lost in gas heating

Oxygen atom mole fraction



Up to 15% even for low power density (0.1 -0.4 W/cm^2)

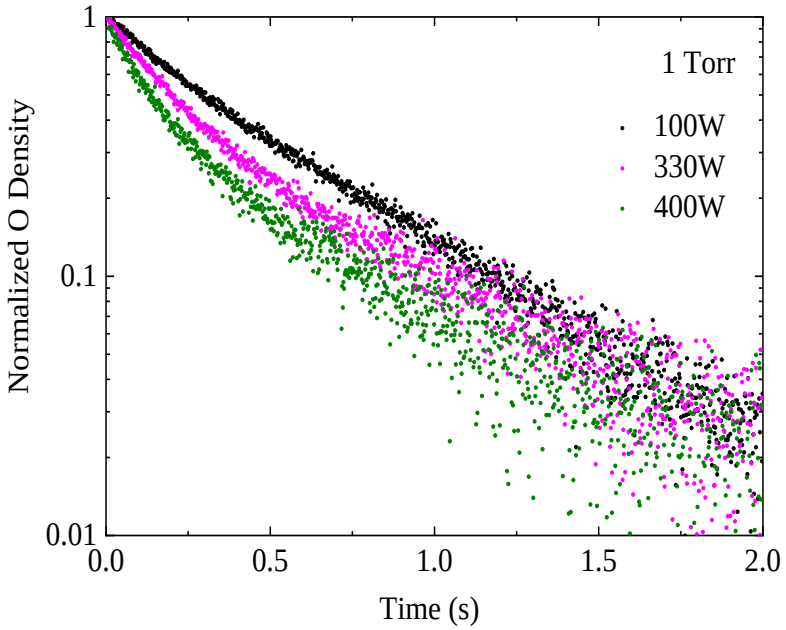
Decreases above 2 Torr
-more power lost in gas heating

Oxygen atom balance:

$$\frac{[O]}{[O_2]} = \frac{2.k_d.n_e}{k_{loss}^O}$$

What is driving the trends?

O atom decay in Afterglow



1 Torr O_2

RF Power	$k_{init}^{O}(s^{-1})$	γ (10^{-4})
100	1.8	1.5
200	4.3	3.2
300	5.7	4.2

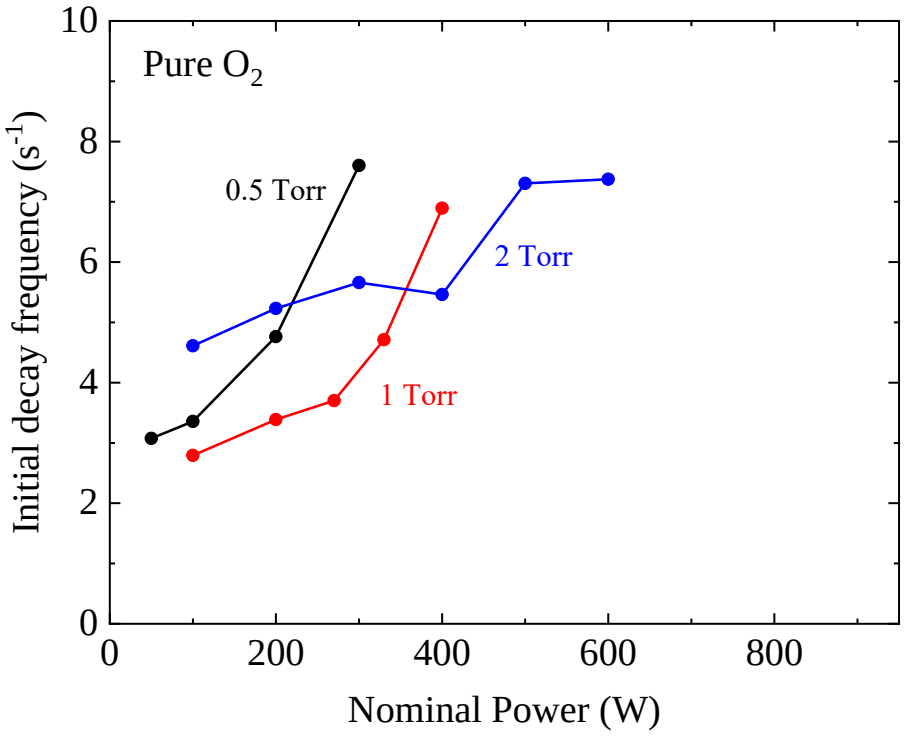
Note : non-exponential decays, but increased initial rate $\Rightarrow$ lower [O]…

