



Cold Atmospheric Plasmas in interactions with materials and liquids for biological applications

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Cold Atmospheric Plasmas in interactions with materials and liquids for biological applications

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In collaboration with: B Held¹, K Gazeli¹, L Marlin¹, E Morel¹, F Girard¹, S Blanc¹, B Grassl¹, S Reynaud¹, P Marcasuzaa¹, C Veclin¹, I Lebouachera¹, F Léonardi¹, Q Hoqui¹, C Nardin¹, X Callies¹, S Arbault², V Badets², P Lefrançois², N Sojic²

¹ *Pau University – IPREM UPPA, France*

² *Univ. Bordeaux, ISM, CNRS UMR 5255, INP Bordeaux, 33400 Talence, France*



Tuesday, July 23, 2019, 11h50-12h30

Québec City Convention Centre
1000, boulevard René-Lévesque Est
Québec QC G1R 5T8
Canada

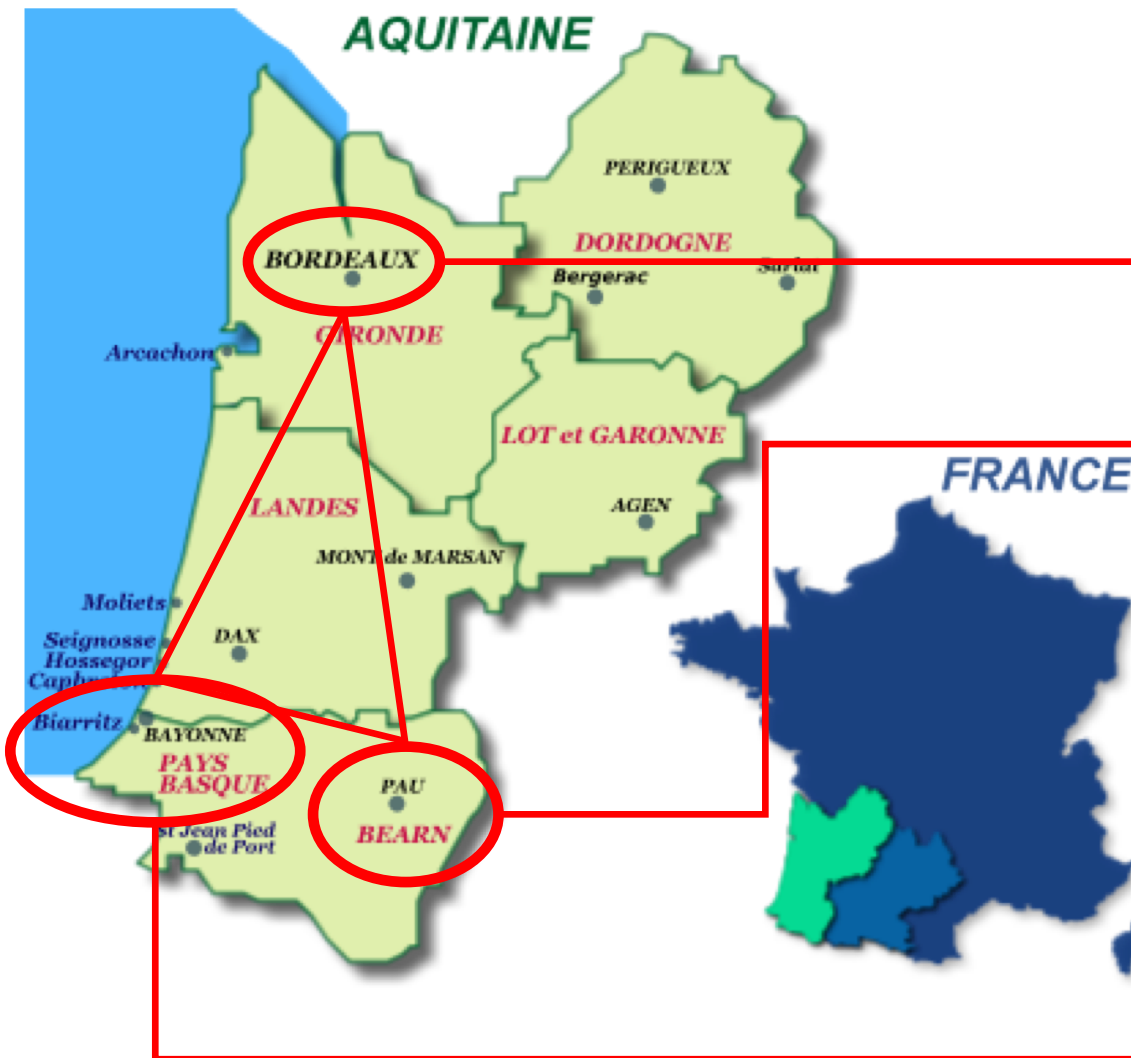


Univ Bordeaux, ENSCBP

Very nice environments



Wines libraries



UPPA – IPREM, Pau



béarnaise

Specialties: GARBURES

basque



UPPA – site Côte basque, Montauray



Why speaking about GARBURES ?

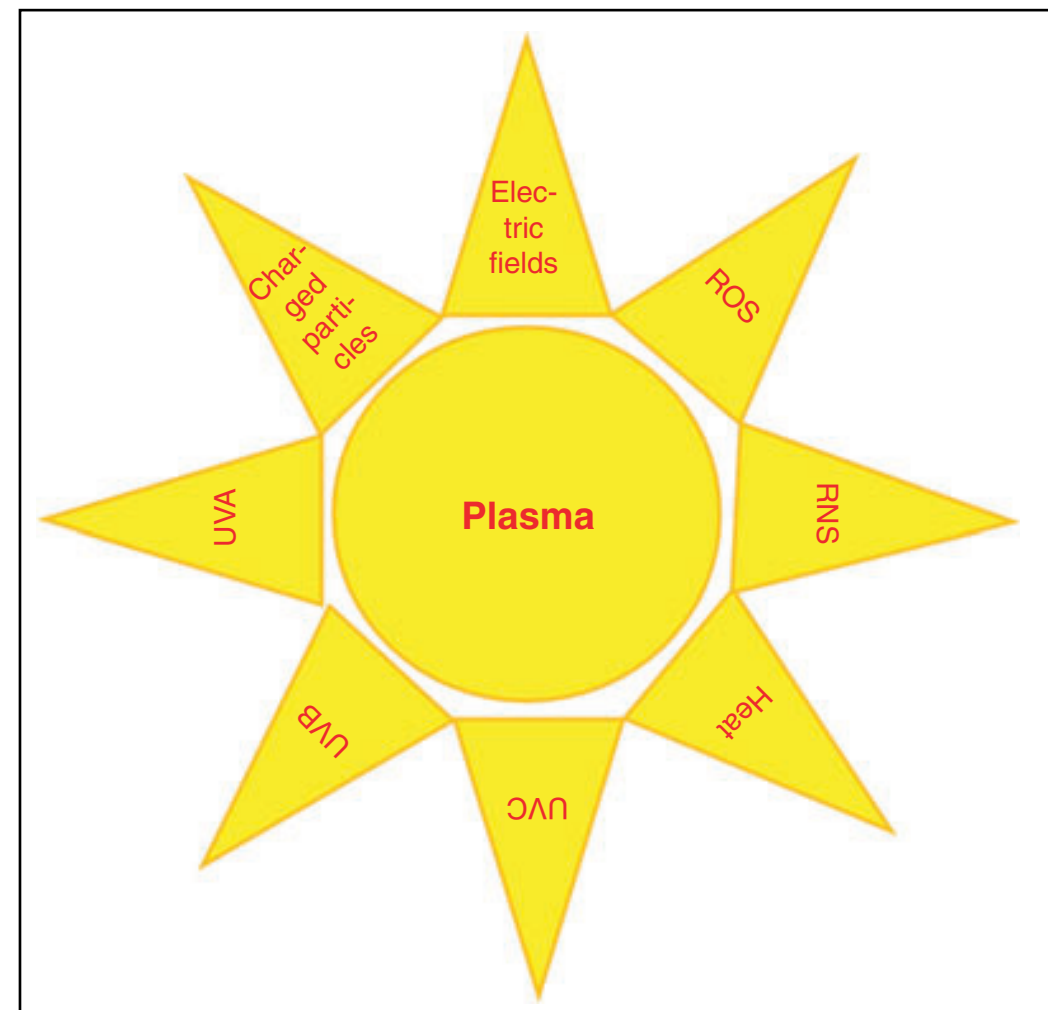


a bit like ...

Plasma Components:

- Neutral particles
- Electrons and Ions
- Electric fields
- Excited Particles: radiative and metastable, radicals, ROS, RNS
- Photons (UV, Visible, IR)

Because GARBURES contains **numerous energy components:** different vegetables (potatoes, pumpkin, leek, turnip, onion, tomato, ...) and different meat (pork, duck, ...)



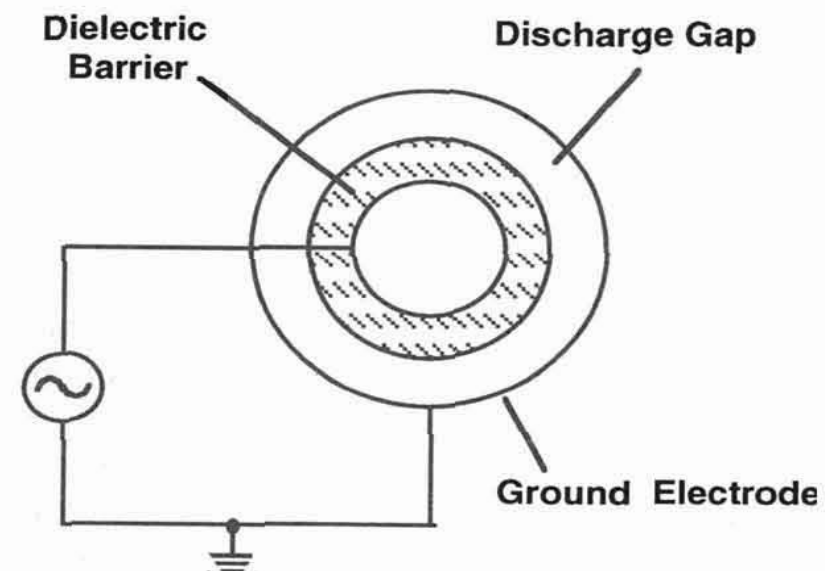
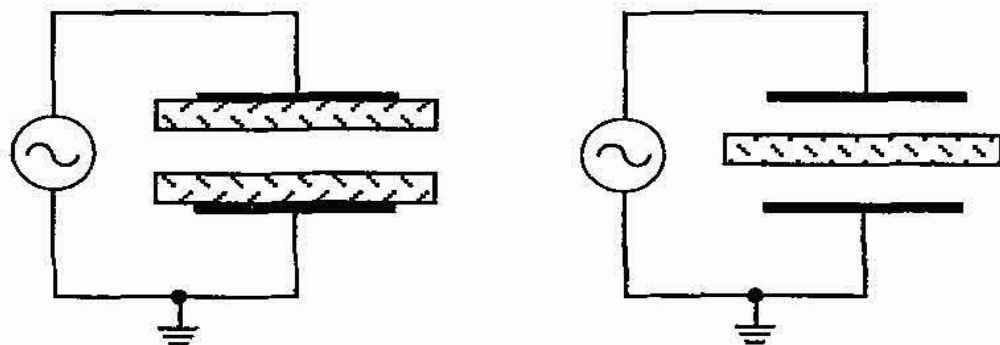
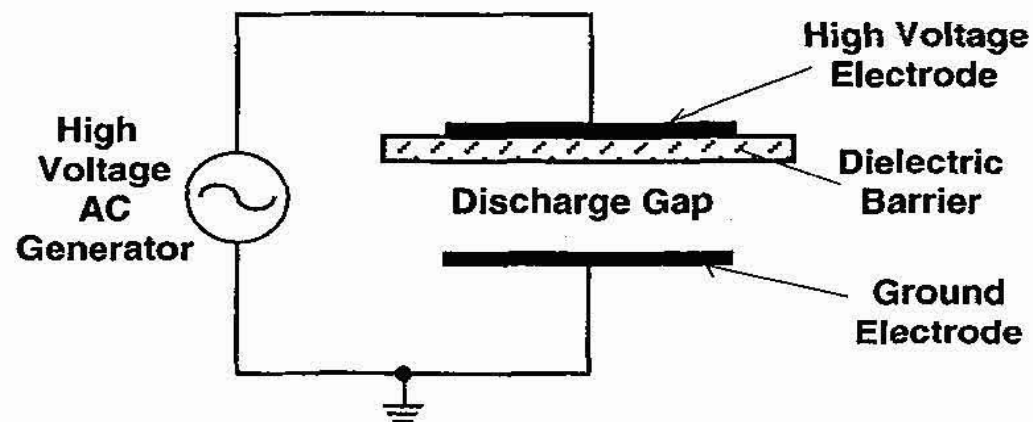
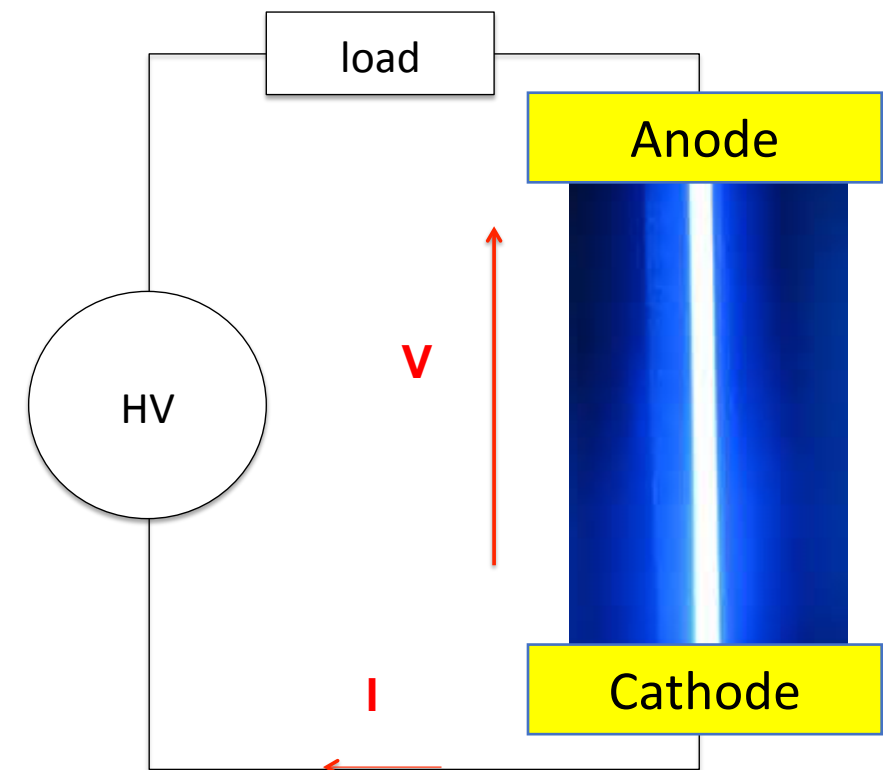
DEFINITION

COLD PLASMA = WEAKLY IONISED GAS

Produced by electrical discharges between two electrodes and by using specific HV power supply

By introducing a dielectric material between the electrodes, and by using pulsed HV power supplies, it is possible to generate cold plasmas at atmospheric pressure and temperatures closed to room temperature:

COLD ATMOSPHERIC PLASMAS (CAPs)



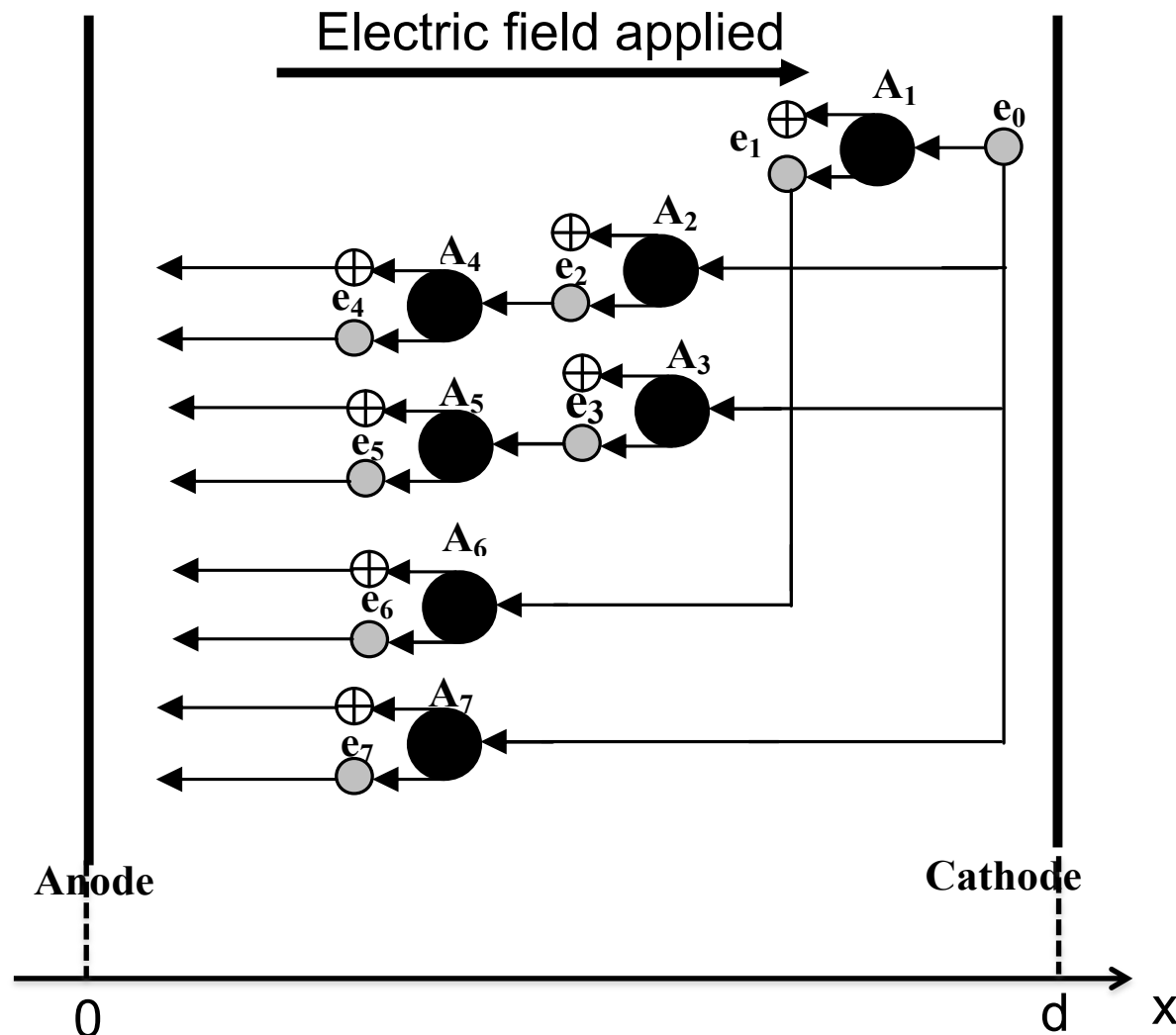
Mechanisms in electrical discharges

Townsend laws: Electronic avalanches in the gap

Ionisation : $A + e^- \Rightarrow A^+ + 2e^- \dots$

Examples of
energy ionisation

Molécules	W_i (eV)
CO ₂	13,7
N ₂	15,5
O ₂	12,2
H ₂	15,4
H ₂ O	12,6



Two important coefficients depending on the nature of gases and electrodes used

1- Multiplication of charges in the gaseous volume characterized by electronic avalanches and defined by the first Townsend coefficient : α

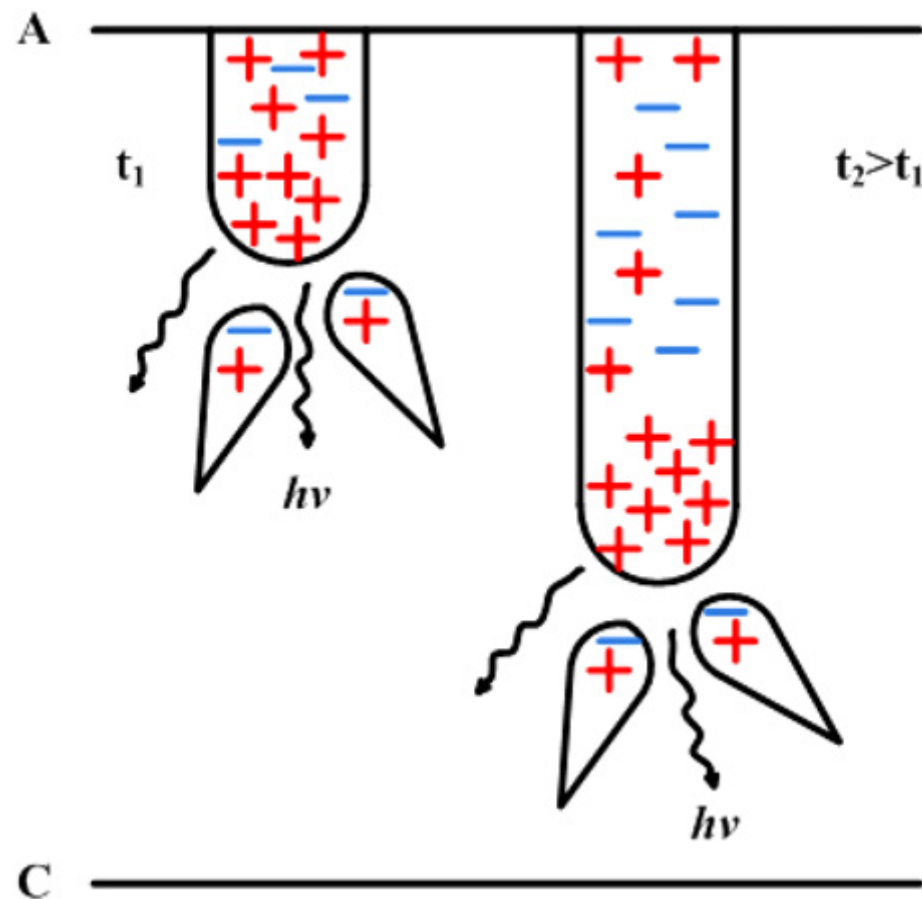
$$n = n_0 \cdot \exp(\alpha x)$$

2- Multiplication of charges due to secondary emission at the cathode and defined by the second Townsend coefficient : γ

Mechanisms in electrical discharges

After the formation of electronic avalanches, and when the space charge field becomes greater than the applied electric field, the space charge field controls the discharge and its dynamics.

