Time-resolved optical emission spectroscopy on CO_2 nanosecond pulsed discharges

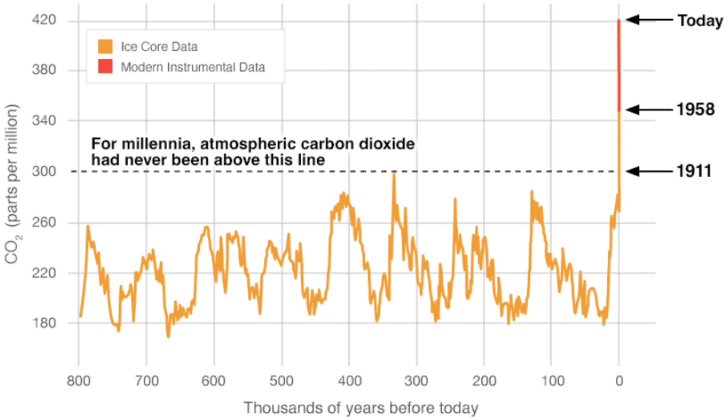
Thesis Presentation

Alberto Appoloni

Master's thesis under the supervision of Prof.Luca Matteo Martini

Global warming

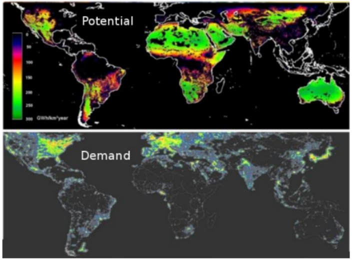
- For centuries CO_2 concentration stable
- In the last decades alarming increase in CO_2 concentration up to 420 ppm due to fossil fuels combustion
- To mitigate the increase we need to reduce the use of fossil fuels

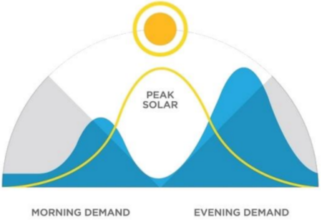


Limitation of Renewable energies

- Variability/intermittency
- Dephasing between production and demand peaks
- Spatial inhomogeneity
- Low energy production for unit surface

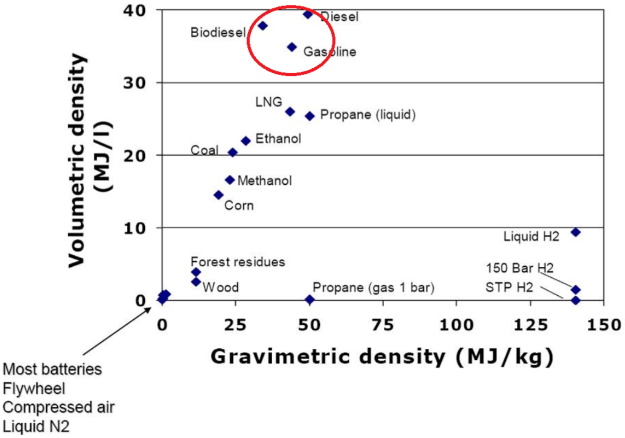
Energy storage is essential





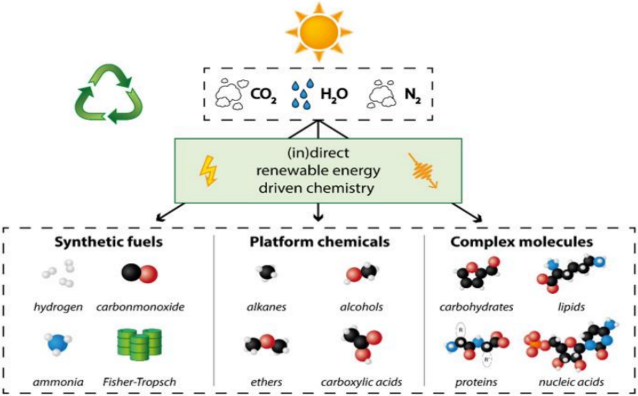
Energy Storage

- Ideal energy vector close to the red circle (Diesel or Gasoline)
- Batteries have a low volumetric and gravimetric density
- Produce fuels artificially is a valuable option



Power-to-X

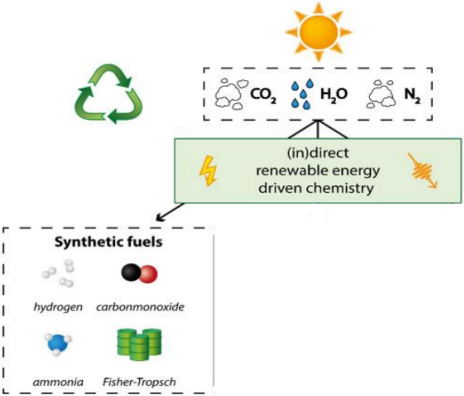
- Use renewable energy to drive chemical reactions
- Abundant molecules can be used to produce synthetic fuels and feedstocks



- Difficult to activate these molecules because very stable

Power-to-X

- Use renewable energy to drive chemical reactions
- Abundant molecules can be used to produce synthetic fuels and feedstocks