$\Rightarrow$ NOT quadratic surface mechanism we saw in glass tube

Increasing flux and energy of ion bombardment

$\Rightarrow$ **Increased surface reactivity**

O atoms in afterglow: initial decay rate



(above 2 Torr gas-phase processes become important)

At low pressure :
Strong increase with power

Ion-induced increase in surface reactivity

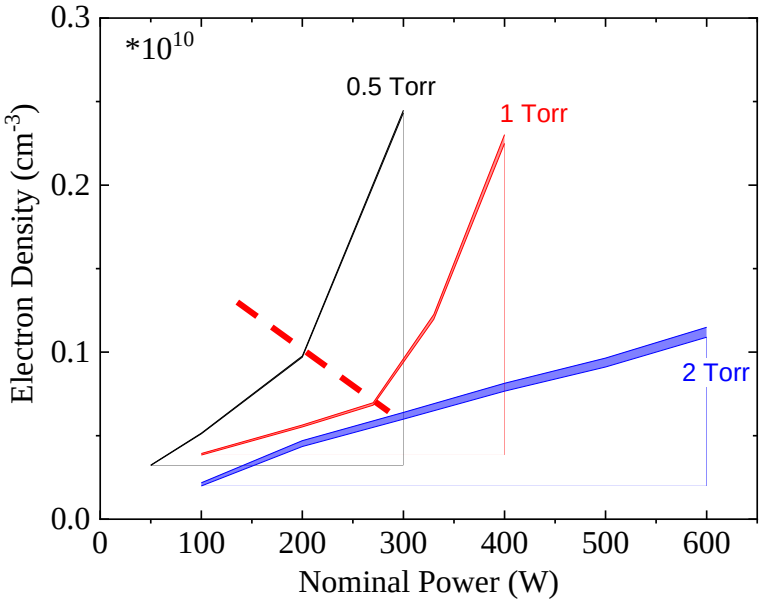
If we assume:

$$k_{loss}^{O} \approx k_{init}^{O}$$

Correlates with drop in [O] with power

But is this the whole story?
How does the electron density change?

Electron Density : Microwave hairpin probe (for ≤ 2 Torr)



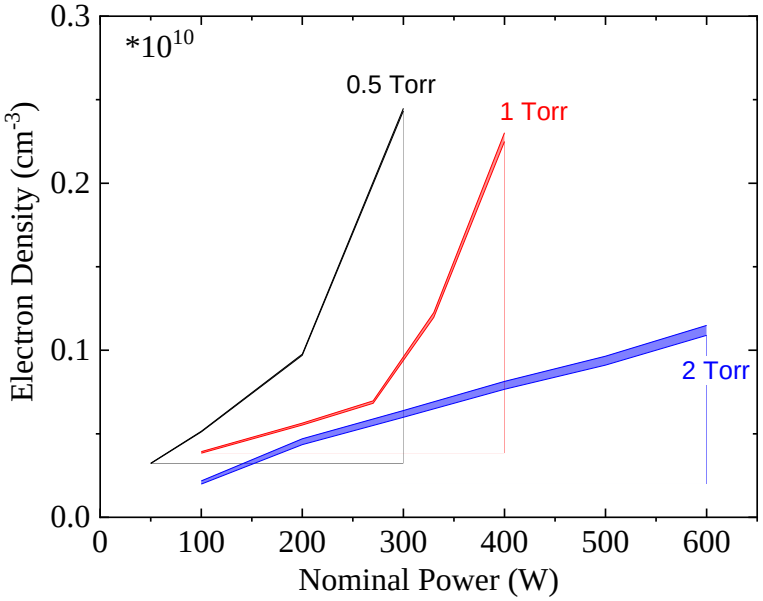
- Increases with power
- Decrease with pressure
- Sharp rise at 0.5 and 1 Torr