We thus obtain an **ionization wave**, which propagates itself due to the space charge field. This ionization wave is called a **STREAMER**

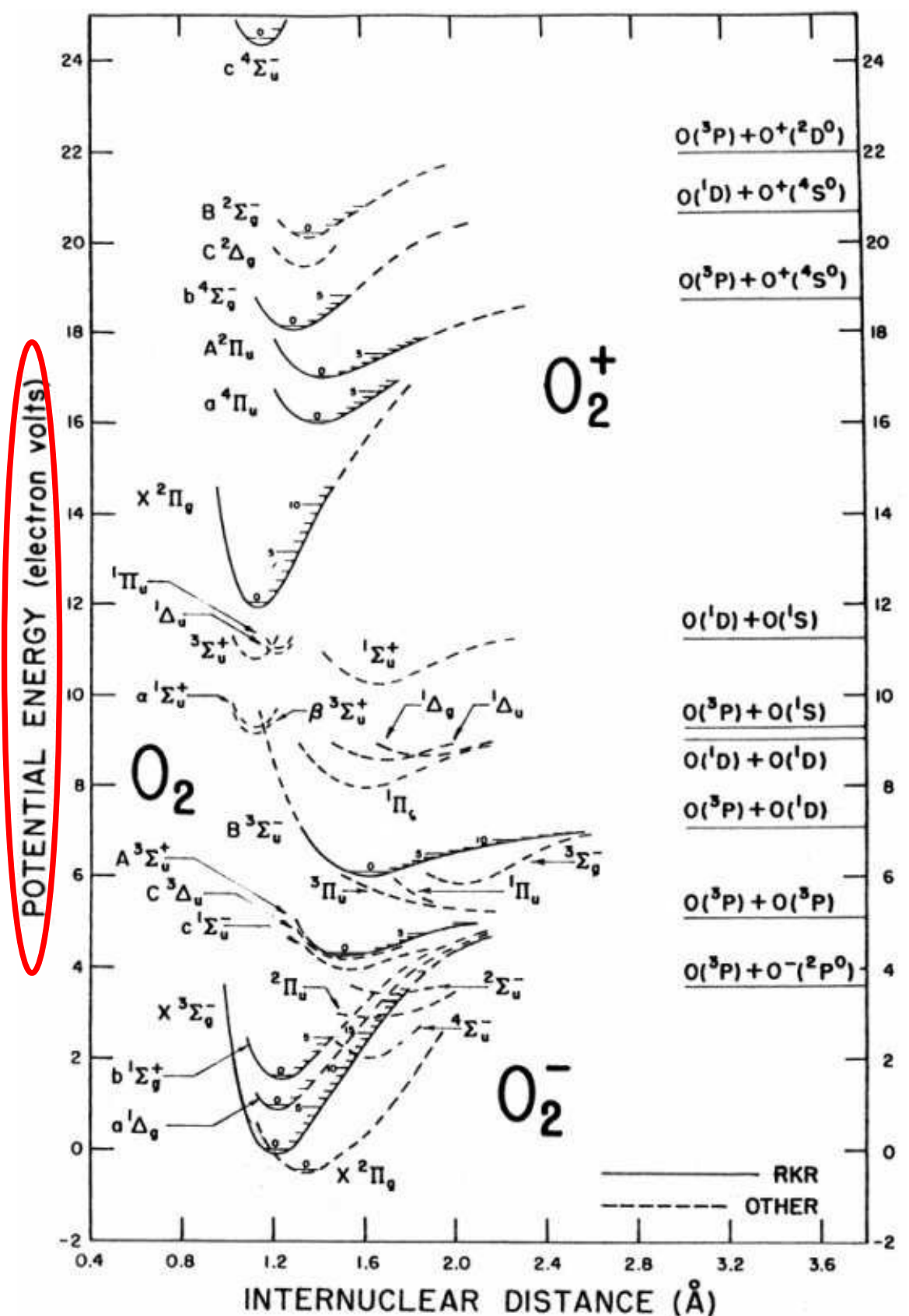
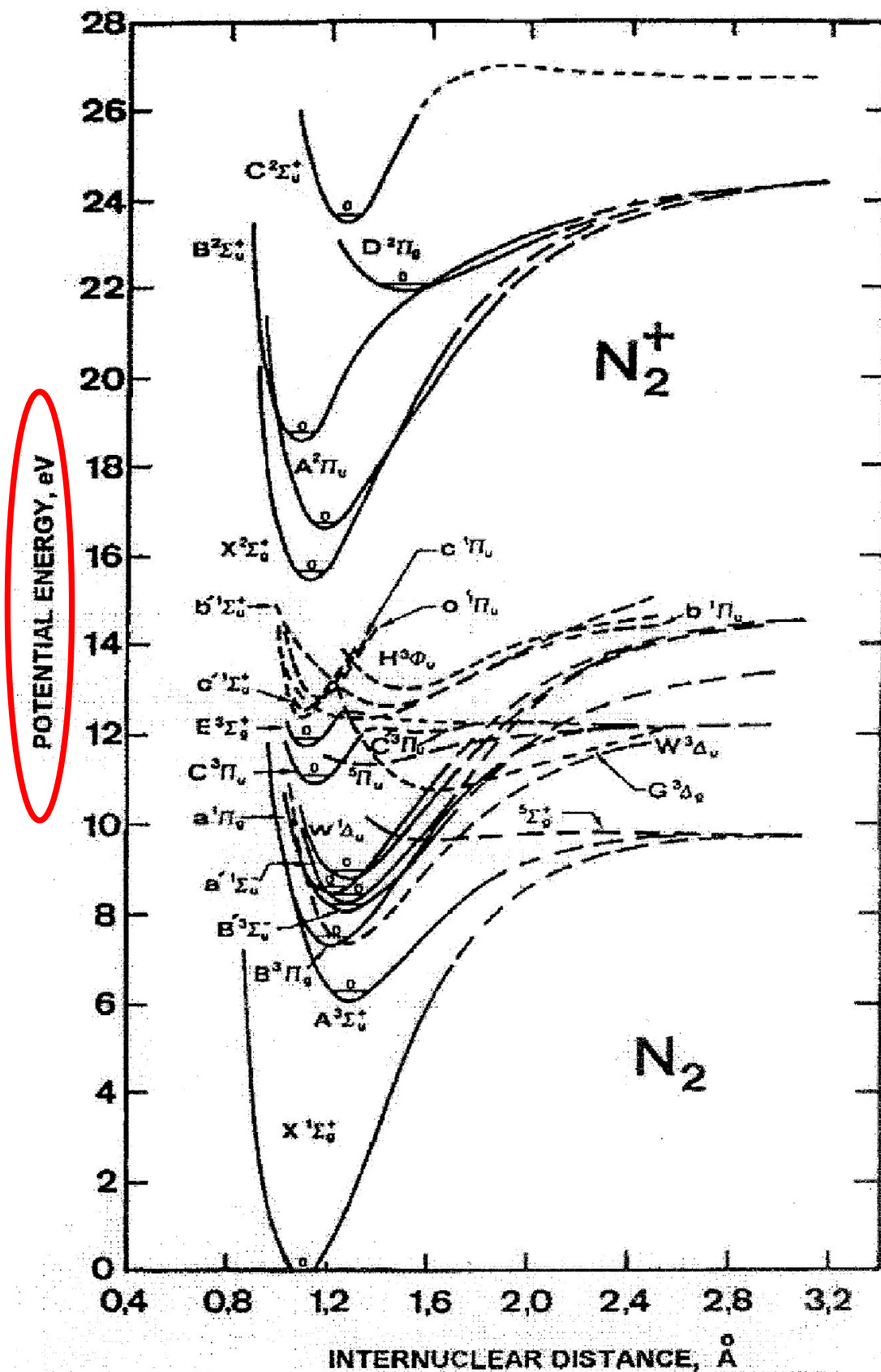


The propagation velocity of streamers is higher than electronic avalanche velocity

10^5 to 10^8 cm.s⁻¹

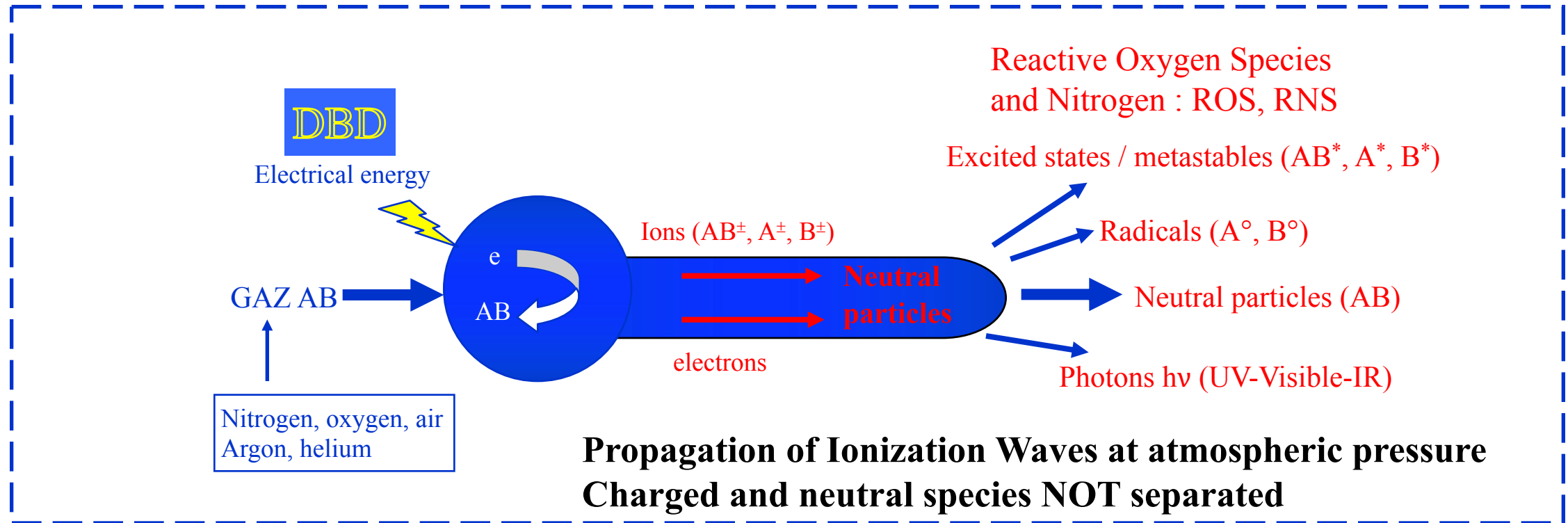
at atmospheric pressure

Electrons are hot in a cold plasma, allowing the production of numerous excited states



Potential energies and diagrams for N₂ and O₂

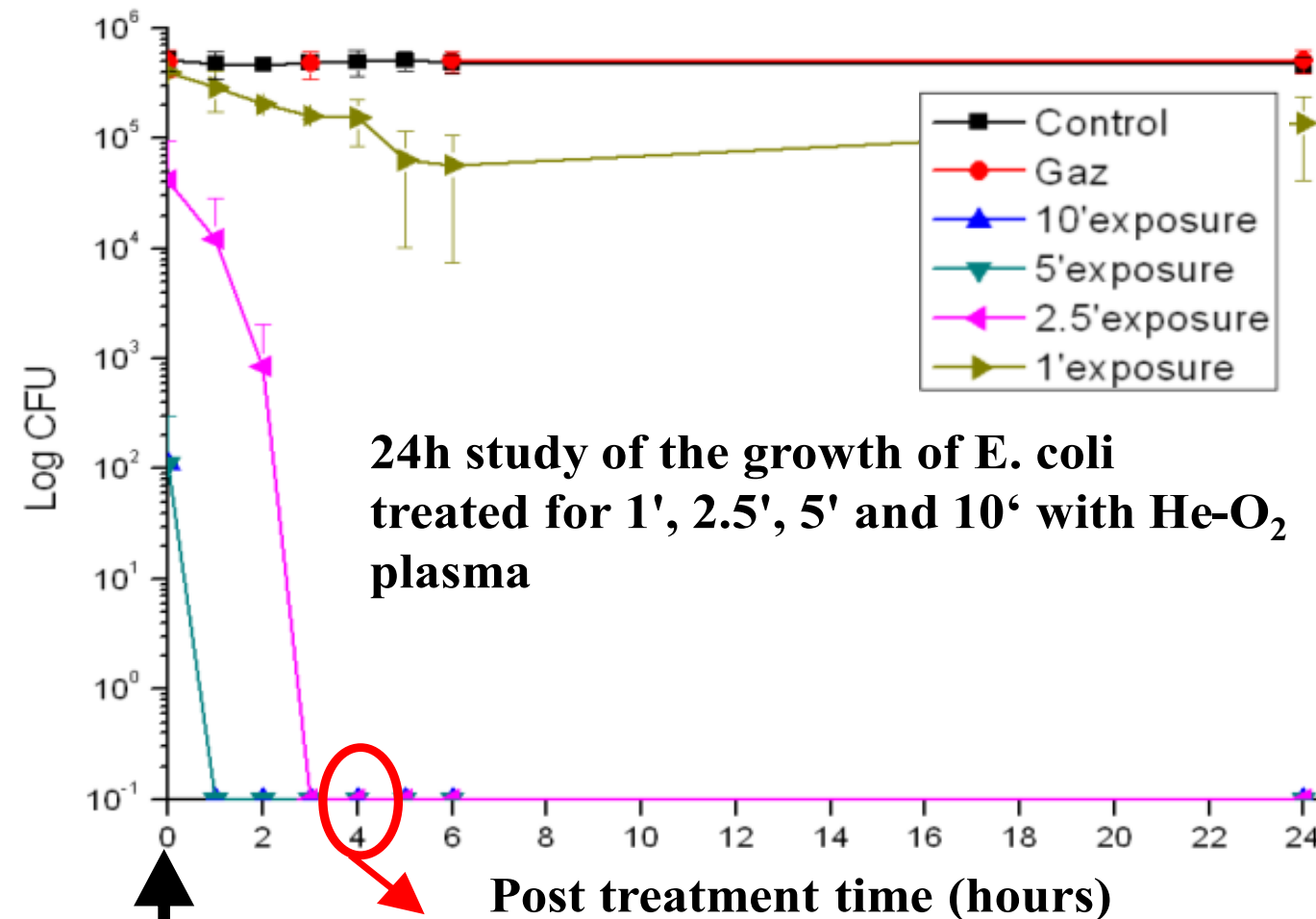
GUIDED IONIZATION WAVE



Gazeli, Clément et al., *Possibility of controlling the chemical pattern of He and Ar “guided streamers” by means of N_2 or O_2 additives*,
J. Appl. Phys. **117**, 093302 (2015)



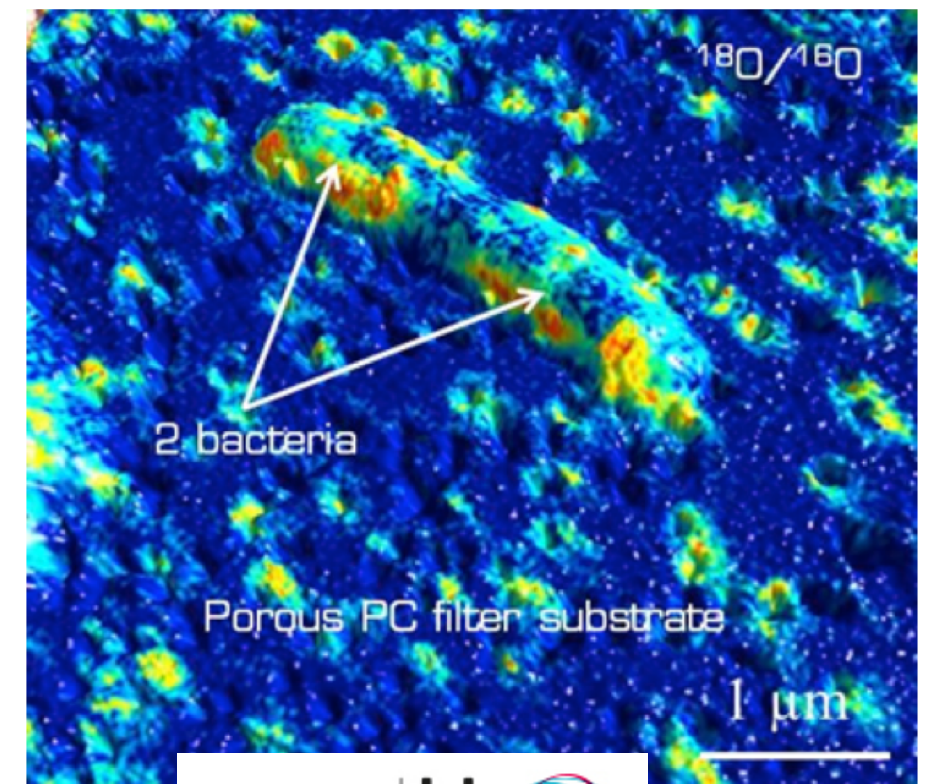
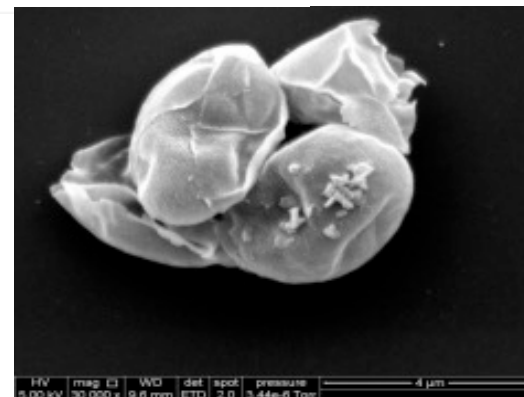
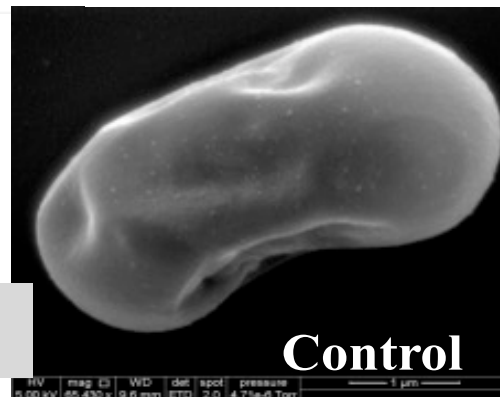
Gazeli, Clément et al., *A study of helium atmospheric-pressure guided streamers for potential biological applications*,
Plasma Sources Sci. Technol. 22 (2013) 025020 (9pp)