- Difficult to activate these molecules because very stable

Conventional thermal processes vs non-thermal processes

- Thermal processes $\rightarrow$ energy equally distributed in all degrees of freedom
- Non-Thermal processes $\rightarrow$ energy **not** equally distributed in all degrees of freedom

Conventional thermal processes vs non-thermal processes

Application of an **electric field** to a gas

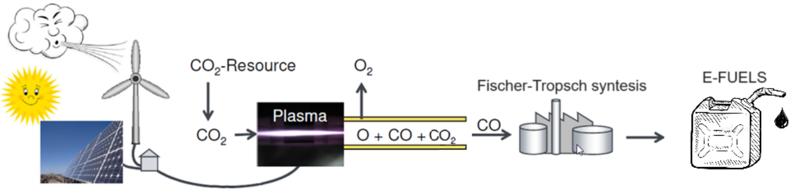
→ Accelerated **electrons** transfer energy to molecules mainly by **inelastic collisions**

→ **Electron-induced** molecular dissociation at low gas temperature

→ **Dissociation** of CO_2

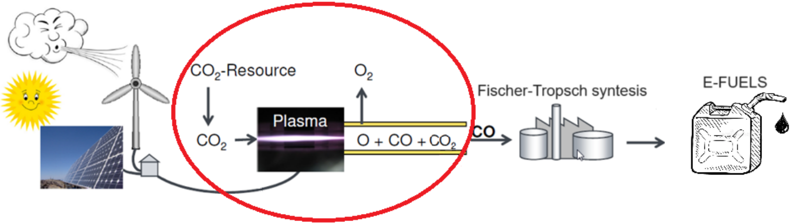
Power-to-Fuel: electrical discharges

- Alternative to thermal processes
- Scalability
- Low inertia



Power-to-Fuel: electrical discharges

- Focus on this part to understand dissociation processes



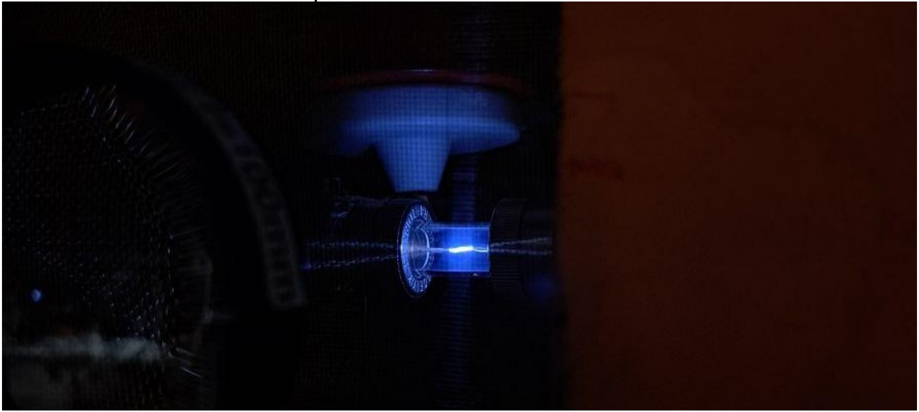
Why nanosecond repetitively pulsed discharges?

Characteristics:

- Rapid voltage variation
- Nanosecond rise times
- FWHM of $\sim$ 10 ns

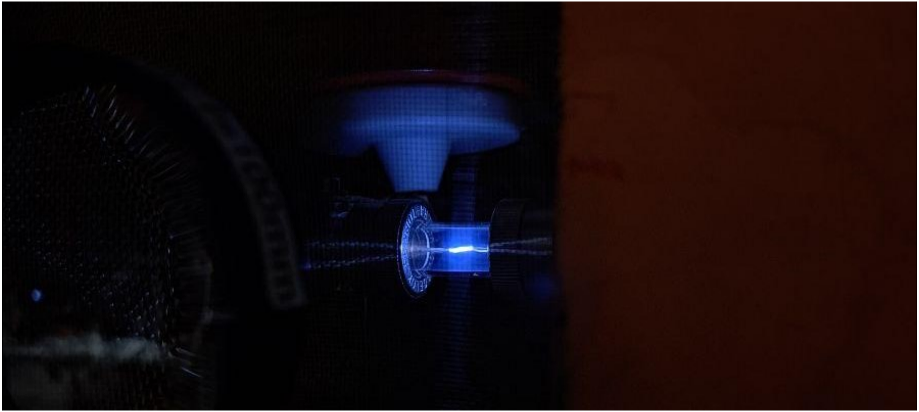
$\longrightarrow$

- Operating at atmospheric pressure
- Enhance non-equilibrium conditions



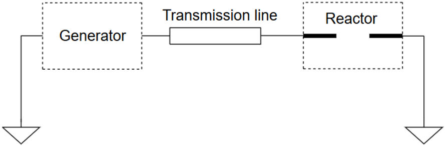
Nanosecond repetively pulsed discharges

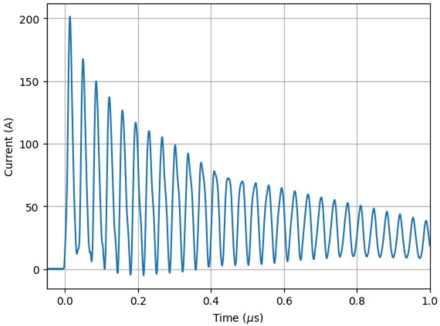
1. Spatial inhomogeneity
2. Temporal inhomogeneity