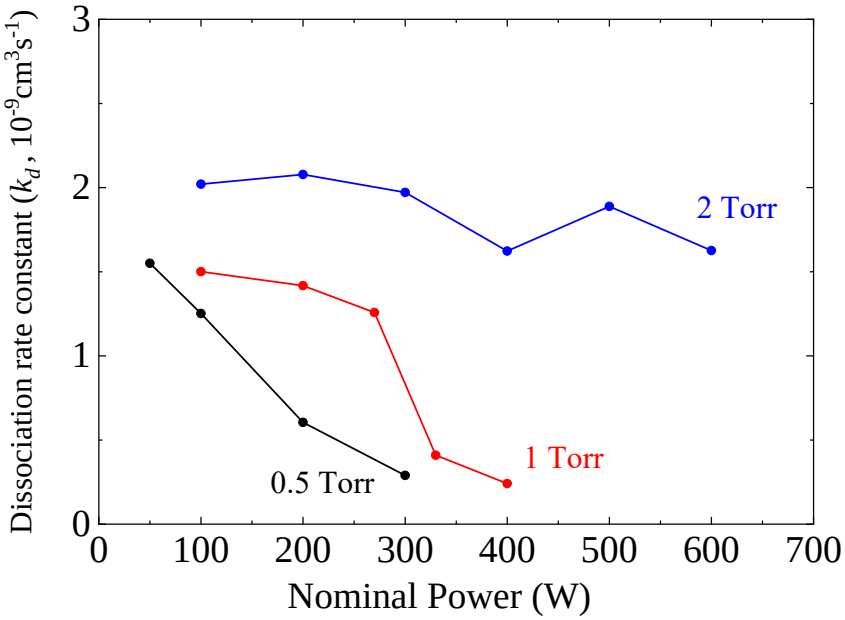
This increase of electron density should cause increased O_2 dissociation….

Estimate the dissociation rate constant:

$$k_d(EEDF) = \frac{[O].k_{loss}^{O}}{[O_2].2.n_e.}$$

O_2 dissociation rate vs pressure and power





$k_d(EEDF) \approx$ constant at 2 Torr

Sharp drop at :