Treatment Distance: 10 mm Away from the Tube Exit
 $Q(\text{He-O}_2:99-1\%) = 2 \text{ slm}$, $V_c = 5 \text{ kV}$, $f = 10 \text{ kHz}$, $r_c = 1\%$

Treatment

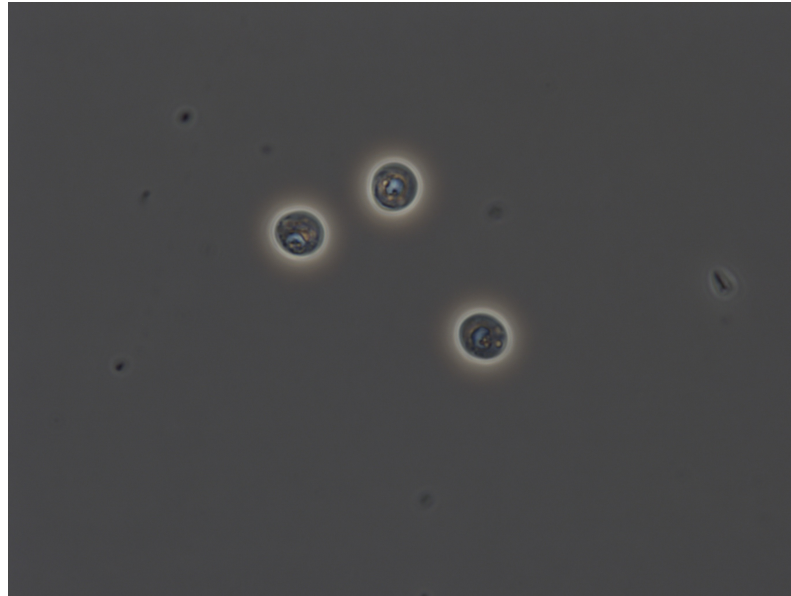
SEM Images



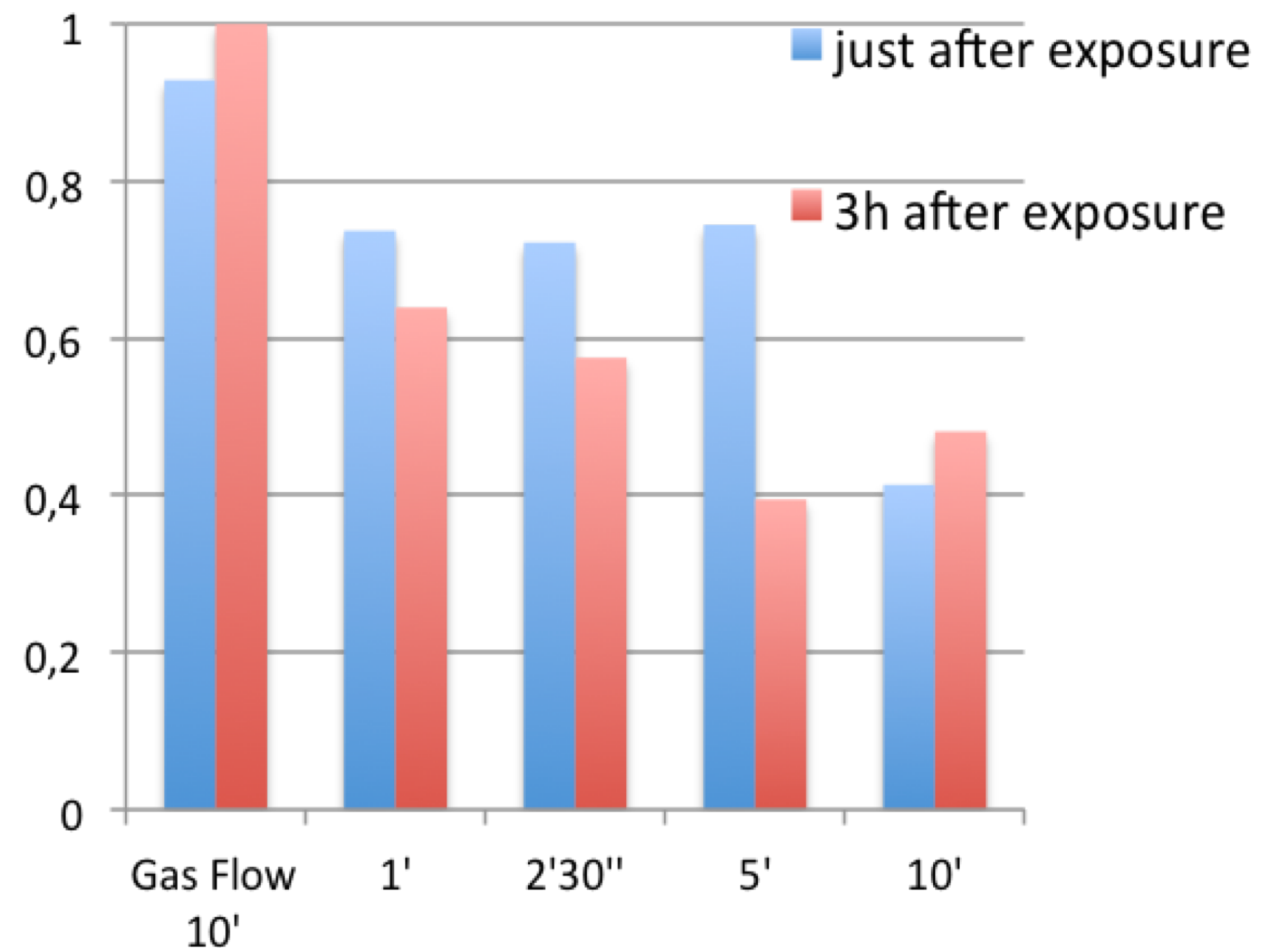
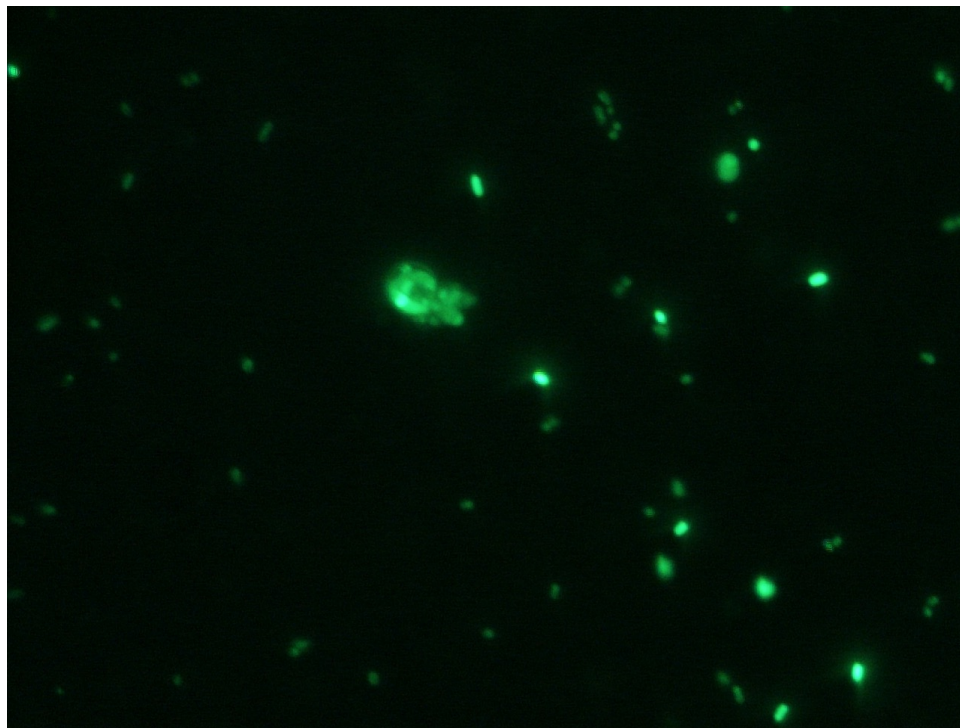
Clément et al., *Study of Reactive Oxygen or/and Nitrogen Species Binding Processes on E. coli Bacteria with Mass Spectrometry Isotopic Nanoimaging*, *New Journal of Physics* 13 (2011) 113040 (12pp)

Duday, Clément et al., *NanoSIMS50 analyses of Ar/¹⁸O plasma-treated Escherichia coli bacteria*, *Plasma Processes and Polymers*, vol 10, Issue 10, p 864–879, 2013

Dezest, Clément et al., *Oxidative modification and electrochemical inactivation of Escherichia coli upon cold atmospheric plasma exposure*, *PLOS One*, 2017, 0173618



Cryptosporidium parvum oocysts are composed of a capsid containing four infectious sporozoites. Cell integrity is well marked by a luminous crown around the oocysts.

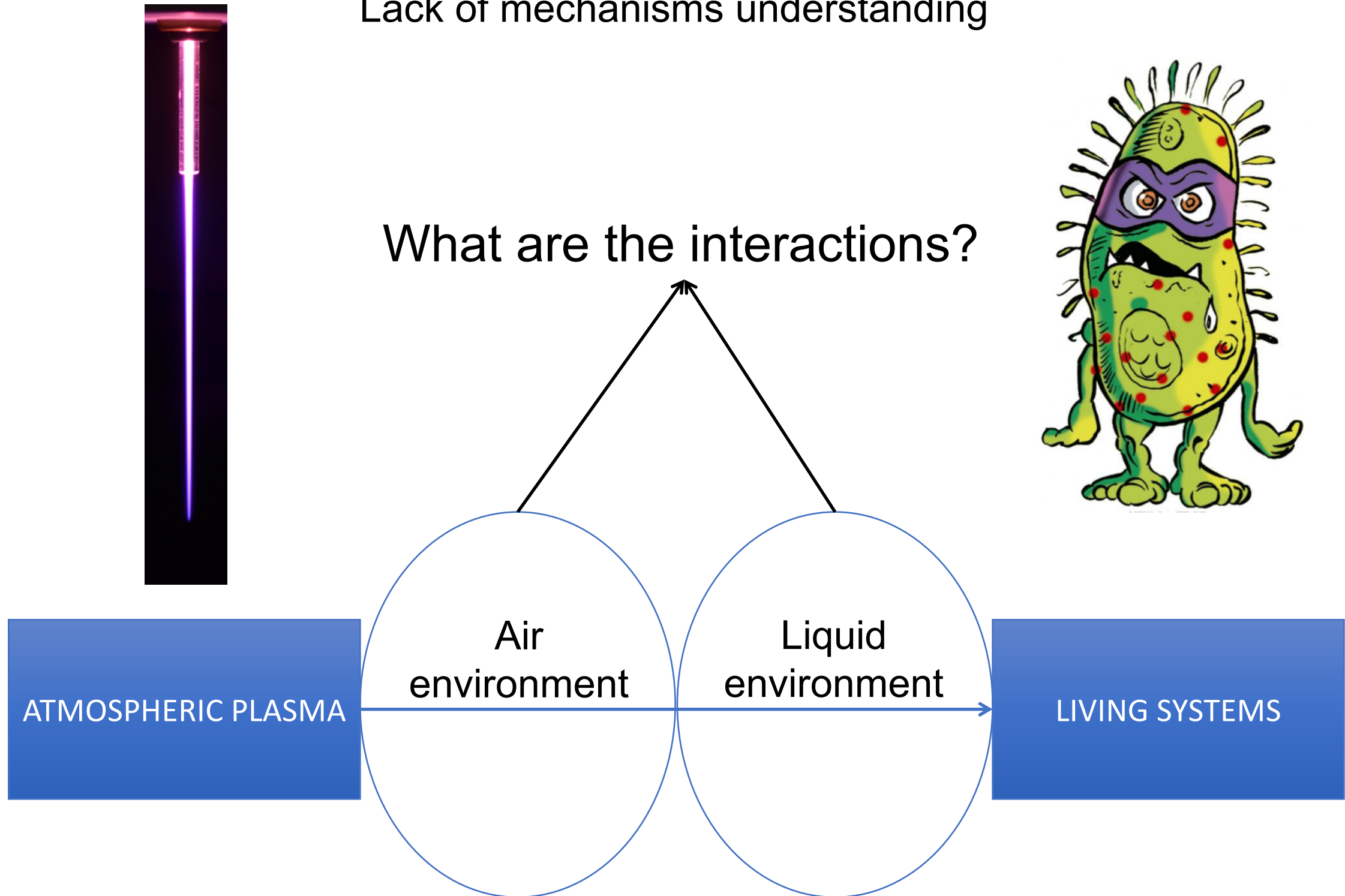
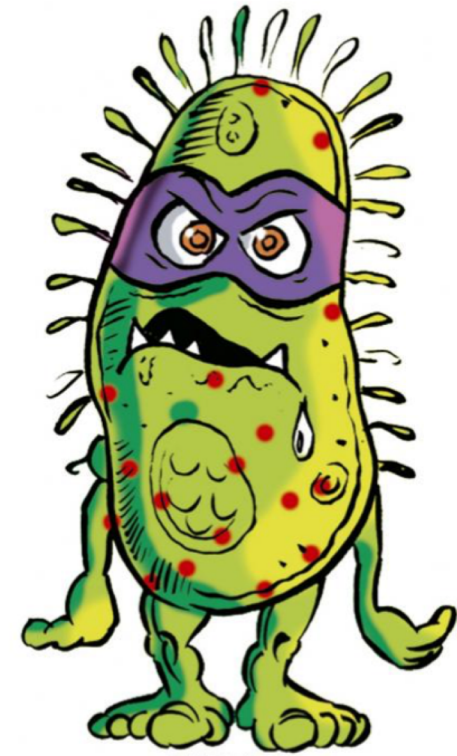


Drs C. Penny, J-P Cambus, A. Valentin

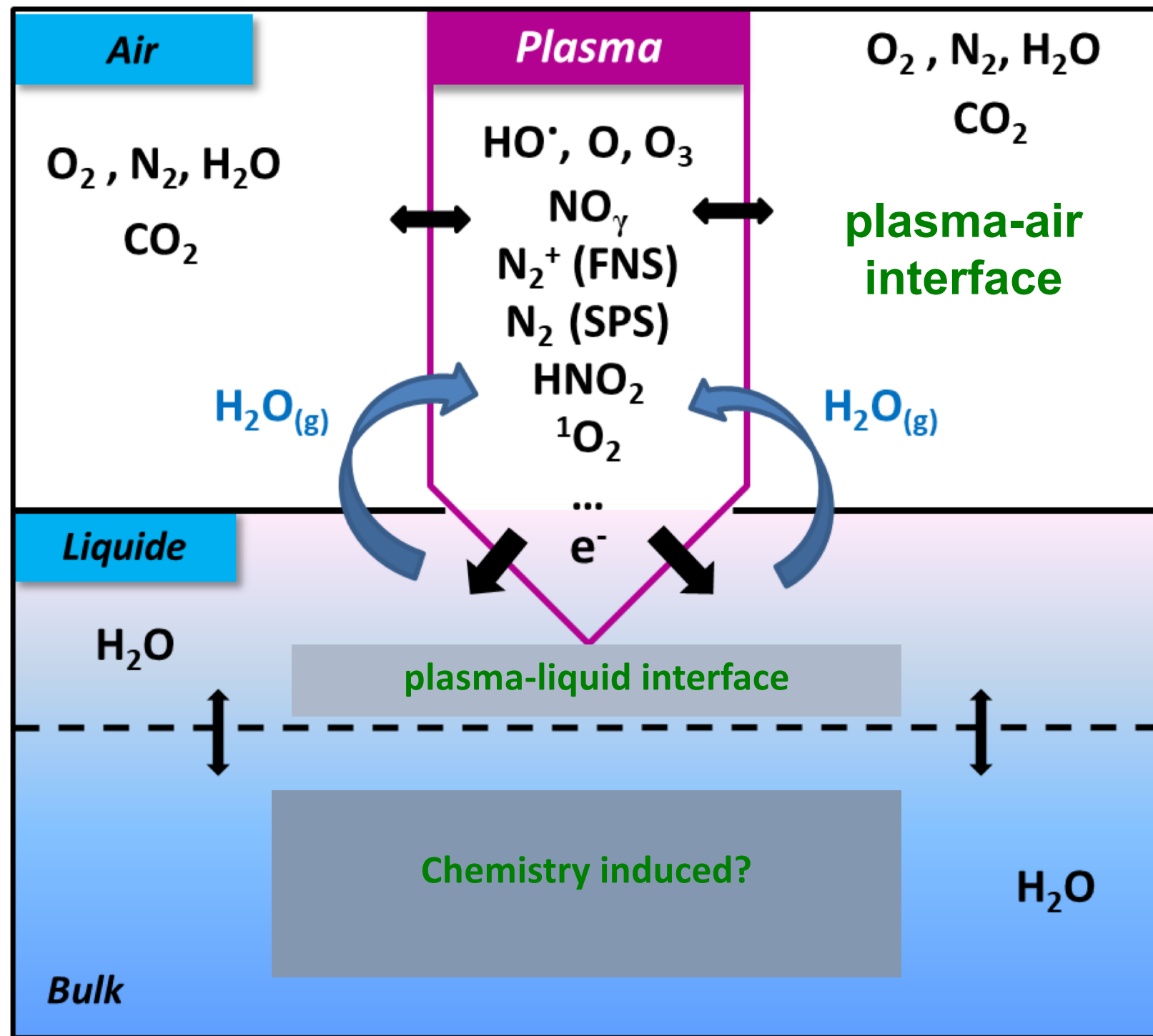
IONIZATION WAVE

Lack of mechanisms understanding

What are the interactions?