Scientific issues

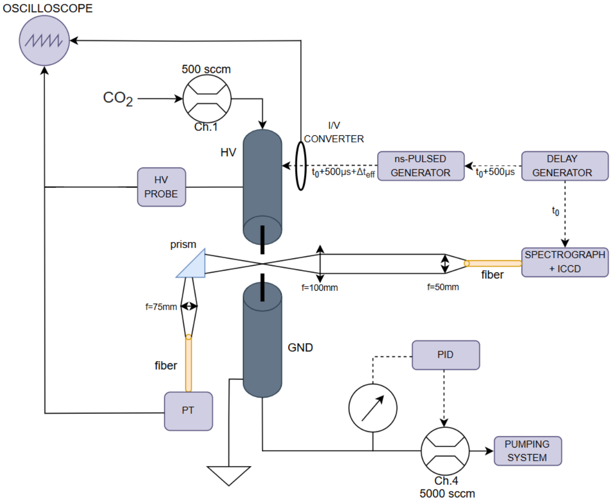
1. Spatial inhomogeneity
2. Temporal inhomogeneity
3. Current reflections



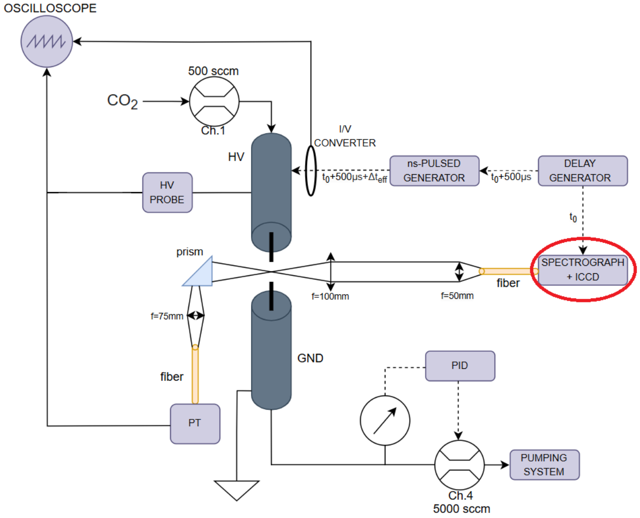


Experimental Setup

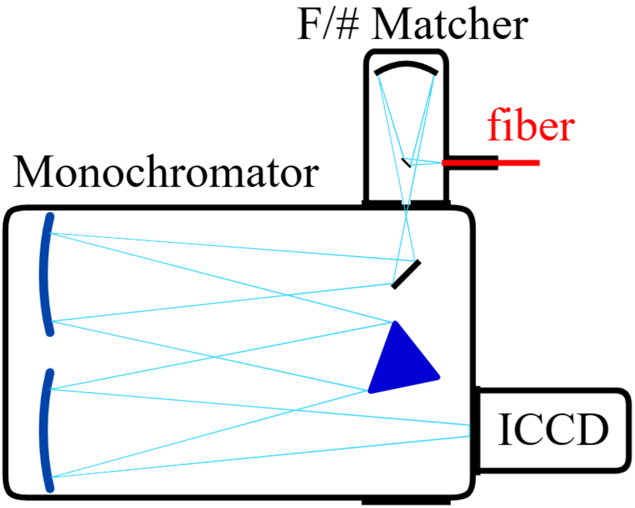
- Generator and spectrograph synchronization is essential to study the temporal evolution of the discharge