1 Torr 270W ($240V_{rms}$)

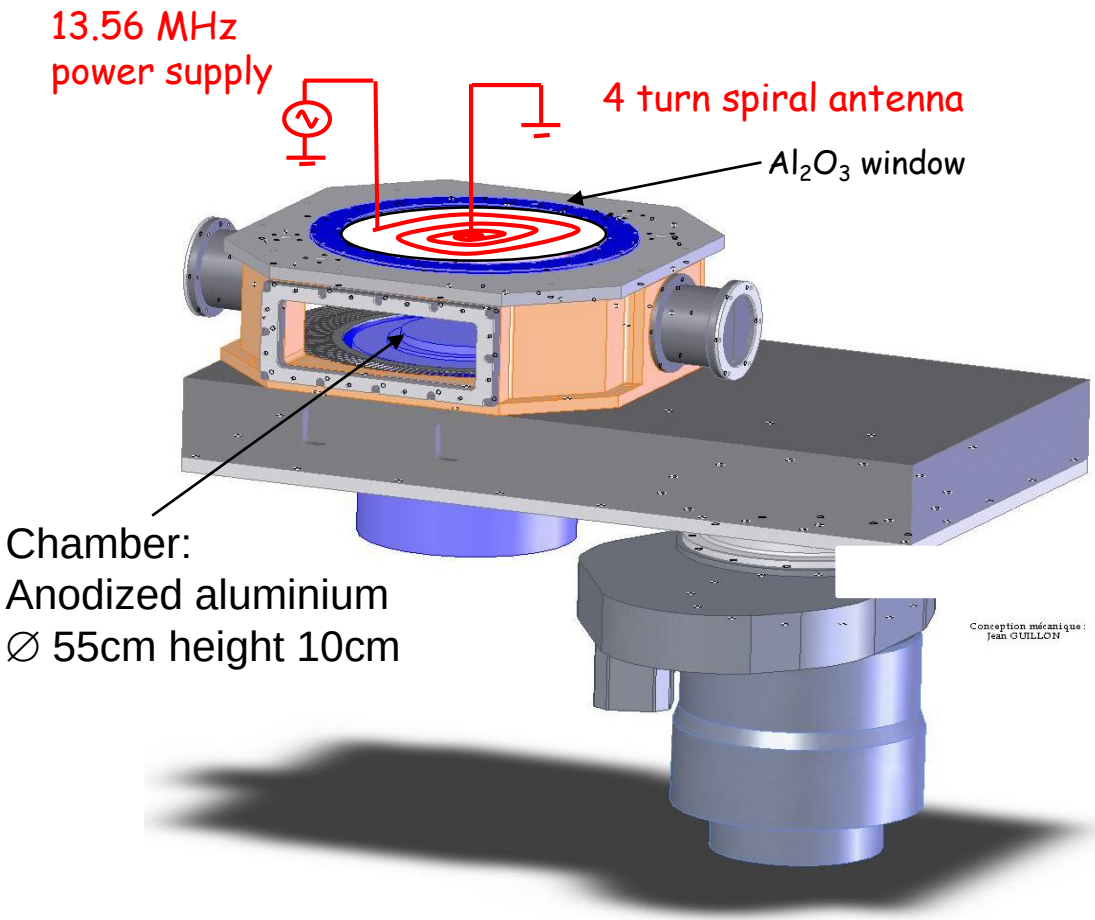
0.5 Torr 100W ($200V_{rms}$)

Low density/high Te →High density low Te

Alpha→Gamma transition?

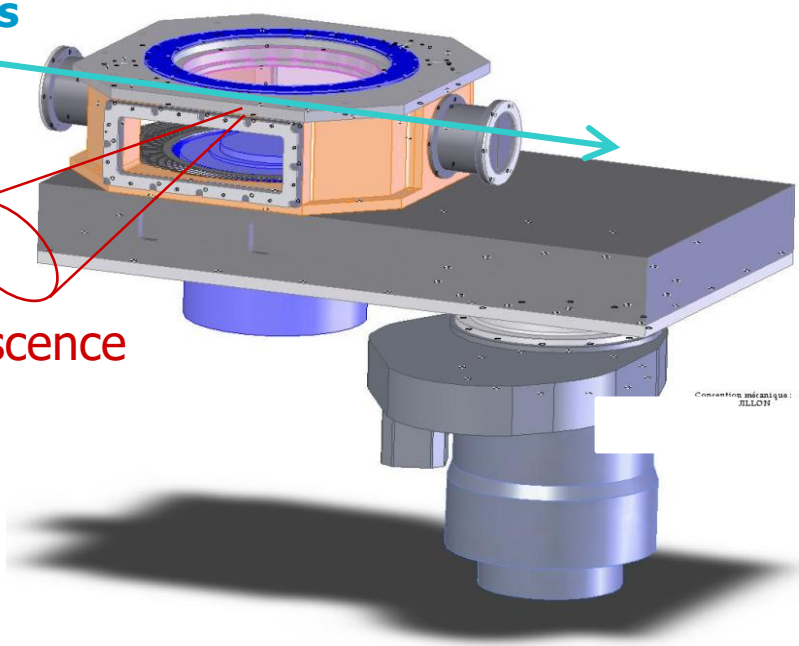
What about much lower pressures?