PLASMA-AIR and PLASMA-LIQUID INTERFACES



phD UPPA
Girard F. Pau

IONIZATION WAVE in interaction with air and water environments

Possible mechanisms

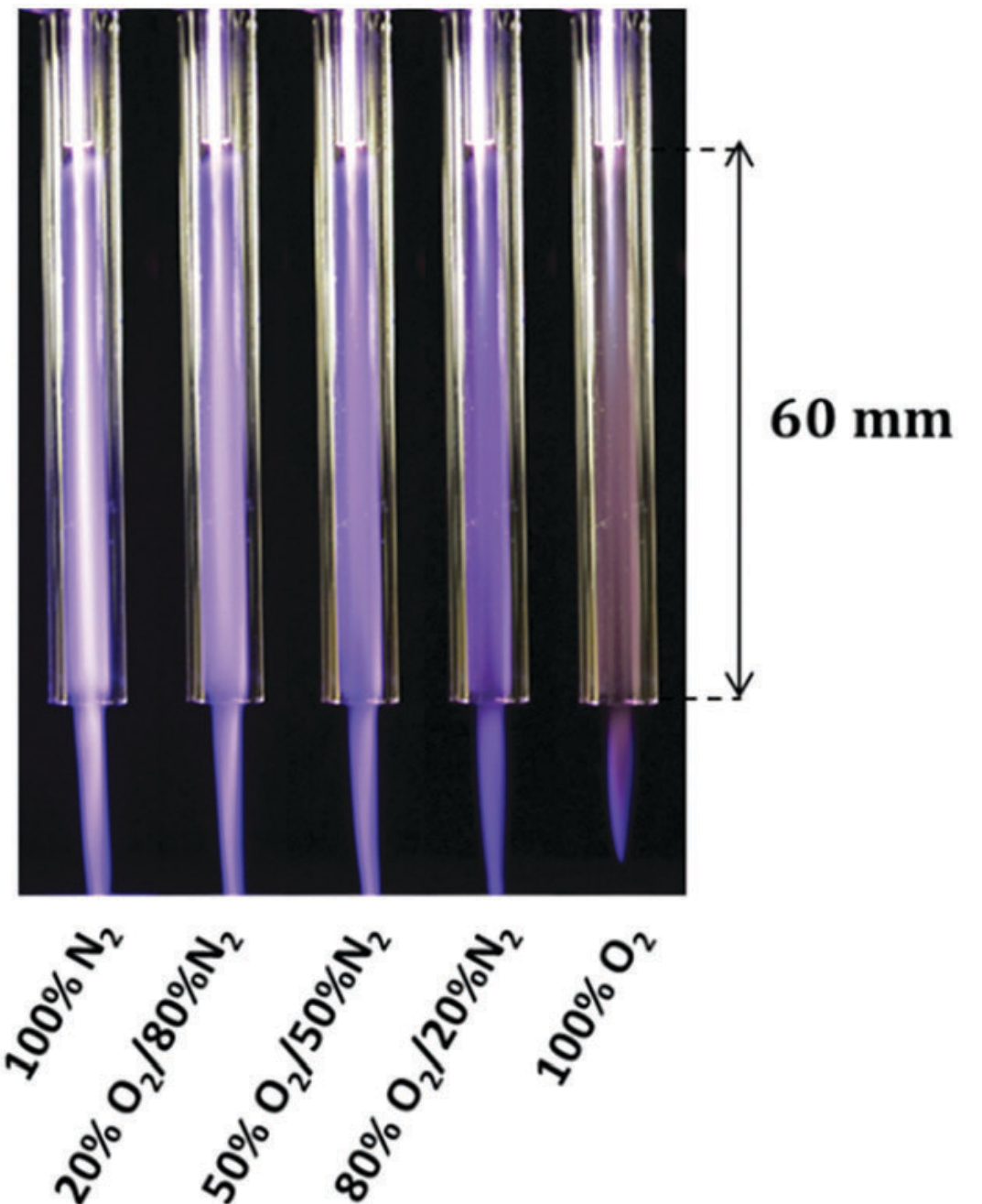
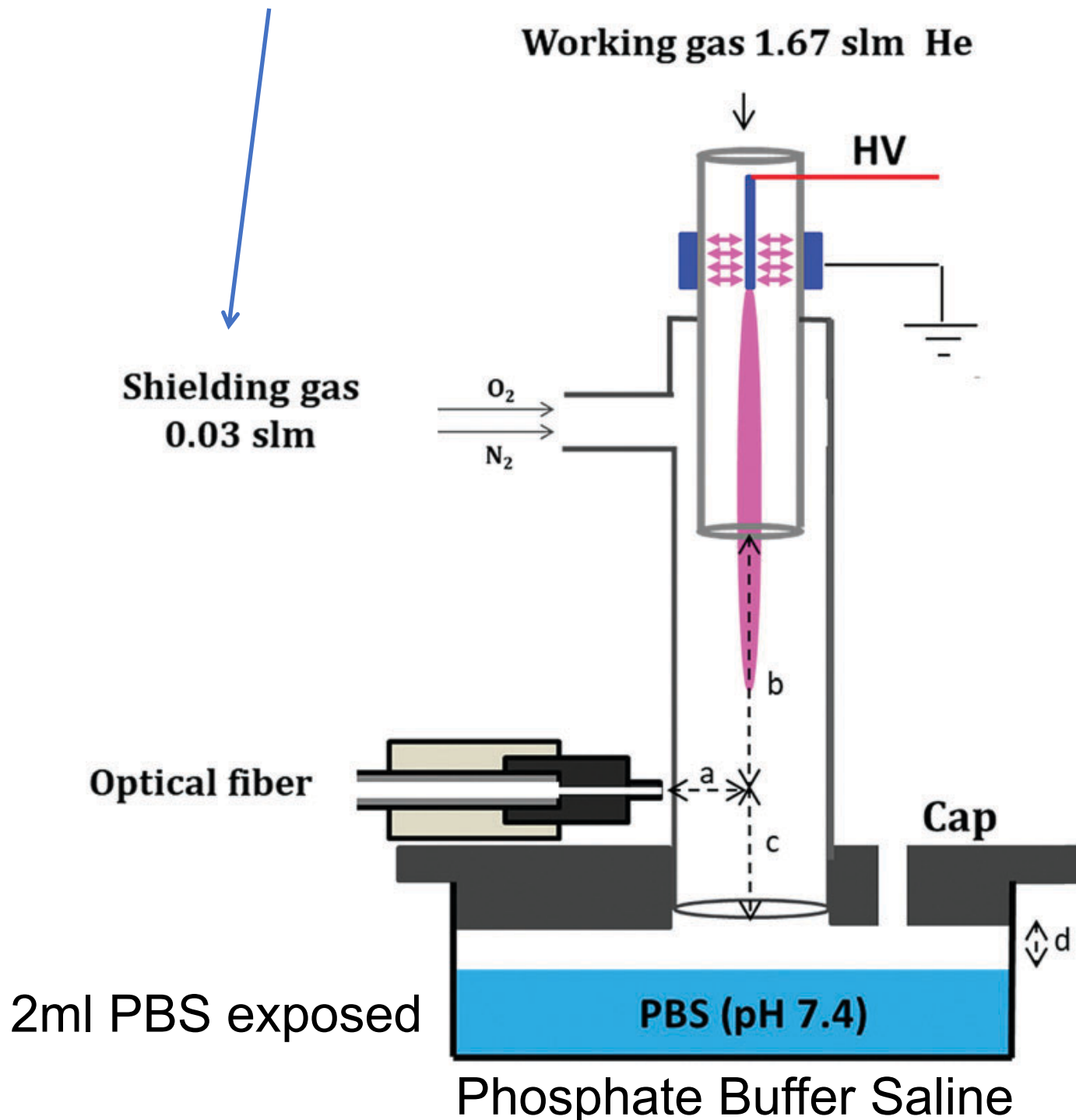


	In the gas	In the liquid (PBS: phosphate buffer saline)
H₂O₂	$\text{HO}^\circ + \text{HO}^\circ \rightarrow \text{H}_2\text{O}_2$ $\text{N}_2 (\text{A}^3\Sigma_u^+) + \text{H}_2\text{O}_{(\text{g})} \rightarrow \text{HO}^\circ + \text{H}^\circ + \text{N}_2$ $\text{N}_2(\text{B}^3\pi) \rightarrow \text{N}_2 (\text{A}^3\Sigma_u^+) + h\nu$ $\text{N}_2 (\text{FPS}) \text{ observed in the plasma: } \text{N}_2(\text{A})$	$\text{HO}^\circ + \text{HO}^\circ \rightarrow \text{H}_2\text{O}_2$
NO₂⁻	$\text{HO}^\circ + \text{NO}^\circ + \text{M} \rightarrow \text{HNO}_2 + \text{M}$ M : collision partner	$\text{HNO}_2 + \text{HPO}_4^{2-} \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{PO}_4^-$
NO₃⁻	$\text{NO}_2^\circ + \text{HO}^\circ + \text{M} \rightarrow \text{HNO}_3 + \text{M}^*$...	$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$...

GAS-LIQUID INTERACTION

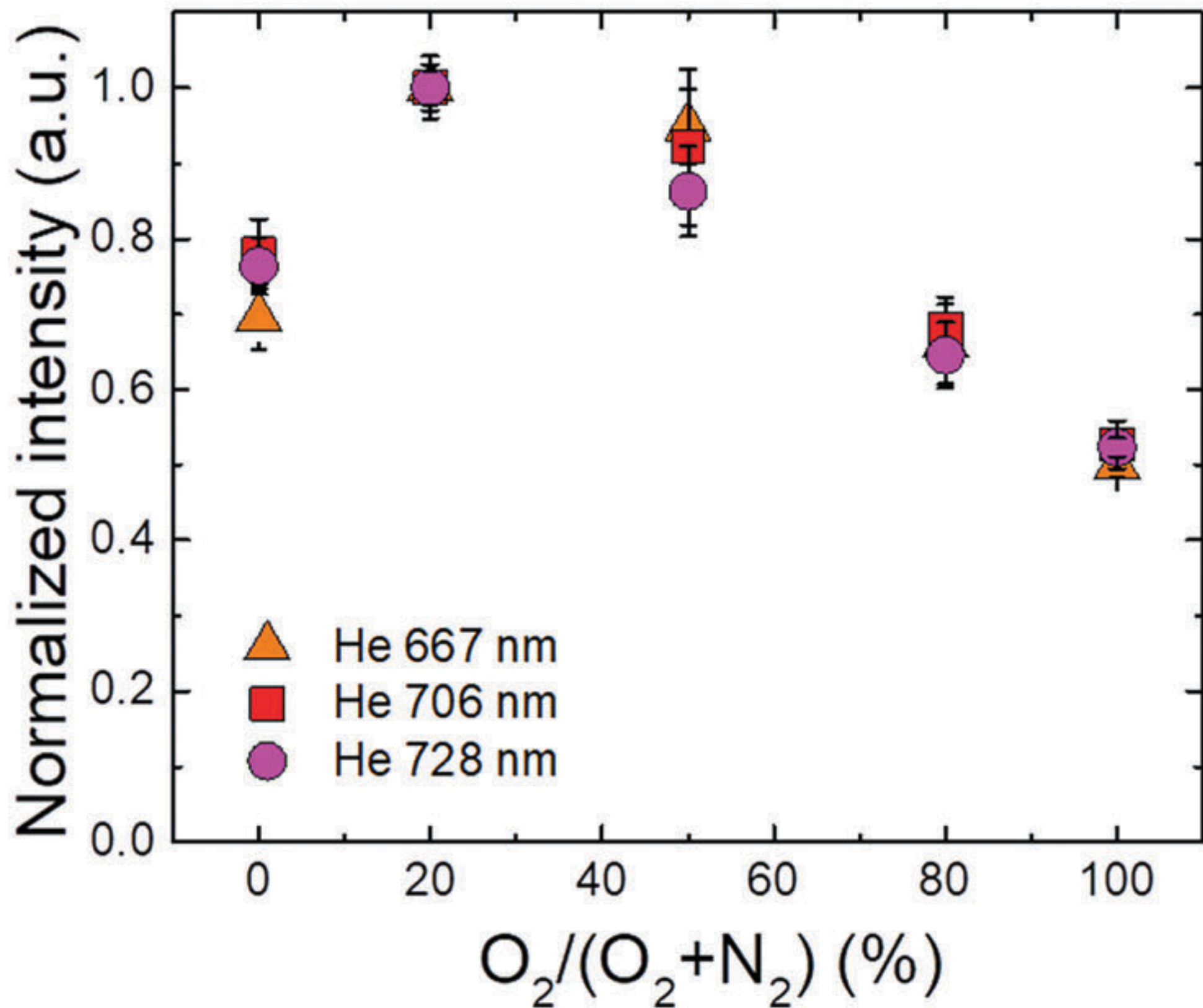
By using a shielding gas device !

Control of the air environment →

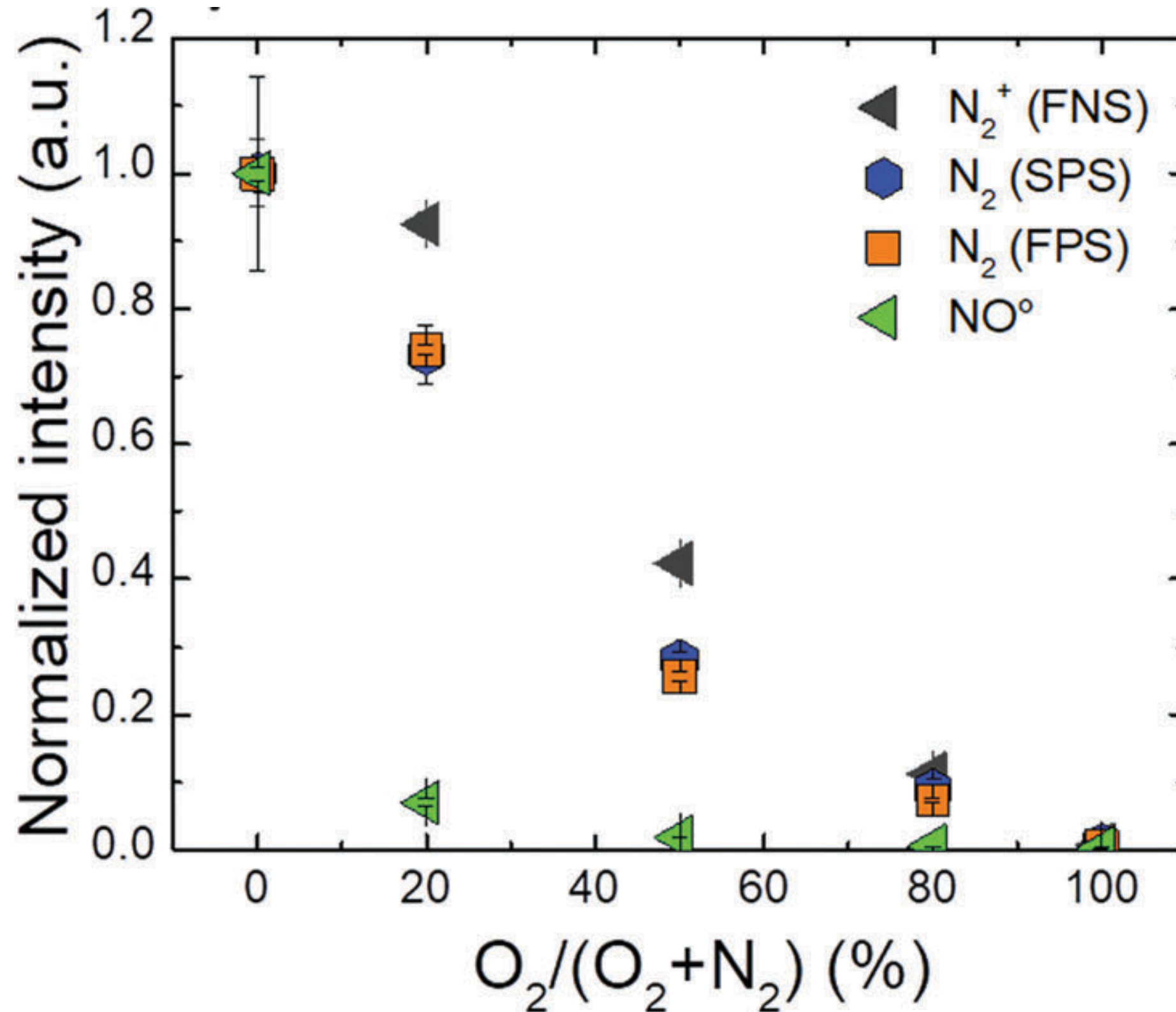


Girard, Clément et al.
Phys. Chem. Chem. Phys.
2018, 20, 9198-9210

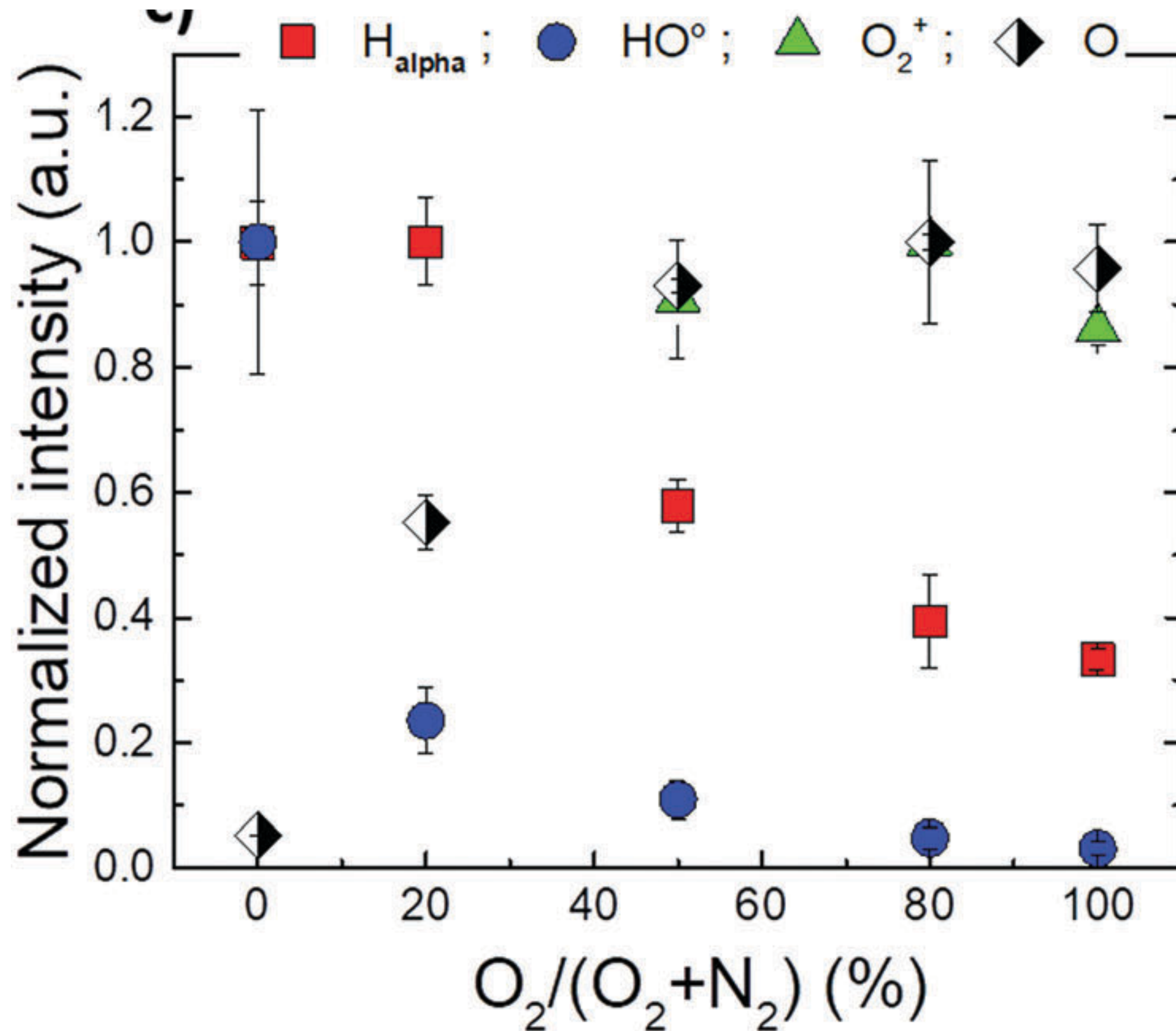
Maximum of excited levels of He
for air mixture



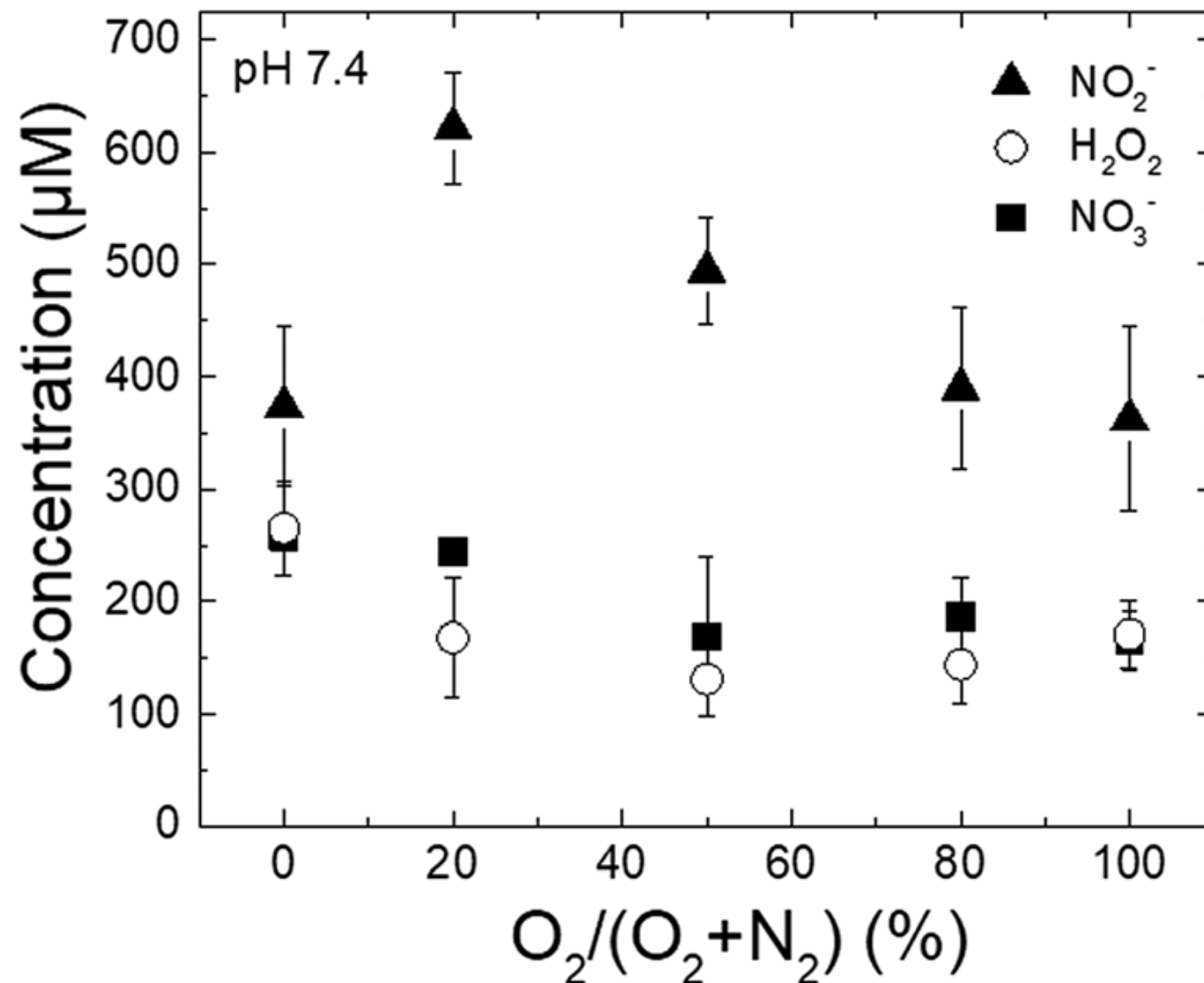
When increasing O₂ %, rapid decrease of
NO and slower decrease of
N₂ (SPS, FPS) and N₂⁺ (FNS)