Experimental Setup

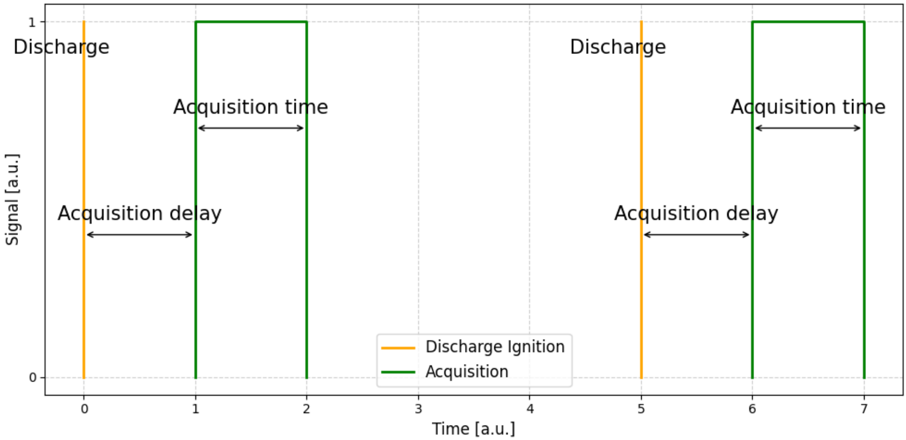


Experimental Setup: Spectrograph



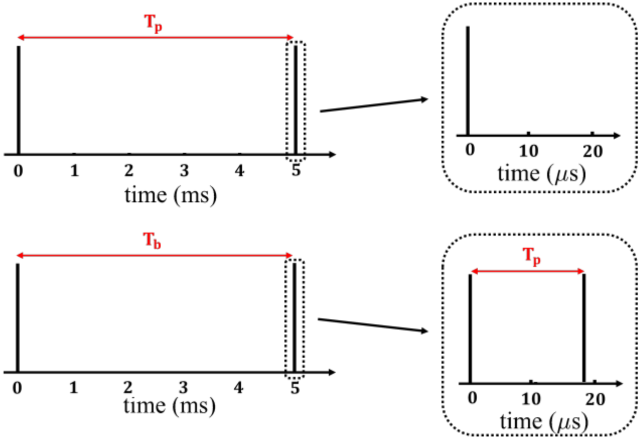
Experimental Setup: Spectrograph

- "Acquisition time" gives the time resolution
- "Acquisition delay" allows the temporal scanning of the discharge



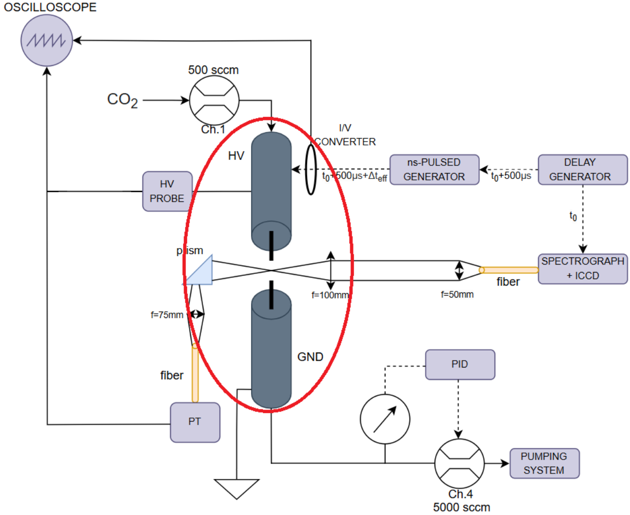
Experimental Setup: mode types

- Continuous mode: 1 pulse each 5 ms
- Burst mode: 2 pulses separated by 18 μs each 5 ms

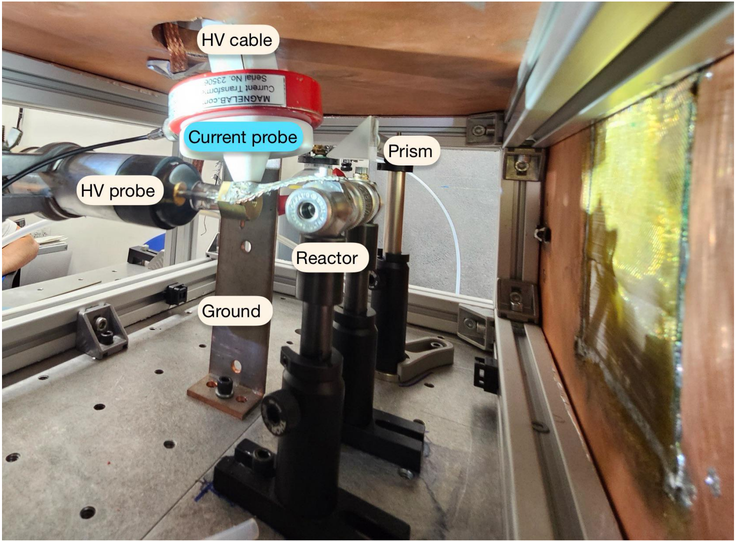


Experimental Setup

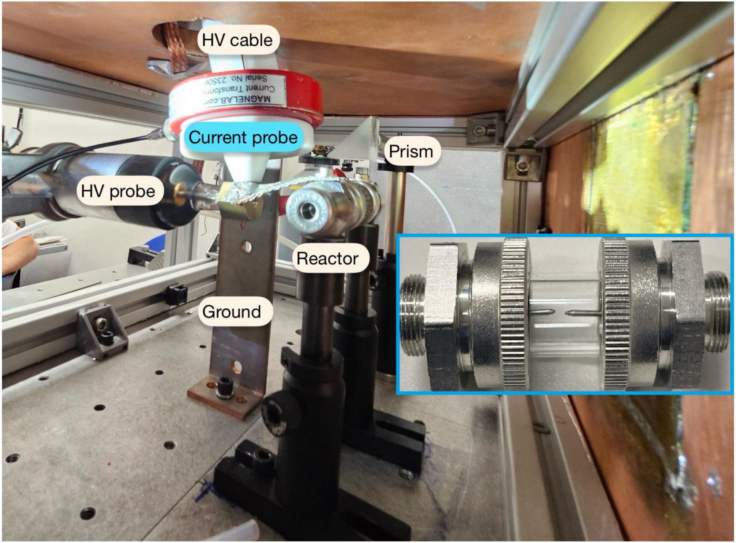
- Electrical diagnostics is essential to measure IV characteristics