Inductively coupled plasma
Oxygen 1-100mTorr

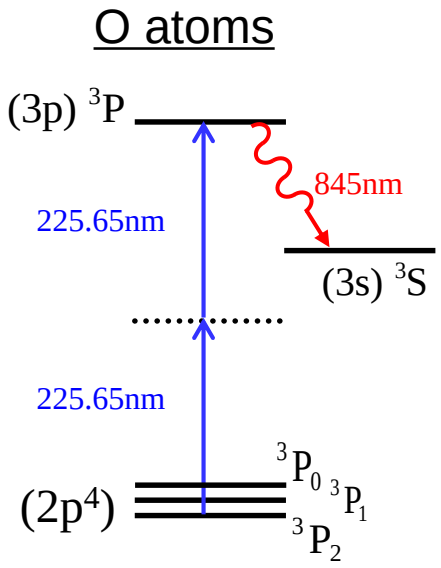


Measuring O atom decay by Two-photon Laser induced fluorescence

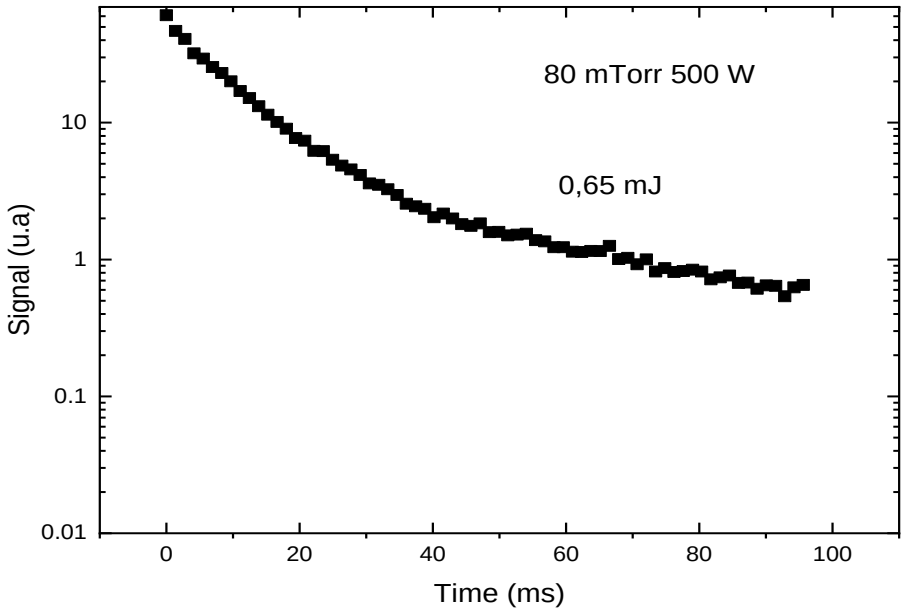
Pulsed
UV laser
1 mJ, 5ns



Fluorescence



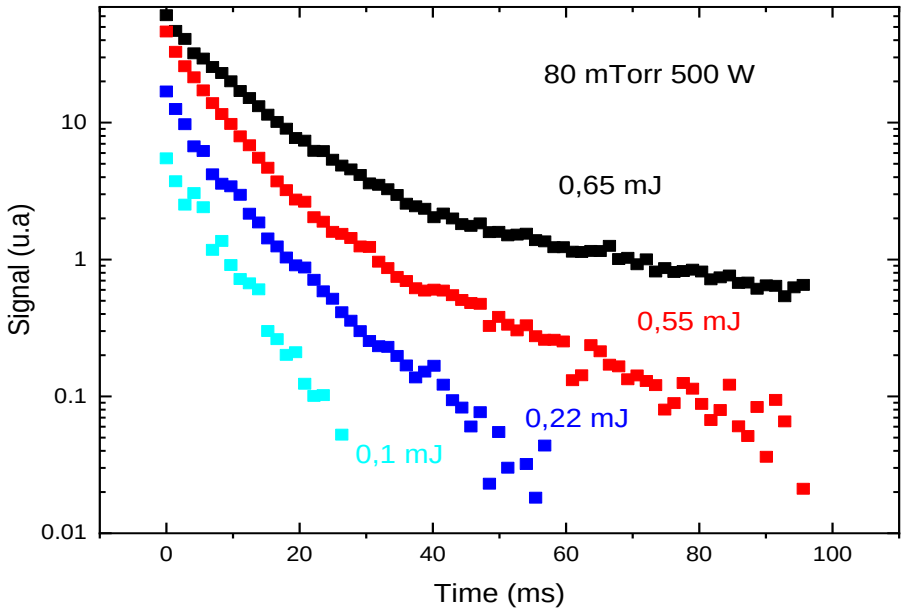
Oxygen recombination in an ICP
O decay by TALIF