When increasing O₂ %, decrease of OH and H, increase of O and O₂⁺



GAS-LIQUID INTERACTION



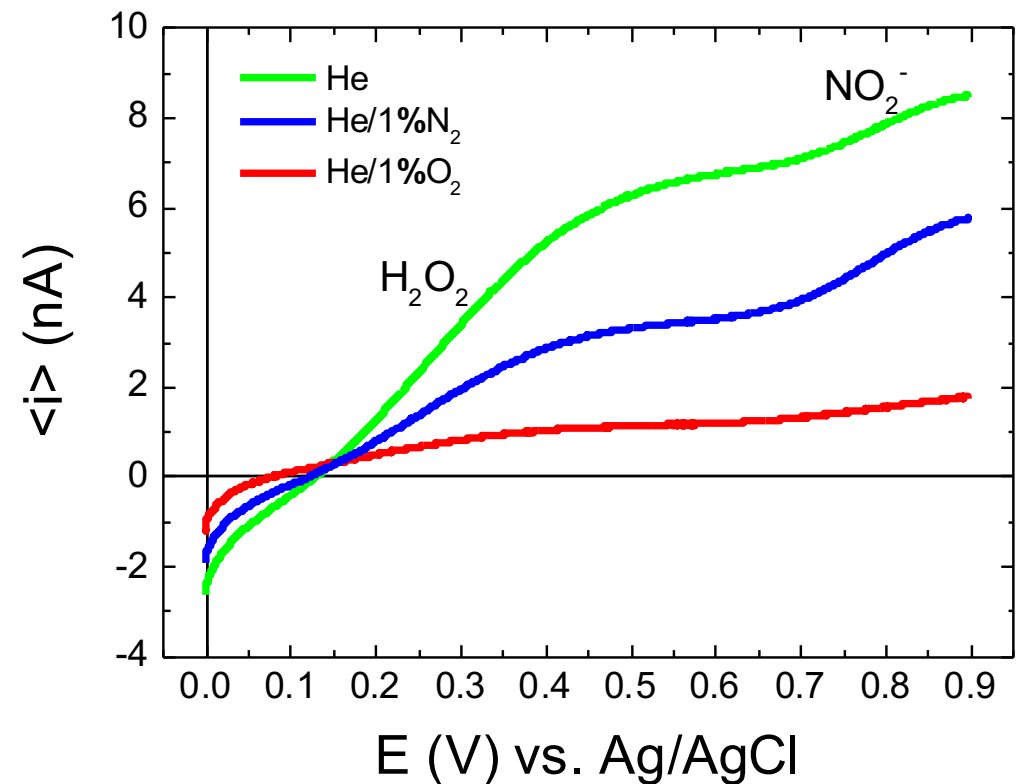
2ml PBS exposed

Girard, Clément et al.

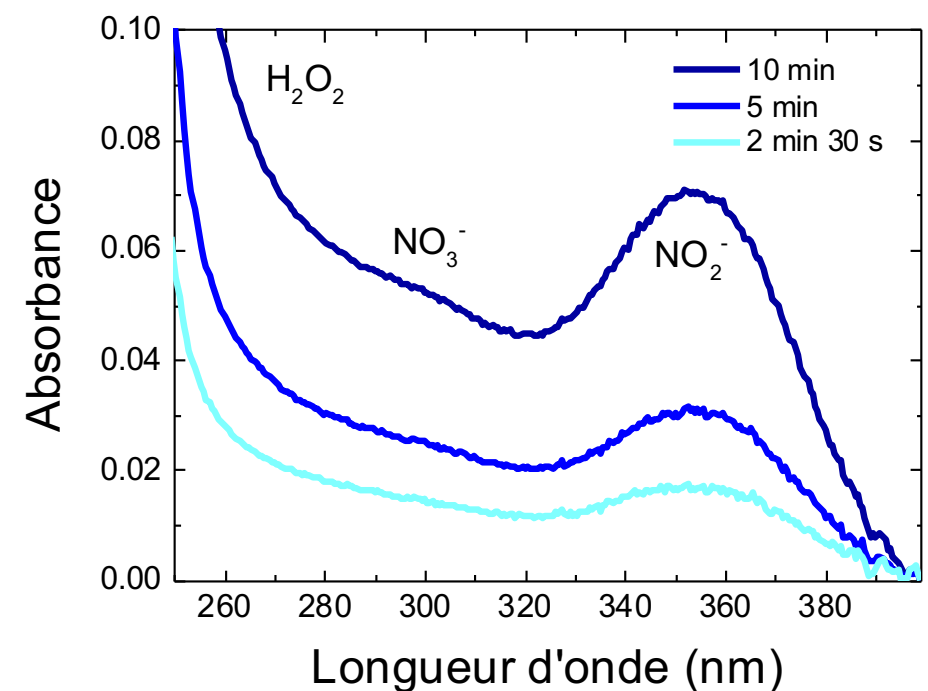
Phys. Chem. Chem. Phys. 2018, 20, 9198-9210

Collab. ENSCBP Bordeaux : S. Arbault, V. Badets, P. Lefrançois

Electrochemistry

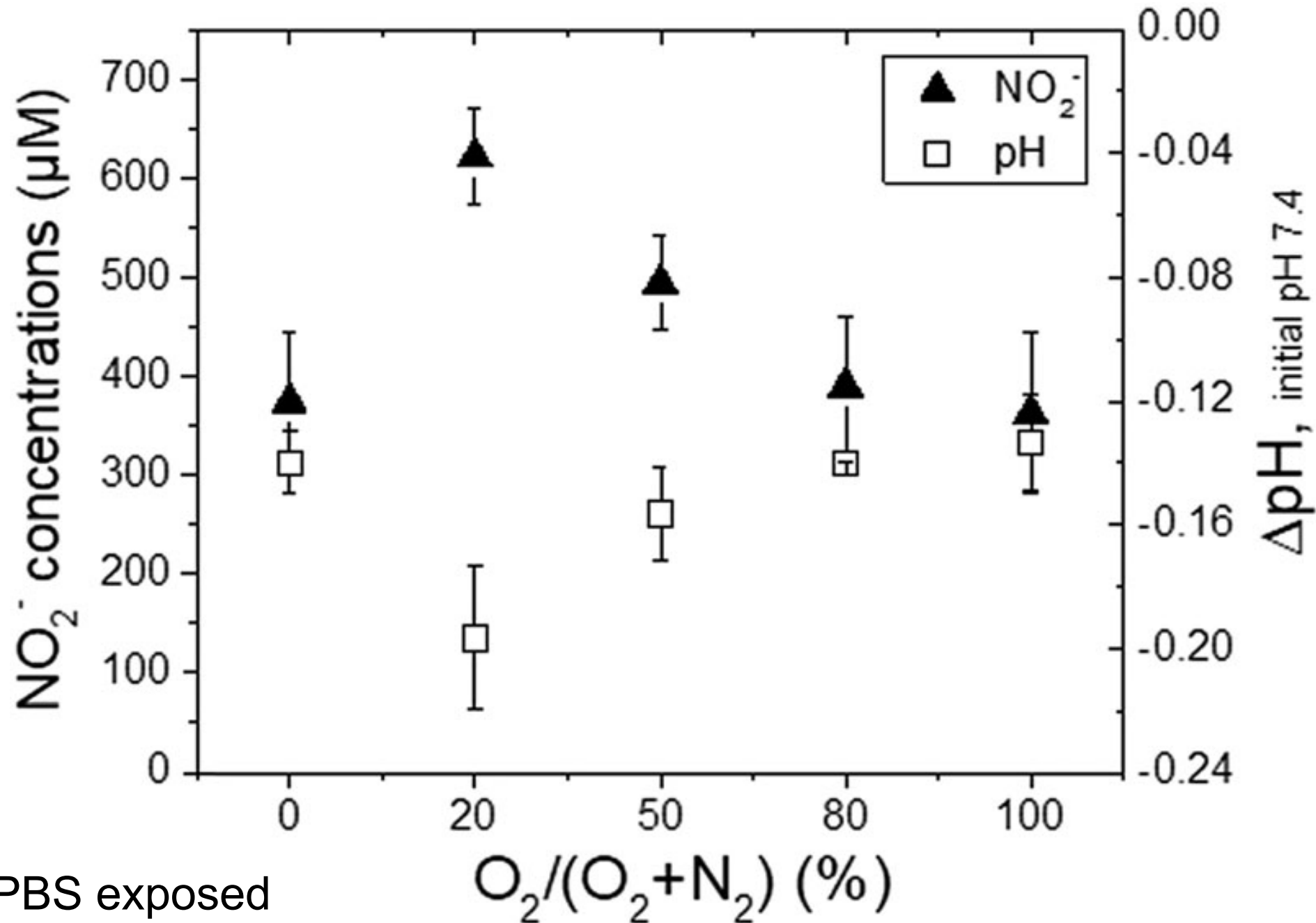


Absorption spectroscopy



GAS-LIQUID INTERACTION

NO_2^- correlated with pH variation in buffered solution (PBS)



2ml PBS exposed

Measured by
Electrochemistry
and Absorption
spectroscopy

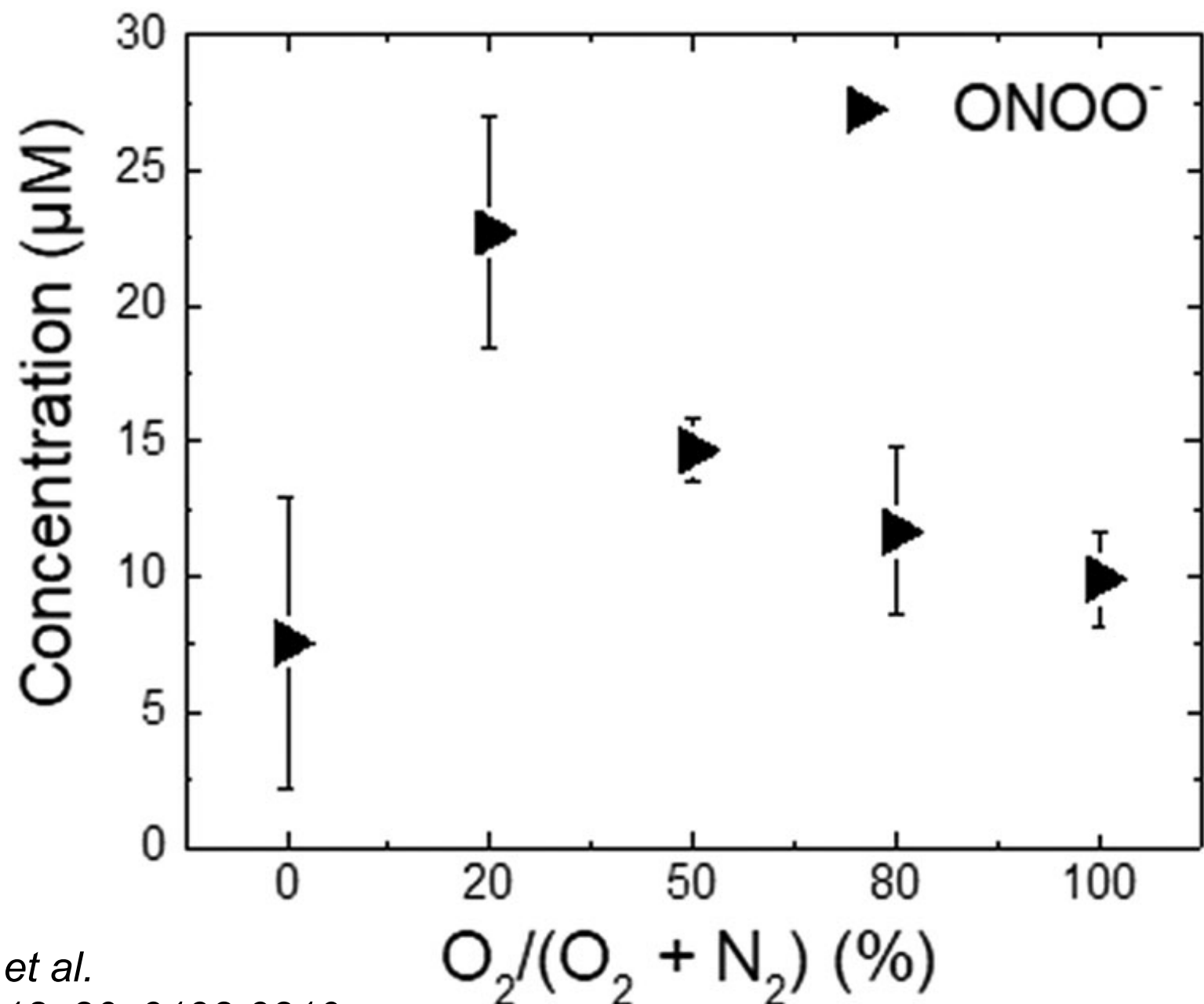
GAS-LIQUID INTERACTION

By changing pH, it is possible to measure unstable Species in solution

pH 12
Buffered solution
2ml PBS

PEROXYNITRITE

Measured by
Absorption
spectroscopy

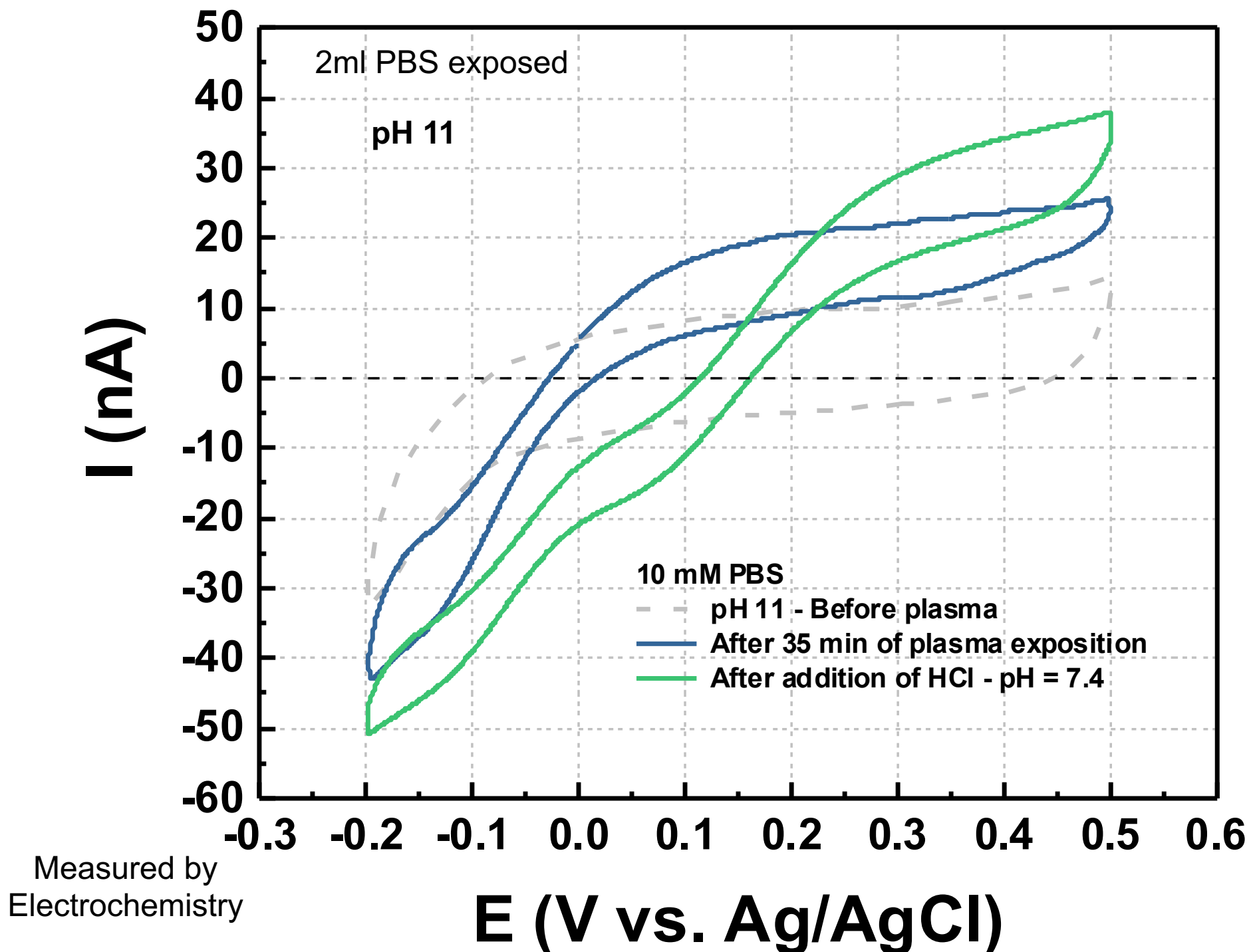


Girard, Clément et al.
Phys. Chem. Chem. Phys. 2018, 20, 9198-9210

GAS-LIQUID INTERACTION

By changing pH, it is possible to measure unstable Species in solution

ANION
SUPEROXYDE $\text{O}_2^{\circ -}$



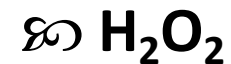
After exposition to
plasma:

1- $\text{O}_2^{\circ -}$ detected in PBS
at pH 11

2- $\text{O}_2^{\circ -}$ is fully
converted to H_2O_2
after ajustement of
pH to 7.4

GAS-LIQUID INTERACTION

Helium plasma produces ROS and RNS including:



Abs. Spectroscopy
Electrochemistry
(20-30 $\mu\text{M}.\text{min}^{-1}$)*



Electrochemistry (not quantified)