Experimental Setup: Electrical diagnostics

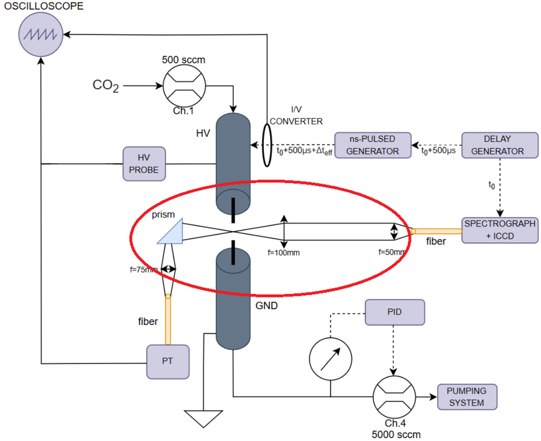


Experimental Setup: Electrical diagnostics

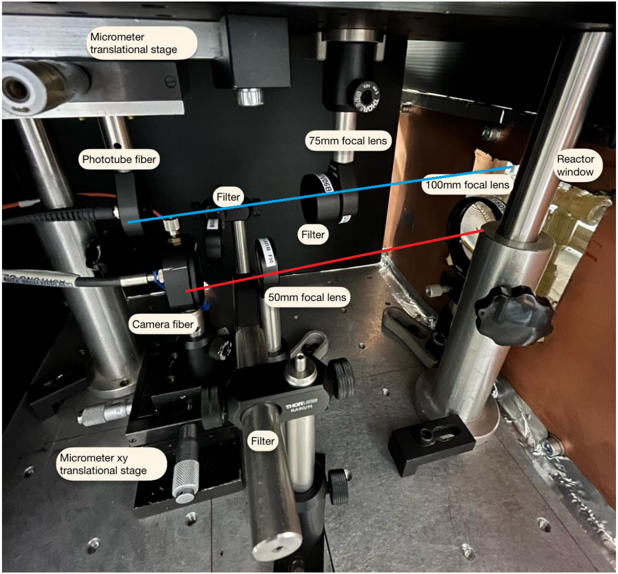


Experimental Setup

- Optical setup directs the light to the spectrograph and to the phototube
- Spectrograph $\rightarrow$ Time-resolved optical emission spectroscopy
- Phototube $\rightarrow$ Time evolution of the spectrally integrated signal

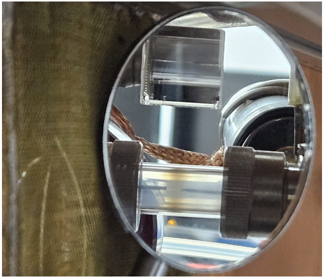


Experimental Setup: Optical Diagnostics



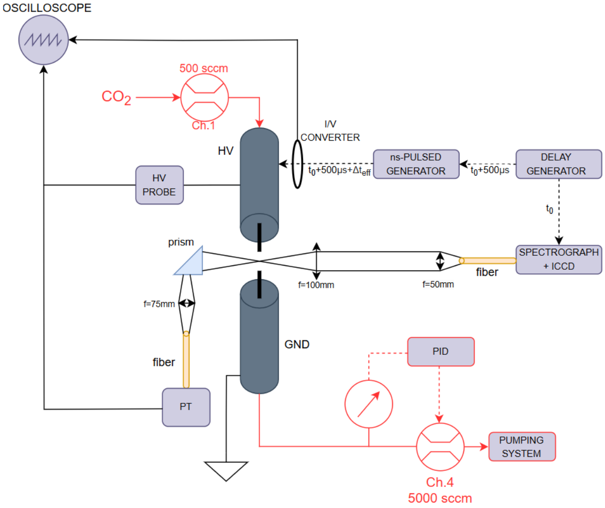
2 pathways:

- Upper → Phototube
- Bottom → Spectrograph



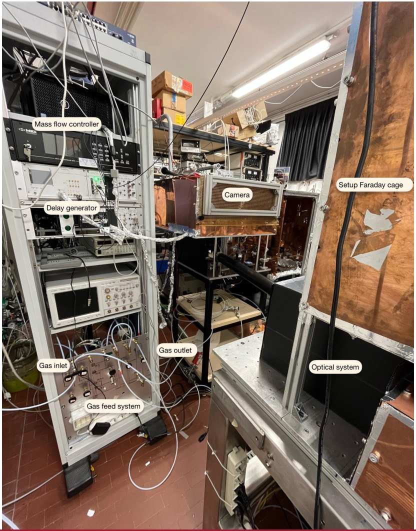
Experimental Setup: Gas feed system

- Pressure regulation



Experimental Setup

- Shielding with Faraday cages
- Space electrical equipment as far apart as possible