Non exponential decay…

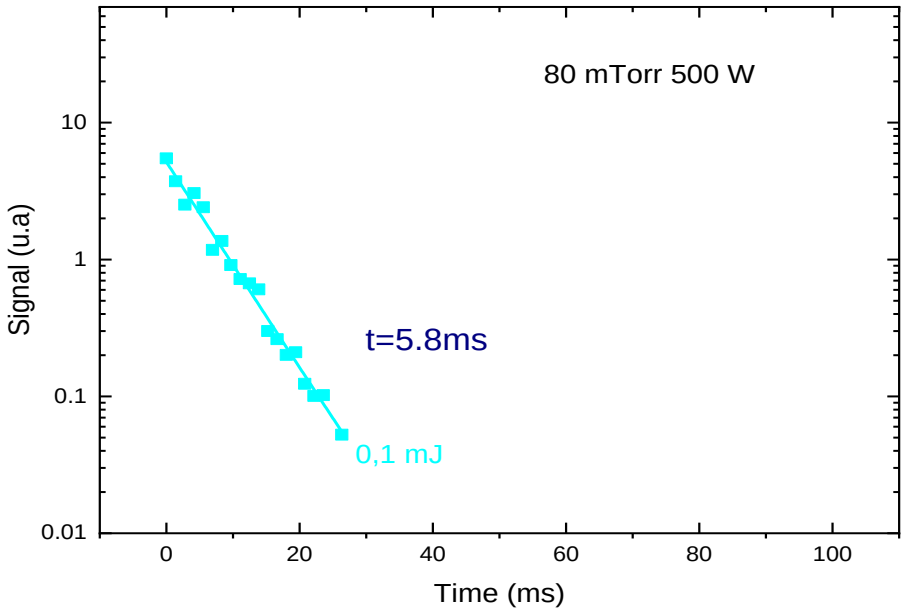
But if we decrease the laser power:

Oxygen recombination in an ICP
O decay by TALIF :Effect of laser energy



O atoms produced by photolysis of O_2 (v) ?

Oxygen recombination in an ICP
O decay by TALIF :Effect of laser energy



τ = 5.8ms

$\rightarrow \gamma = 0.084$

Two orders of magnitude bigger than high-pressure DC glow or RF CCP (surface = Al_2O_3)

Much higher ion flux/ neutral flux ratio

Surface recombination rate increases dramatically as pressure is reduced

Conclusions

Surface recombination is much more complex than simple constant γ

<u>O atoms on glass or Al_2O_3 :</u>

At higher pressures (<1 Torr)

- γ is small (< 10^{-3}), may depend on surface history..
- Depends on surface and gas temperature, fluxes of particles
- additional quadratic term appears for high O flux

At low-pressure/high plasma density:

- γ much higher (0.1 vs 10^{-3})
- influence of energetic ion bombardment (especially Ar^+)

Closely coupled Experiment and Simulation/theory approach is essential

- plasma, gas phase and surface chemistry needed
- This is a still a work in progress!

Acknowledgements

- Applied Materials
- Comet Plasma Control Technologies
- Federation Plas@par
- China Scholarship Council