Abs. Spectroscopy
(0.2-1.2 $\mu\text{M}.\text{min}^{-1}$)*

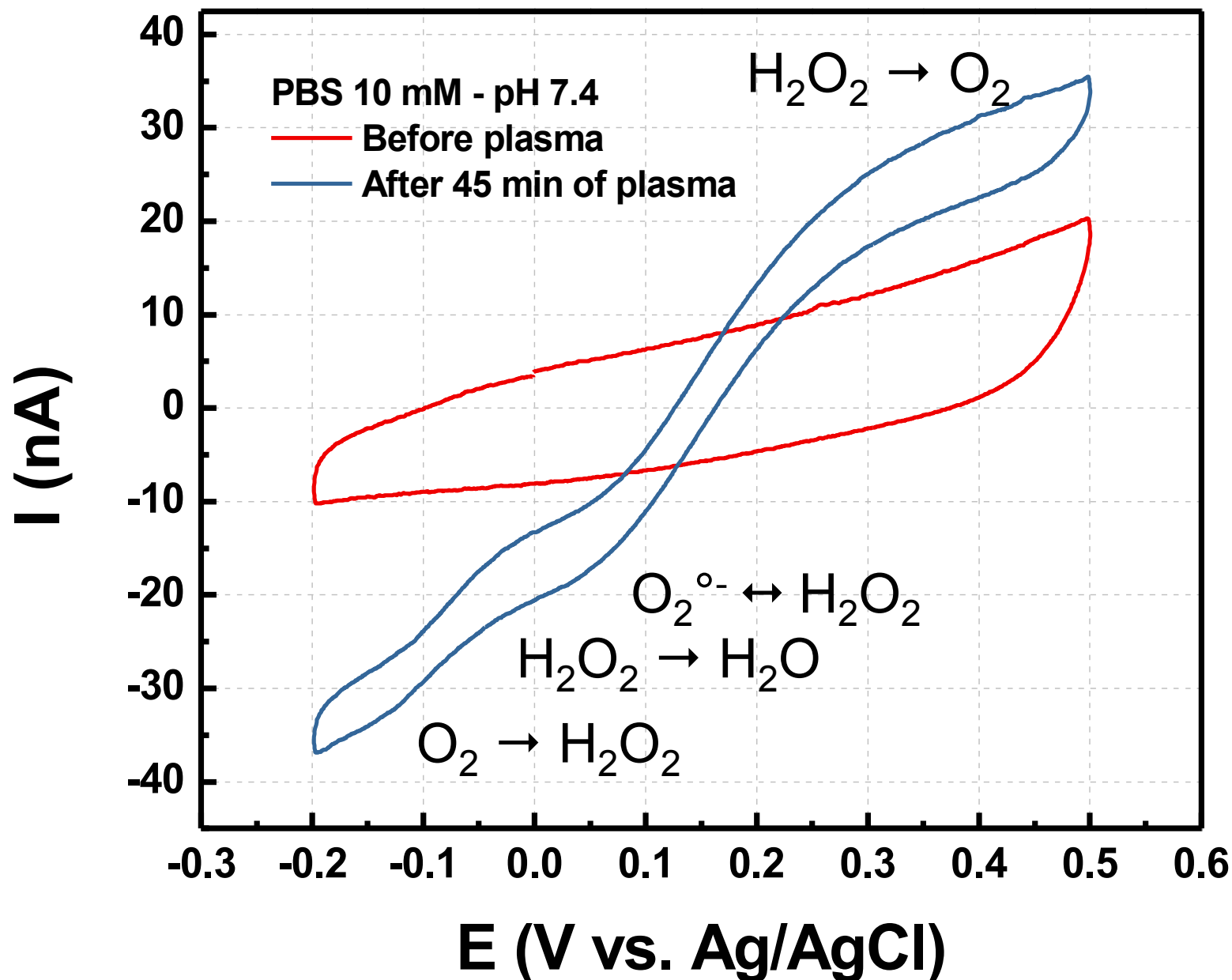


Abs. Spectroscopy
Electrochemistry
(30-45 $\mu\text{M}.\text{min}^{-1}$)*



Abs. Spectroscopy
(30-45 $\mu\text{M}.\text{min}^{-1}$)*

** With N_2 as shielding gas*



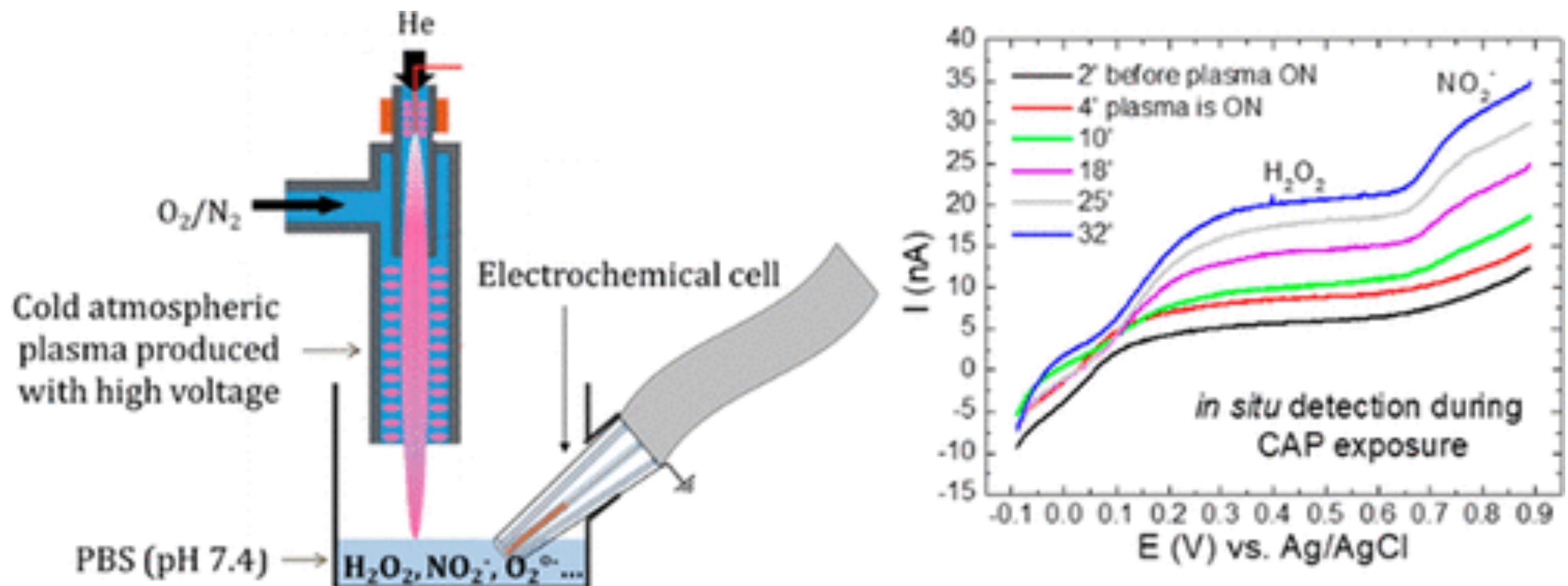
GAS-LIQUID INTERACTION in situ, during plasma exposure

Electrical fields implied in ionization waves are in the order of magnitude of some **10kV.cm⁻¹**

Sretenovic, G. et al., J.Appl.Phys. 452 2017, 121 (12), 123304.

Razavizadeh, S. et al., Plasma Sources Sci. 454 Technol. 2018, 27 (7), 075016.

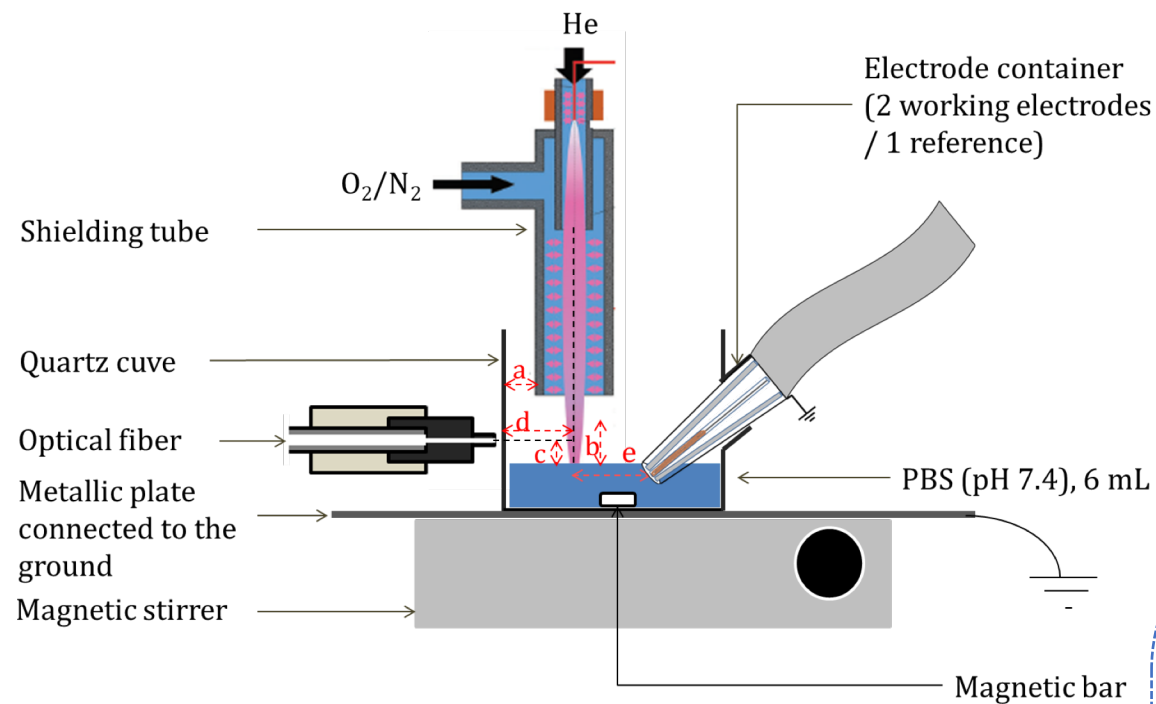
Difficulties to measure very low faradaic currents, in the **nA range**, in the presence of high electric fields used for plasma formation



Reactive oxygen species generated by cold atmospheric plasmas in aqueous solution: Successful Electrochemical Monitoring in Situ under a High Voltage System, Girard, Clément et al., *Analytical Chemistry*, 2019

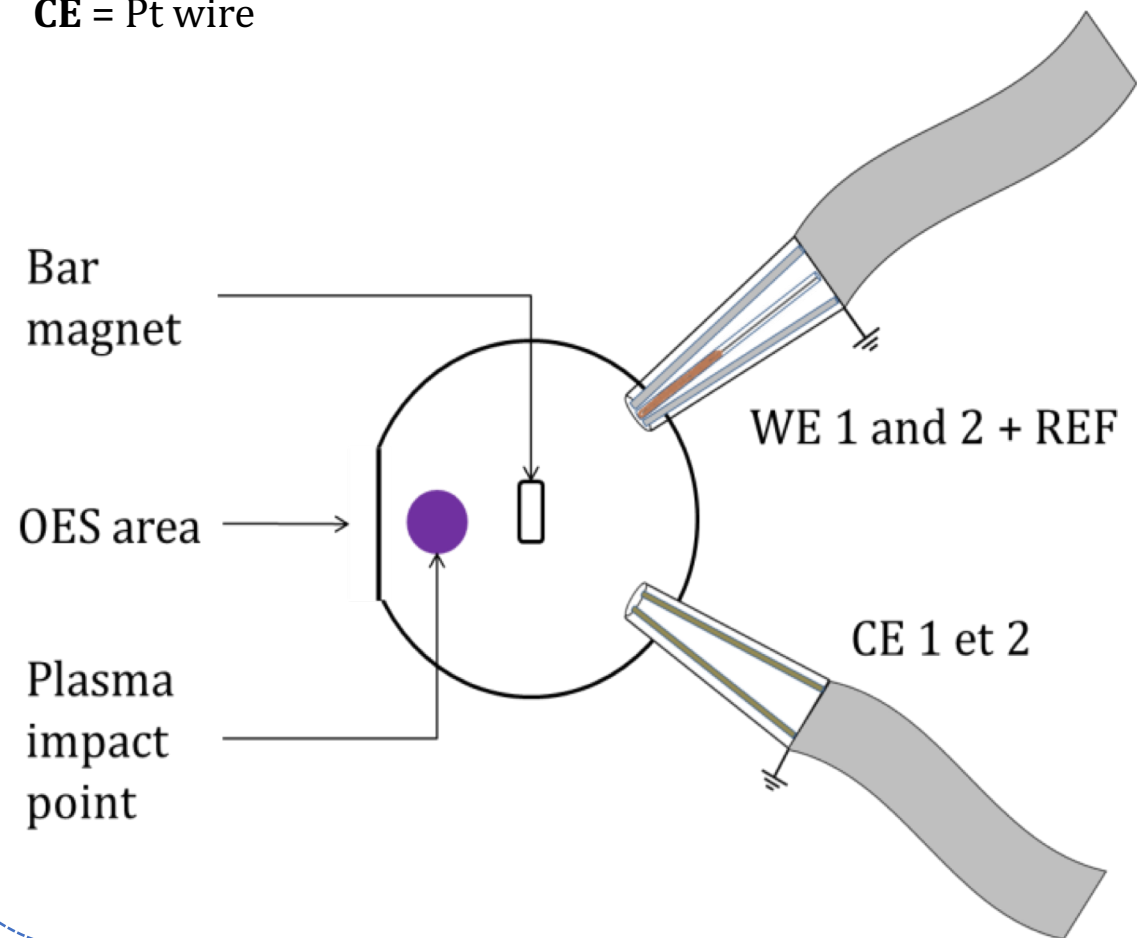
<https://doi.org/10.1021/acs.analchem.9b01912>

GAS-LIQUID INTERACTION in situ, during plasma exposure

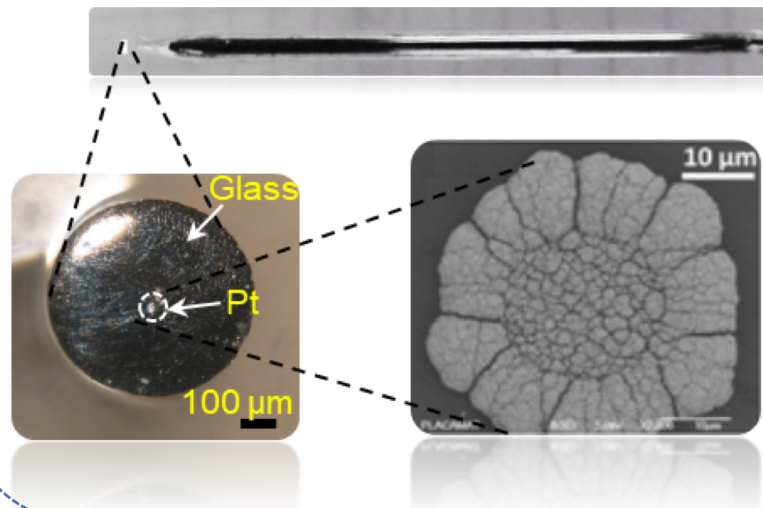


Different types of shielded electrodes used during plasma exposure

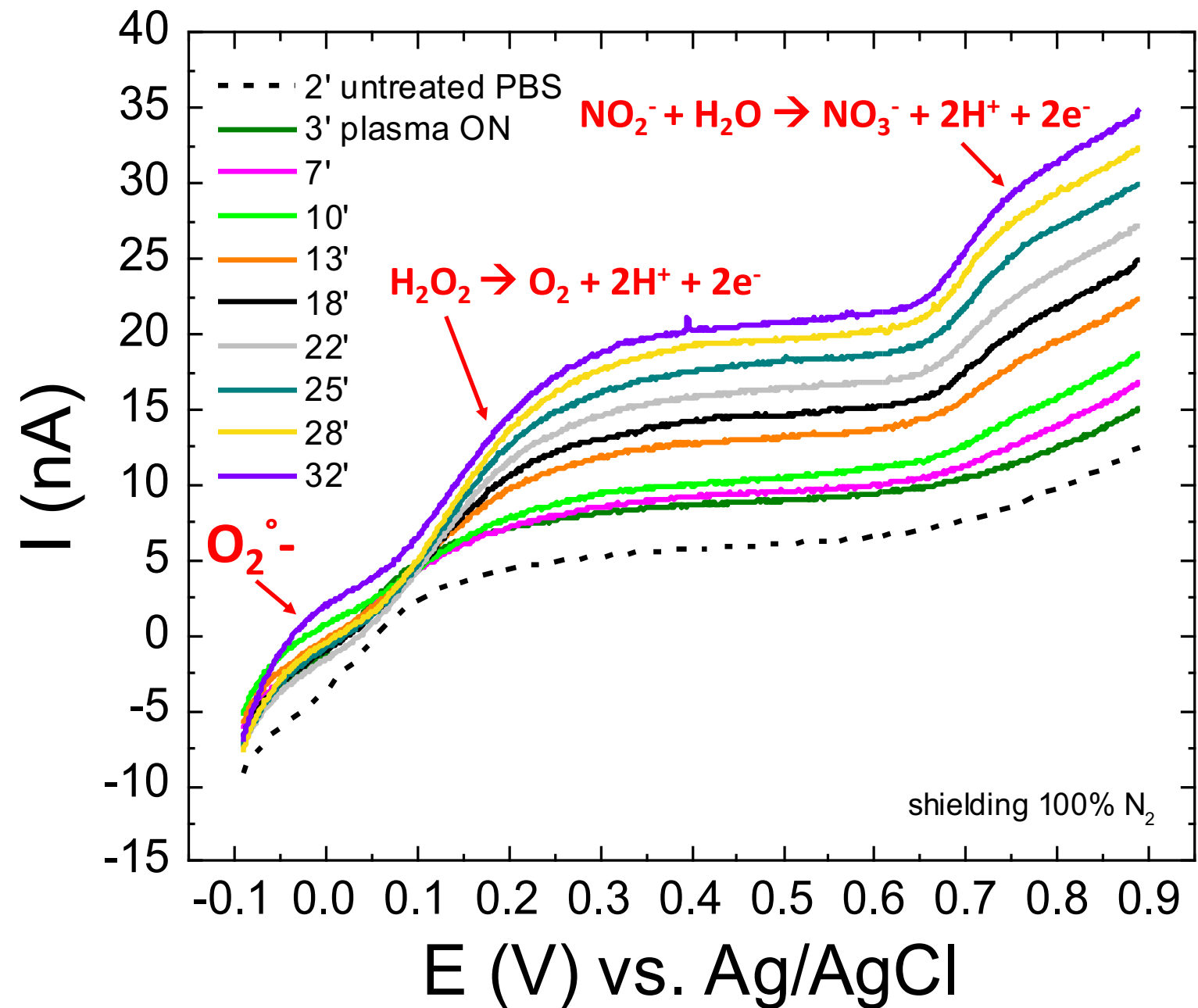
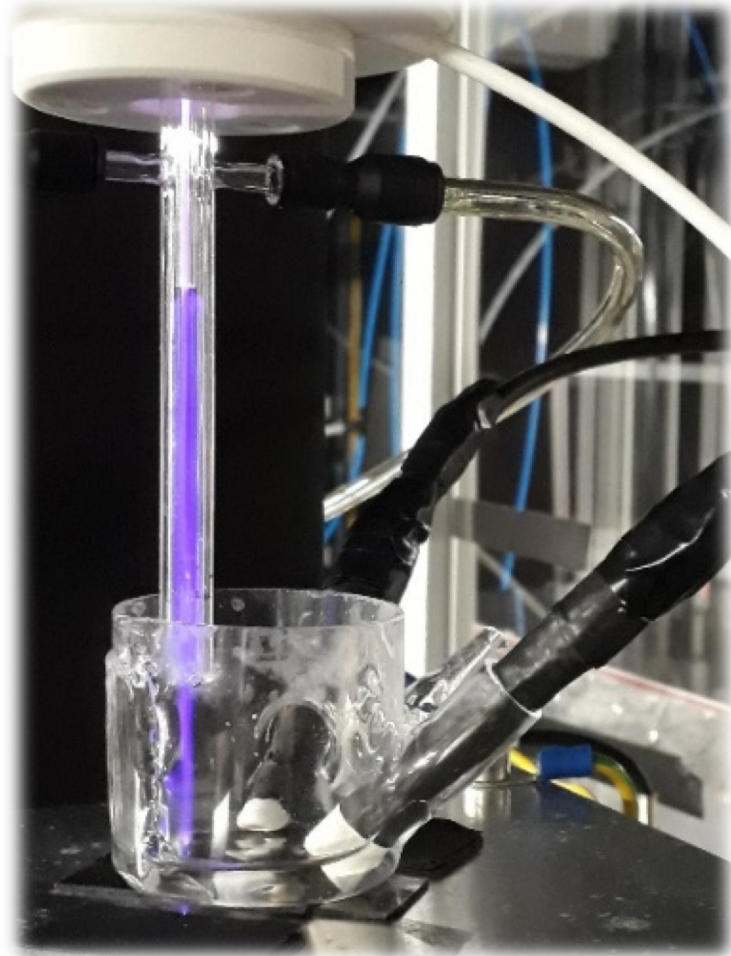
WE = Platinized Pt disk ($25\ \mu\text{m}$ $\varnothing$, $37.5\ \mu\text{C}$)
Ref = Ag/AgCl wire
CE = Pt wire



Black Pt working electrode (enhanced selectivity and sensibility)