Scientific issues

1. Spatial inhomogeneity
2. Temporal inhomogeneity

Scientific issues

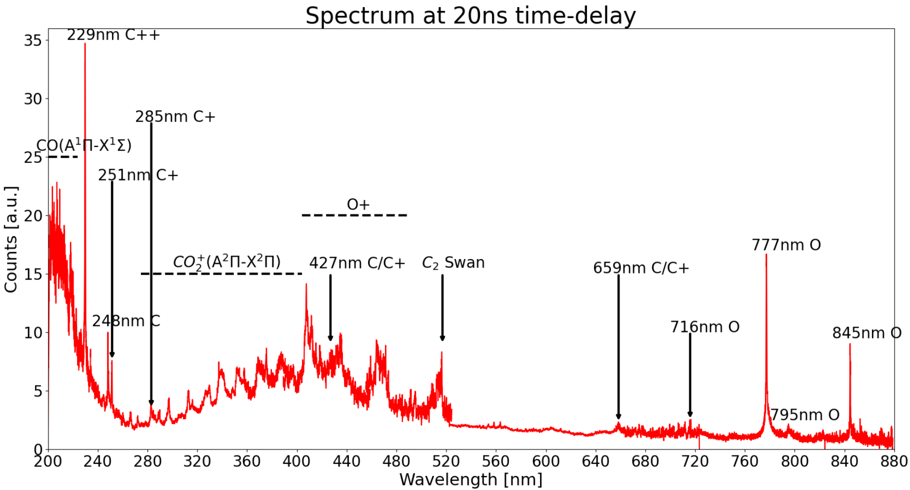
1. Spatial inhomogeneity
2. Temporal inhomogeneity

Configurations:

1. Electrodes gap: 5.5 mm, **center**, continuous mode, line not matched
2. Electrodes gap: 5.5 mm, **cathode**, continuous mode, line not matched

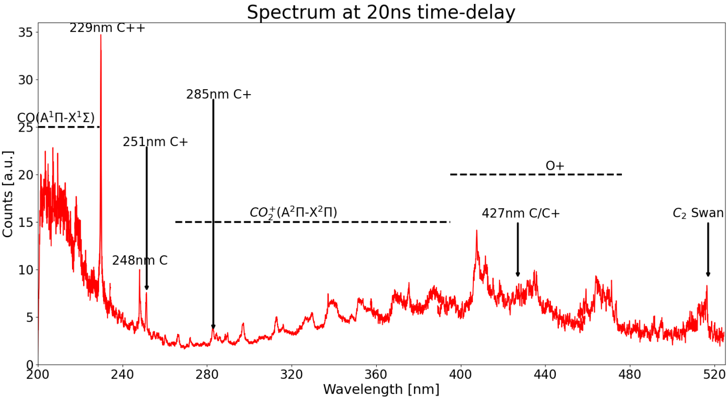
Time-resolved optical emission spectroscopy(TR-OES) at the center

- Characterization of the atomic and molecular emissions



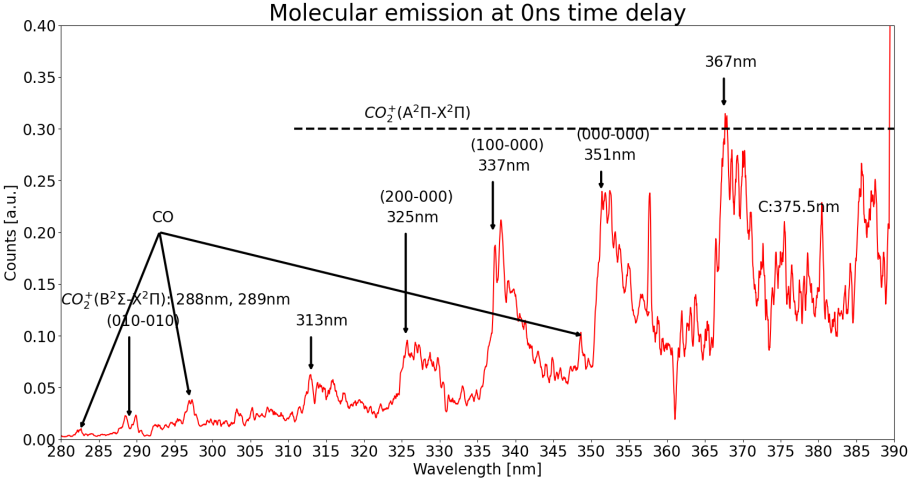
TR-OES: Zoom in the 200-530 nm range

- C^{++} emission is the most prominent
- O^{+} emission in the 400-480 nm range
- ${CO_2}^{+}$ Fox Duffendack Barker system $(A^2\Pi - X^2\Pi)$ in the range 280-450 nm
- CO fourth positive system $(A^1\Pi - X^1\Sigma)$ in the range 200-250 nm