GAS-LIQUID INTERACTION in situ, during plasma exposure

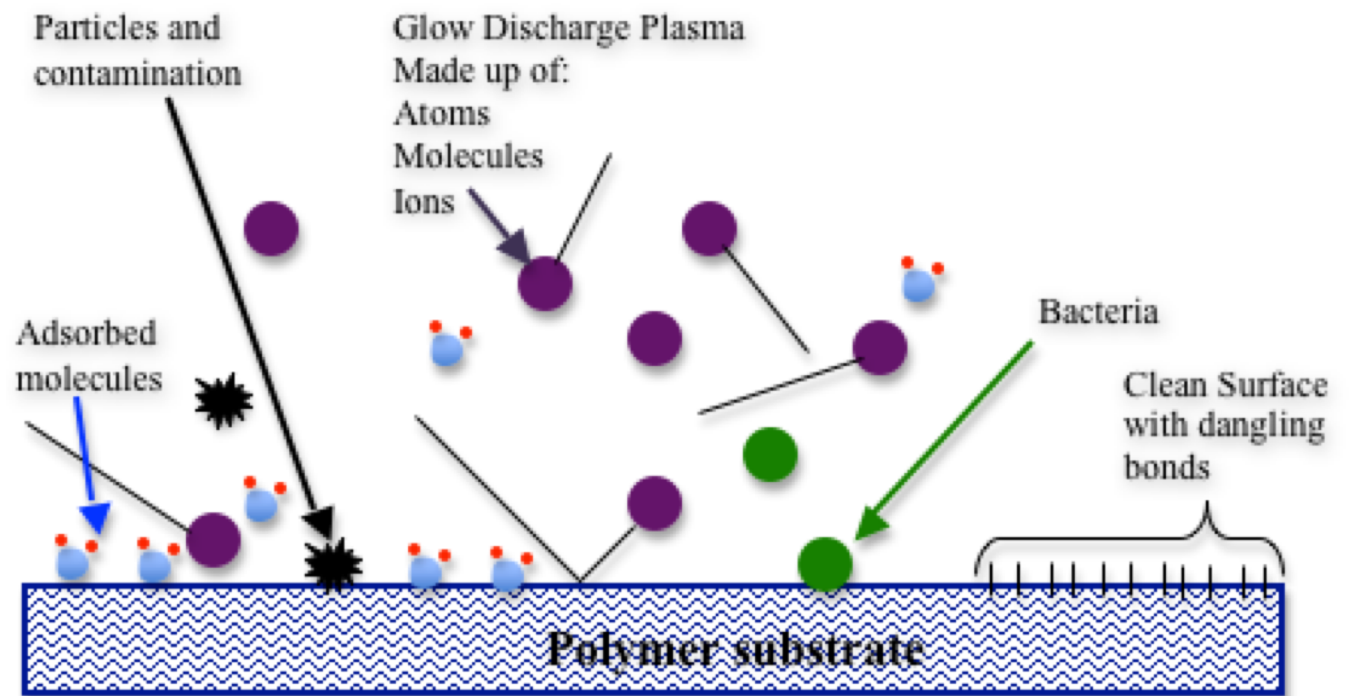


**Possibility to follow long-lived and short-lived RONS
produced in PBS during plasma exposure**

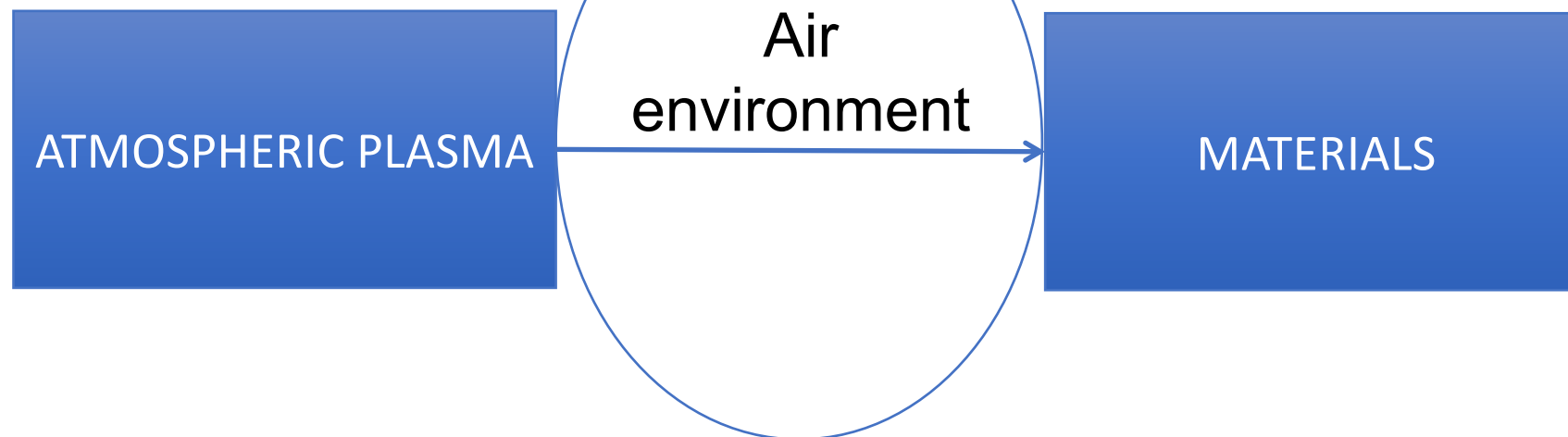
IONIZATION WAVE in interaction with materials

Lack of mechanisms understanding

What are the interactions?



https://en.wikipedia.org/wiki/Biomaterial_Surface_Modifications



Numerous applications

Cleaning

Etching

Functionalization

Coating

Sterilization

Enhanced cell growth

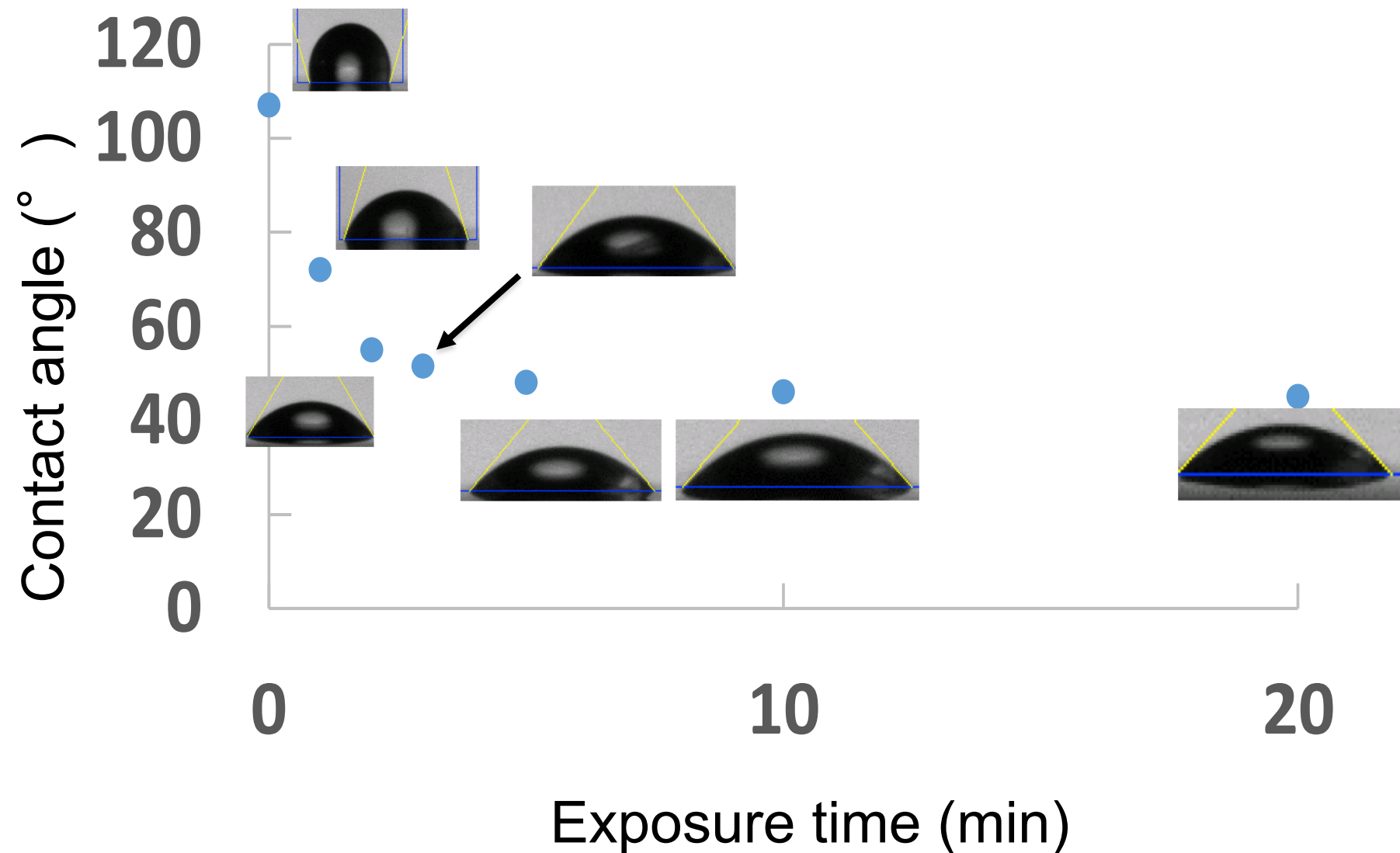
...

These atmospheric plasmas can be used for polymer surface treatments ...

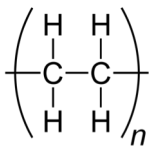
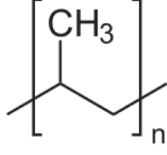
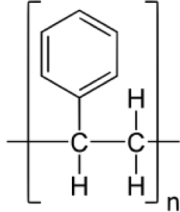
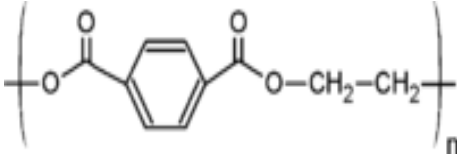
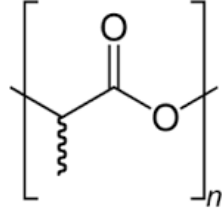


Plasma He + 1% O₂

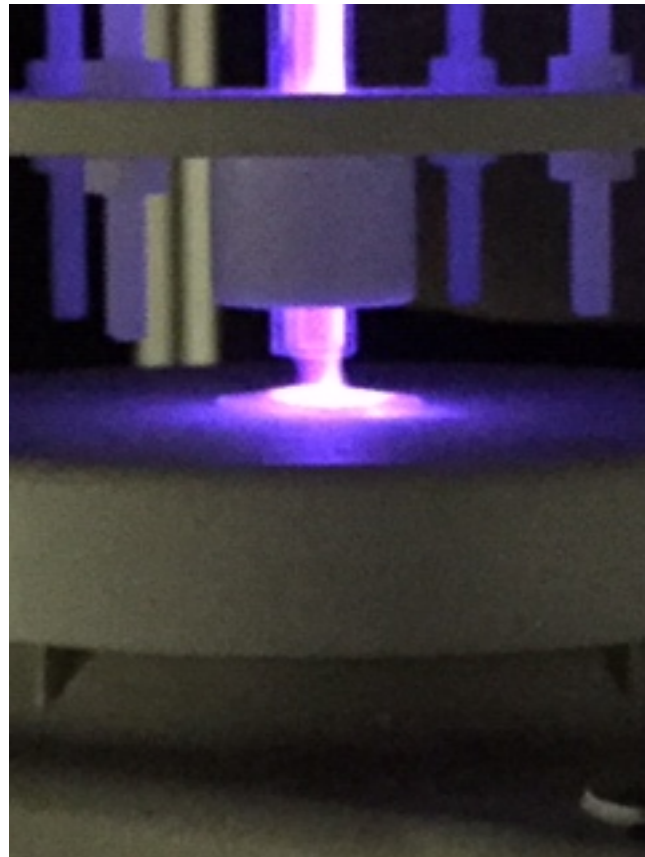
Exposition of Thermoplastic Polyurethane (TPU)
Wettability analyses of the surfaces exposed



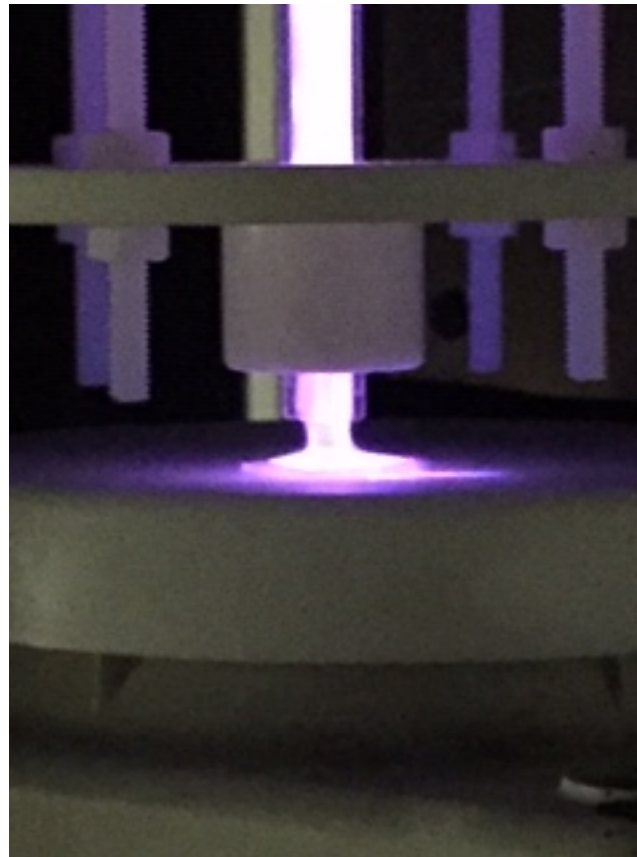
Different types of polymers exposed...