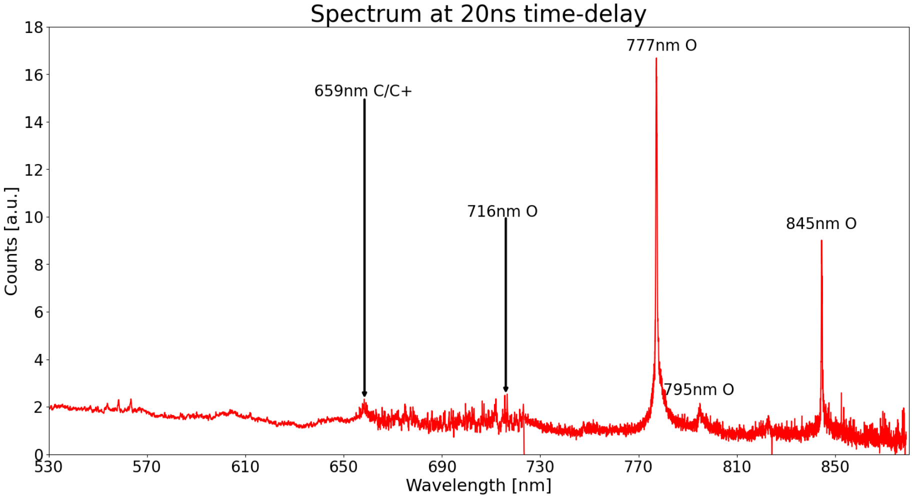
TR-OES: Molecular emissions

- Ionization CO_2^+
- Certain degree of dissociation CO



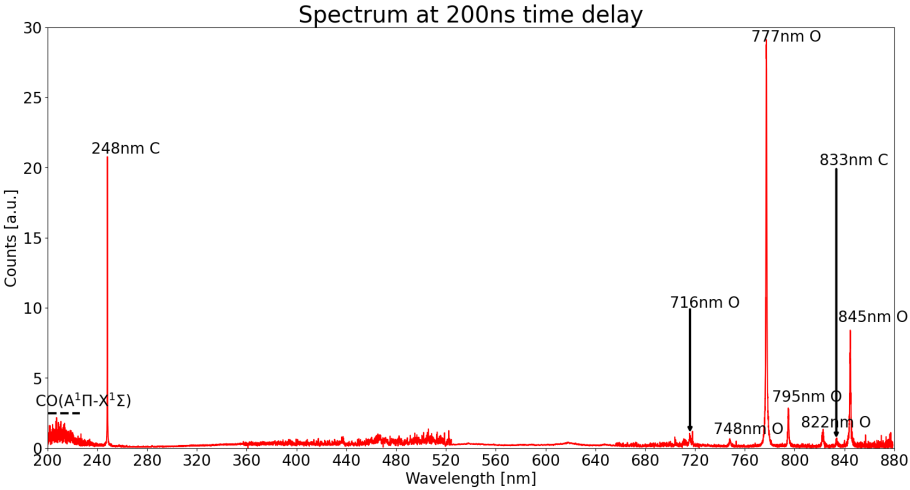
TR-OES: Zoom in the 530-880 nm range

- 777 nm O emission is the most prominent



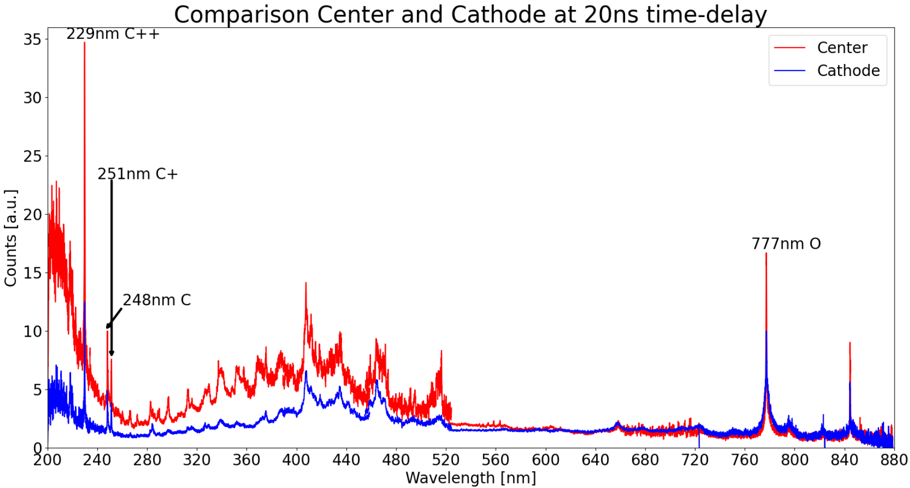
TR-OES: Center

- Dominance of neutral species emission



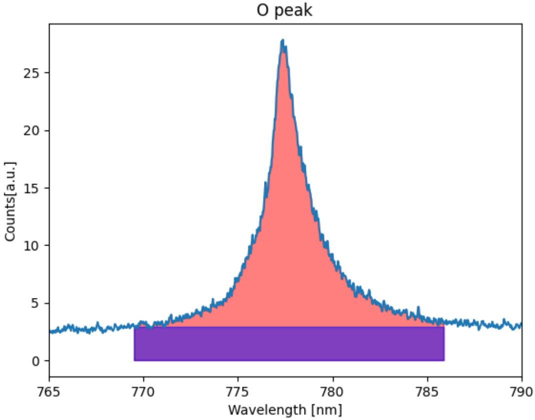
TR-OES: Comparison spectrum center and cathode