PE	PP	PS	PET	PLA
				

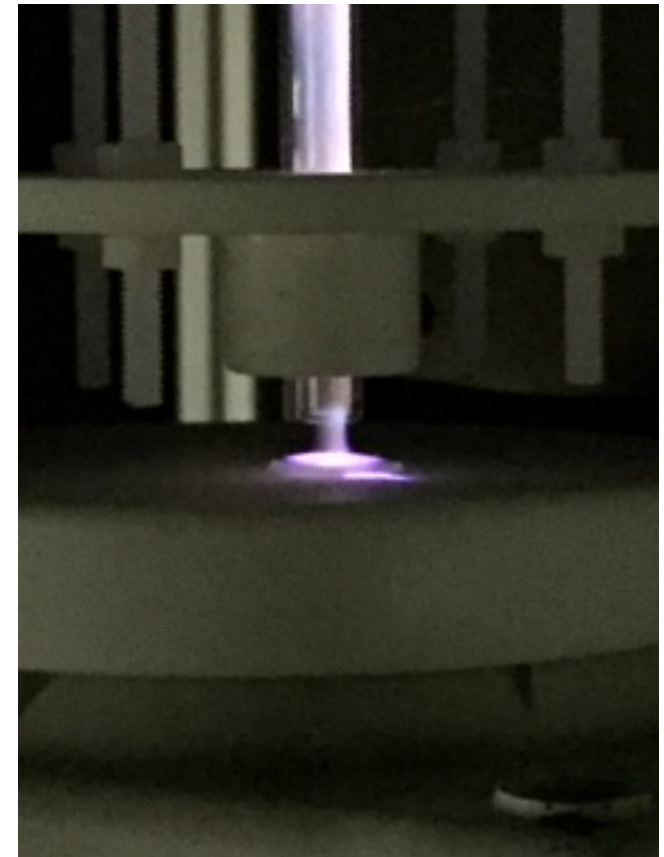
He - N2 CAP



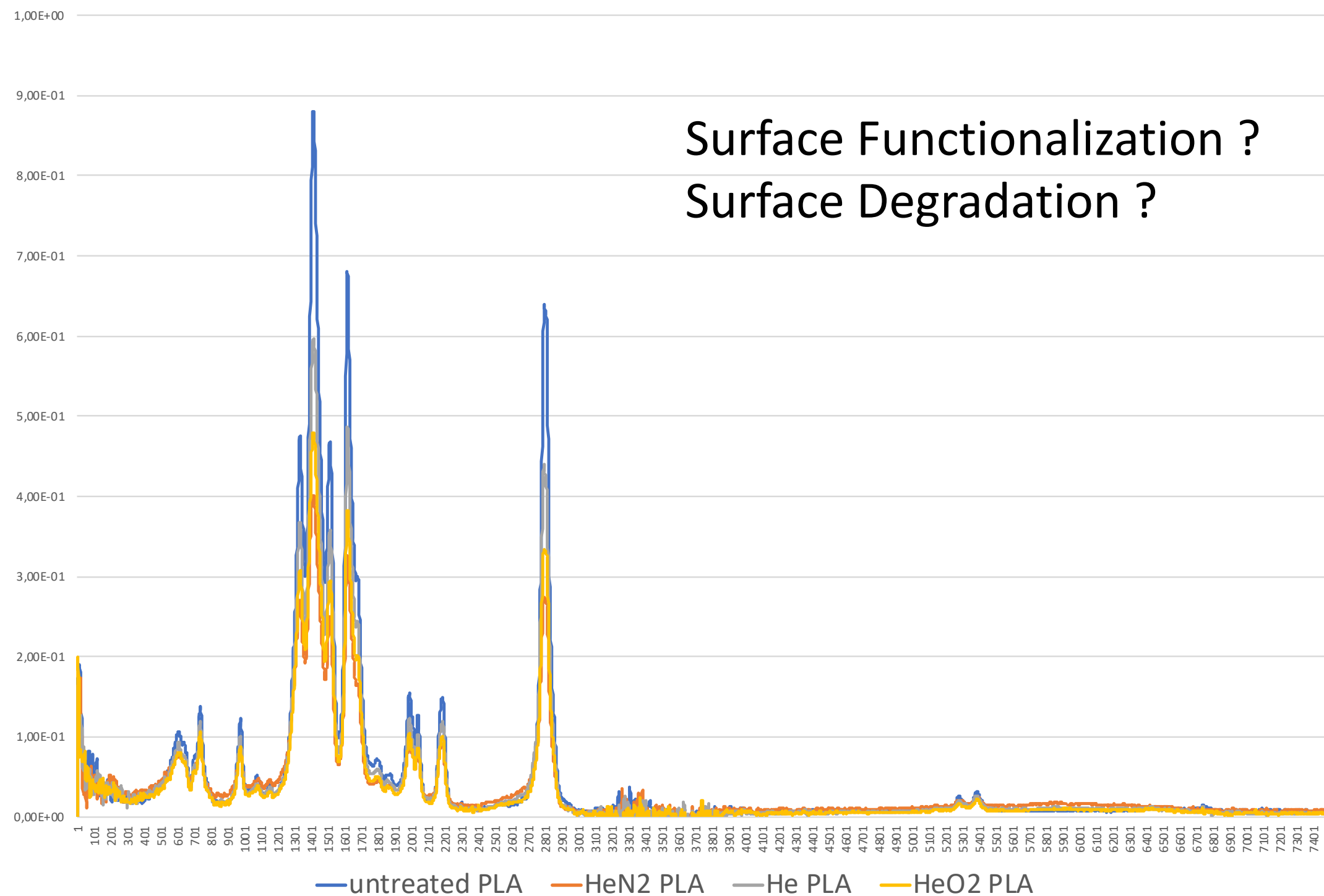
He CAP



He - O2 CAP

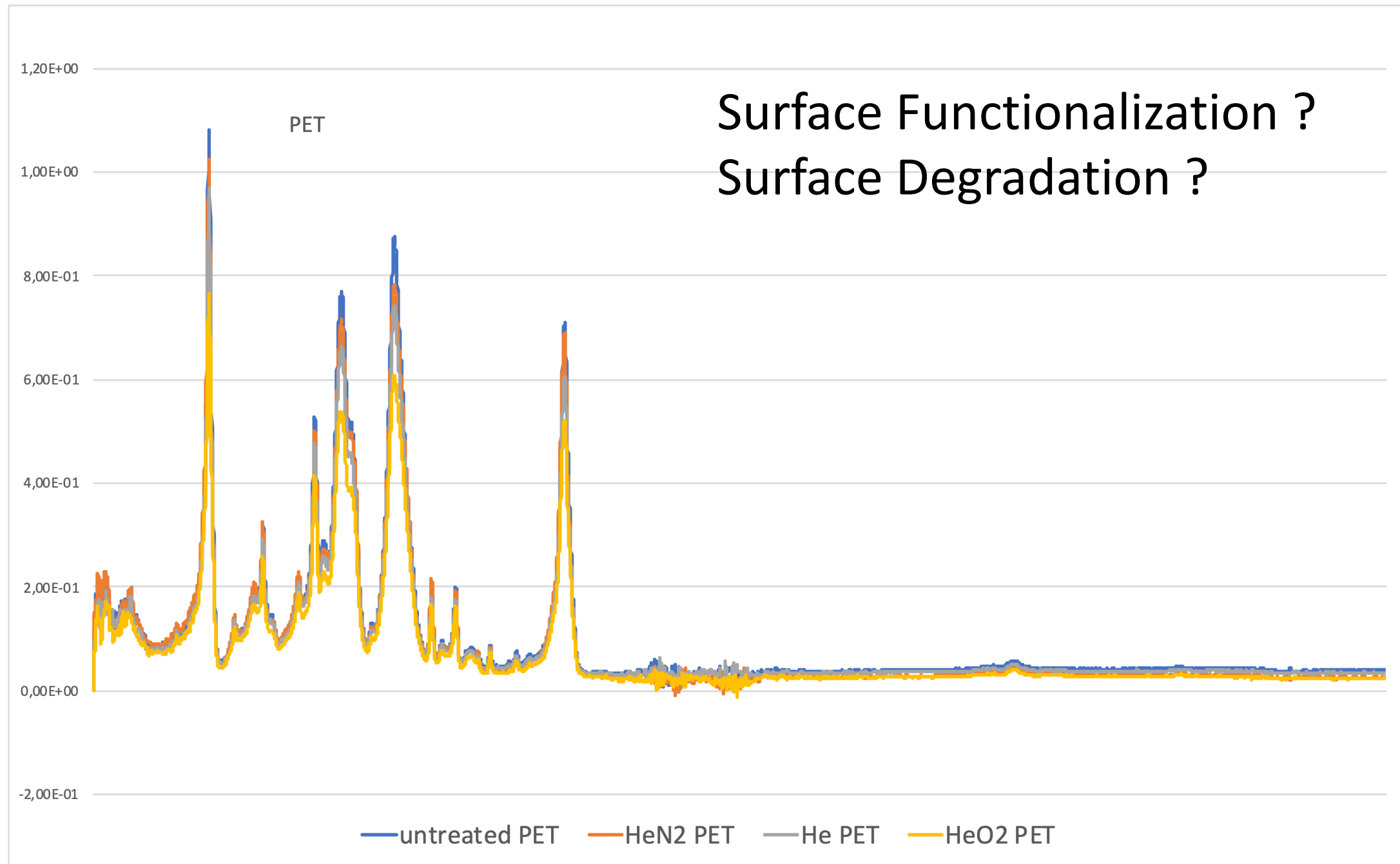


IR-ATR analyses of PLA substrates exposed



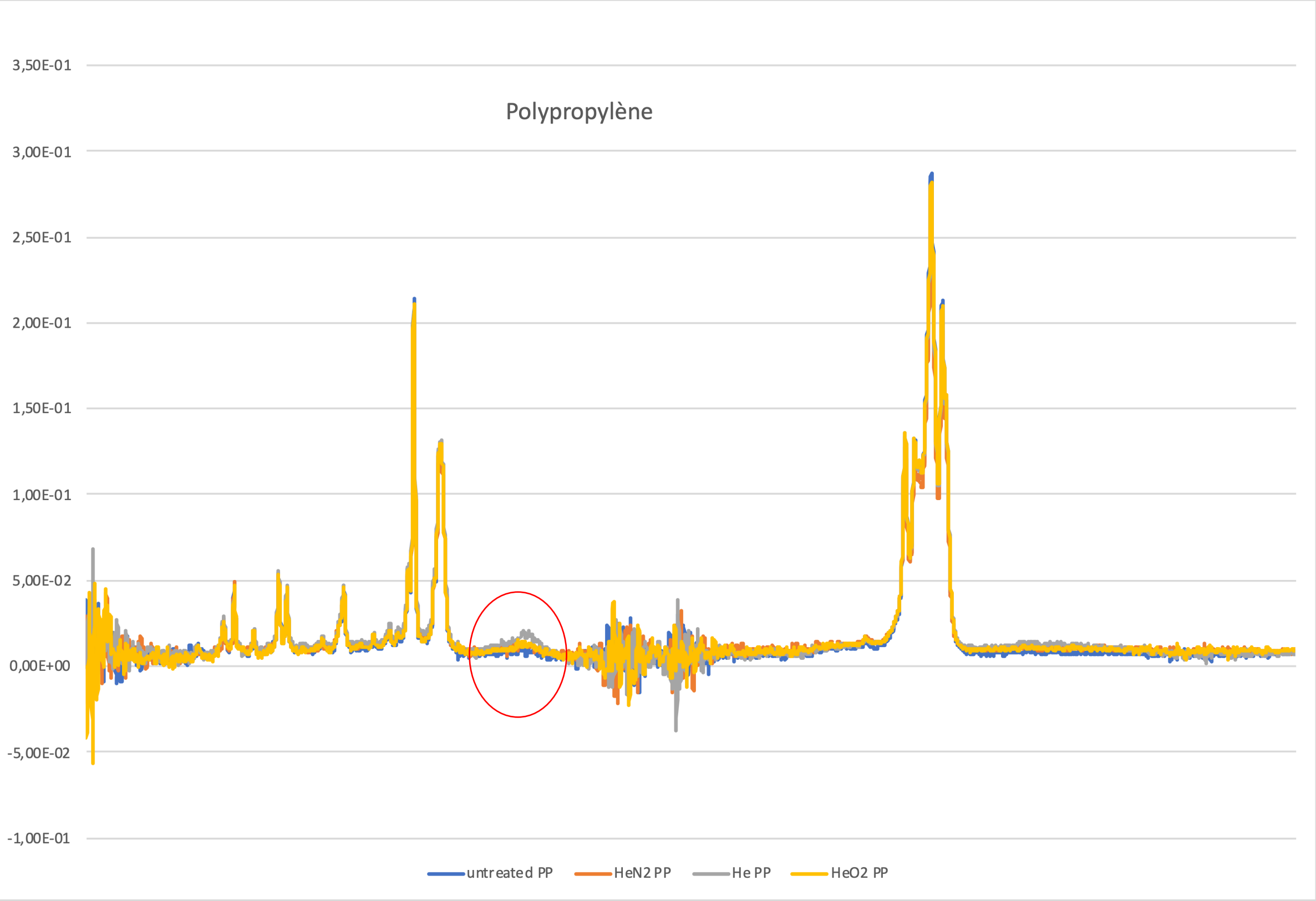
Another example

IR-ATR analyses of PET substrates exposed



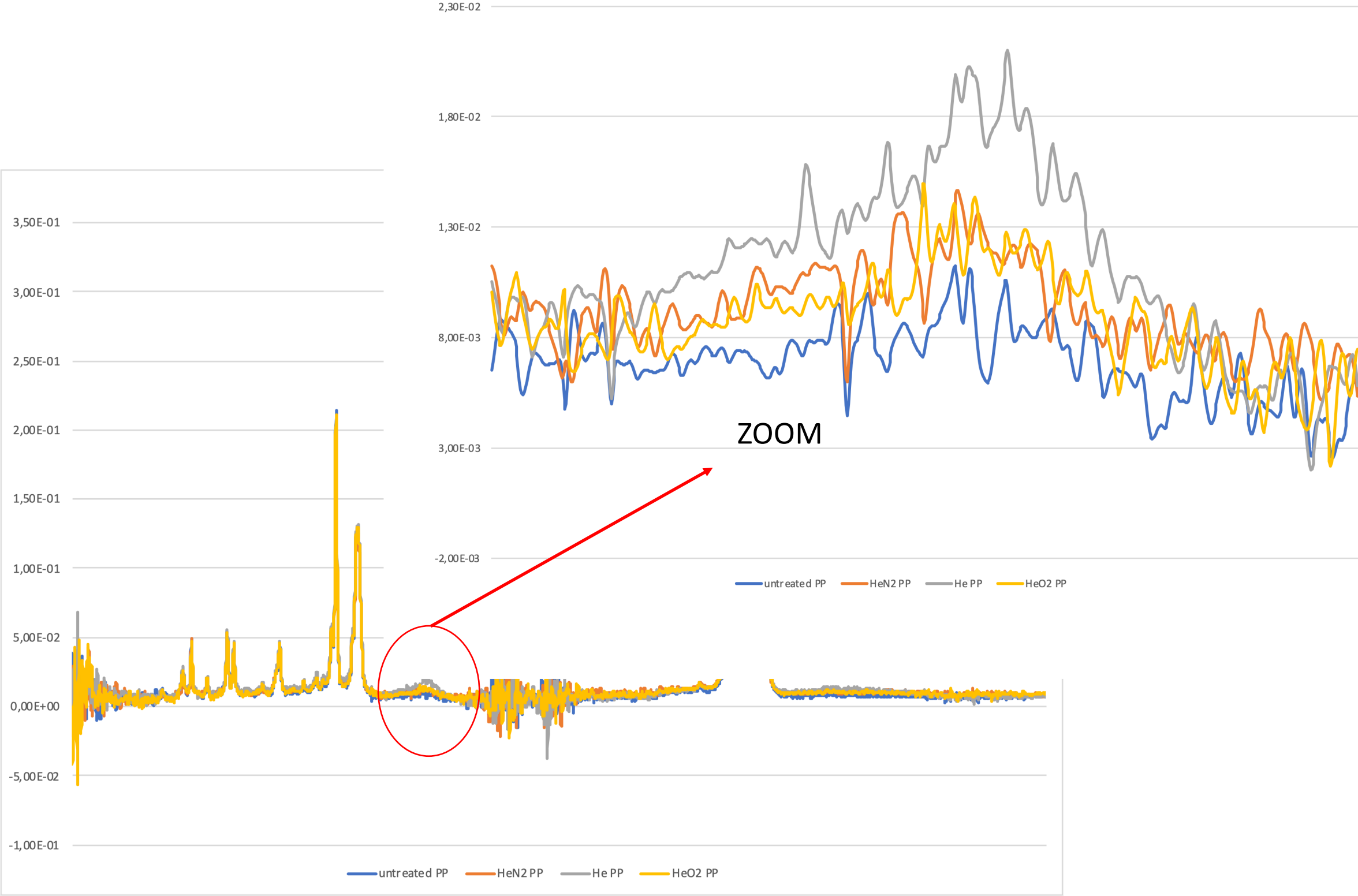
Another example

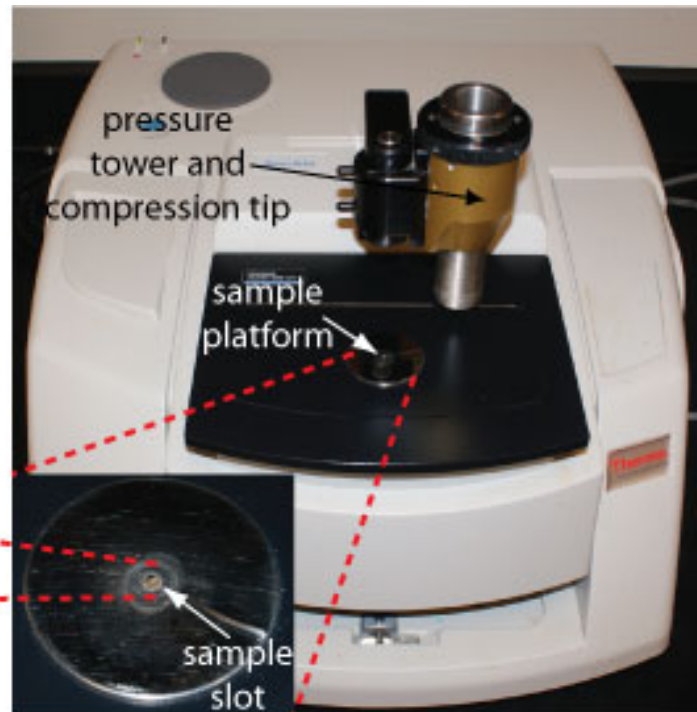
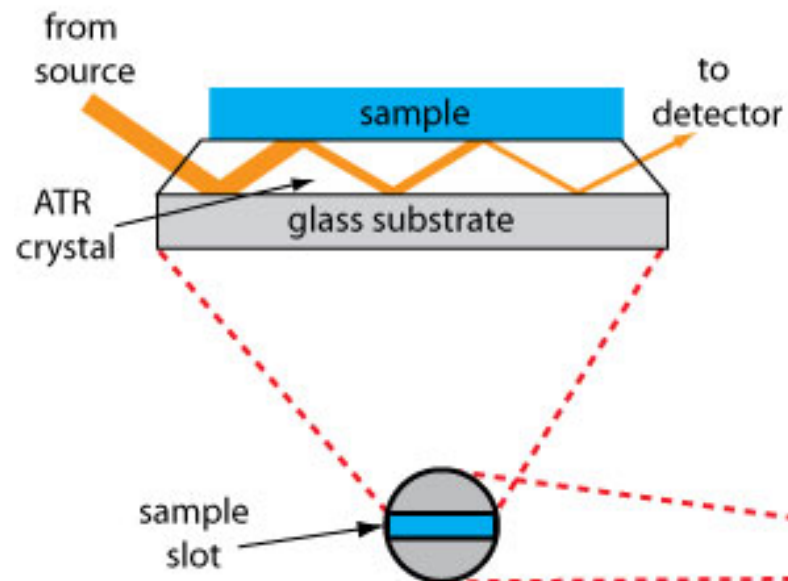
IR-ATR analyses of PP substrates exposed



Another example

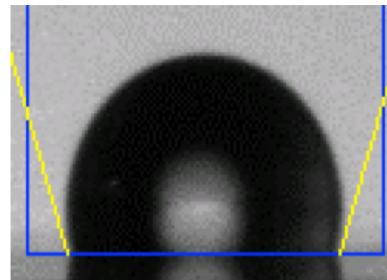
IR-ATR analyses of PP substrates exposed





IR ATR is a simple method to follow qualitatively surface oxydation

As well as wetabilty analyses



Before plasma exposure



After plasma exposure

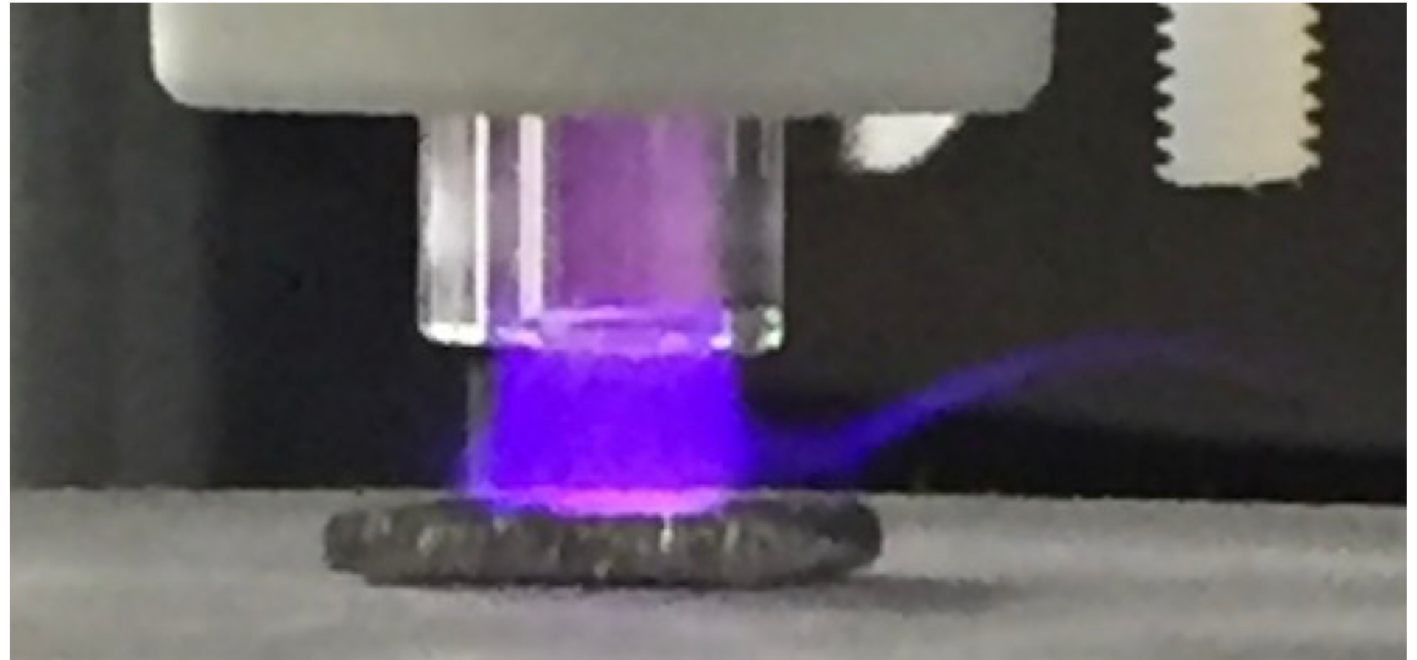
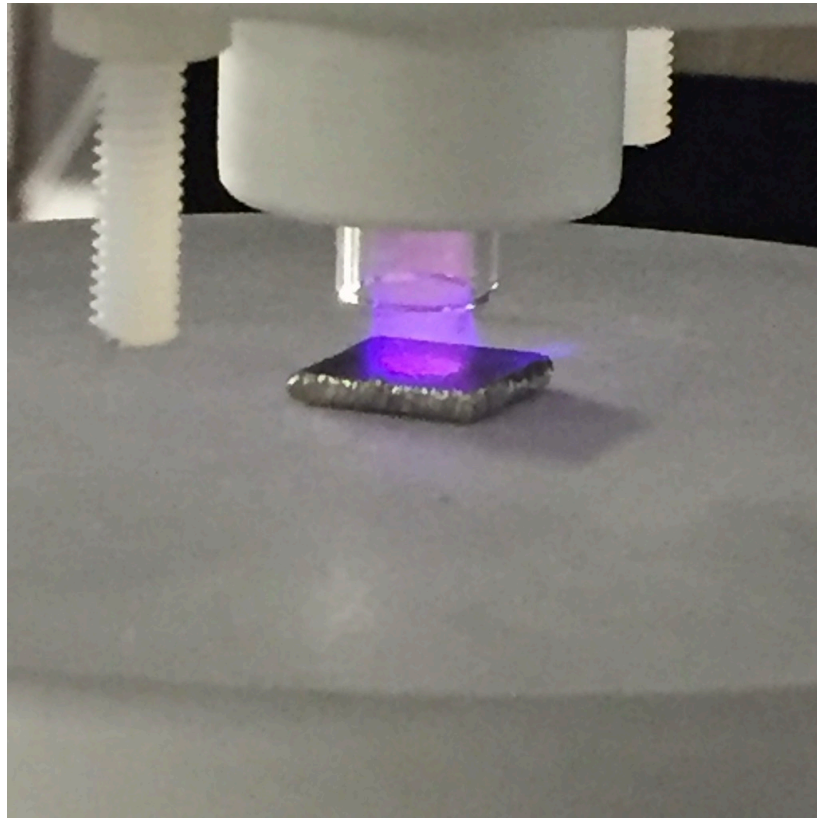
But ...

chemical characterizations are needed (XPS)

Surface aging must be controlled, which is linked to the gaseous media in which the samples are stored!

Work in progress...

Steel processing tests

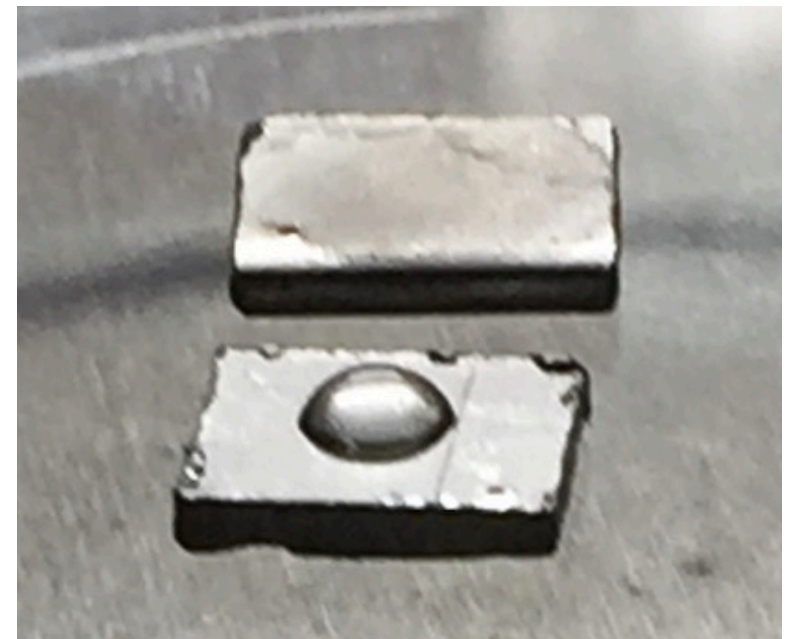


The plasma bounces on the surface

First wettability tests
Water drop spreading

Cleaning ?

Work in progress...



CONCLUSION

Ionization waves produced at atmospheric pressure are very interesting processes for the production of reactive species usefull for biomedical applications

Discharges mechanisms have to be studied for the production of these reactive species: charges, radicals and excited states, photons

Electrochemistry methods are very usefull to follow the production of chemical species produced in liquids during plasma exposures

The control of the environments (gas and liquid) is capital for a better understanding of the interactions mechanisms between plasmas and liquids or solid materials

Finally

« Garbures » are complex to analyse and difficult to reproduce, but we love to cook and we can sometimes find new recipes !



le ragoût de pattes de cochon
« pig's leg stew »



The « POUTINE »

Merci

To the organising committee
To Cora Roy for her help and
of course to Diego Mantovani



and THANK YOU FOR YOUR ATTENTION