- Same emission profile feautures at the center and at the cathode
- Interesting to study the time evolution of the atomic lines



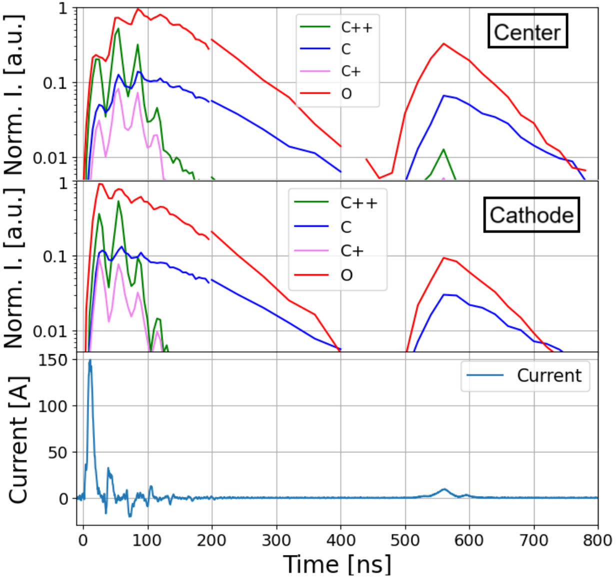
Emission line integration

- C line at 247.86 nm;
- C^+ doublet at 250.91 nm and 251.21 nm;
- C^{++} at 229.68 nm;
- O triplet at 777.19 nm, 777.42 nm and 777.54 nm.



TR-OES: Comparison center and cathode

- Integrated emission lines and Phototube signal follow current reflections
- At the cathode, the most prominent peak is the first one
- At the center, the most prominent peak is the third one



Scientific issues

1. Spatial inhomogeneity
2. Temporal inhomogeneity
3. Current reflections

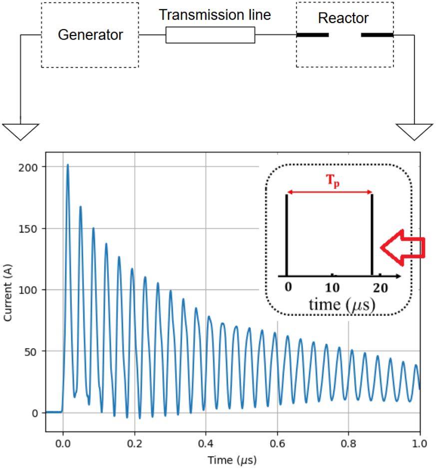
Scientific issues

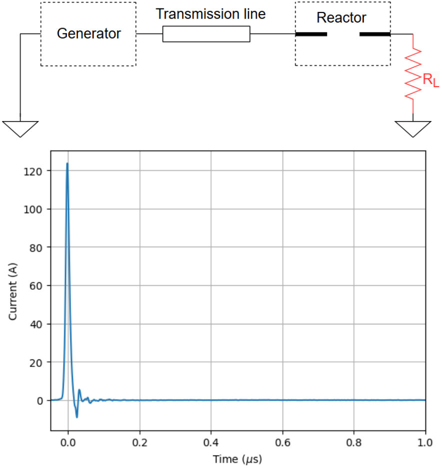
1. Spatial inhomogeneity
2. Temporal inhomogeneity
3. Current reflections

Configurations:

1. Electrodes gap: 2.4 mm, burst mode, line **not matched**
2. Electrodes gap: 2.4 mm, burst mode, line **matched**

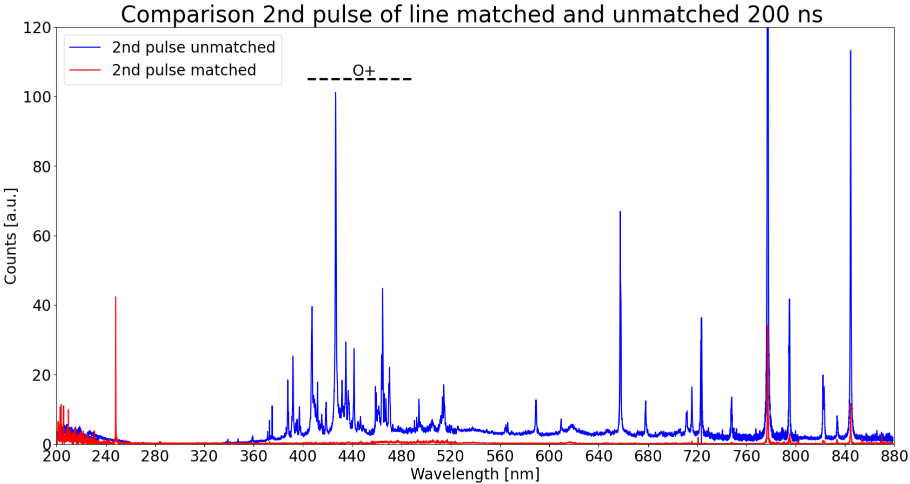
Preliminary steps: Impedance matching





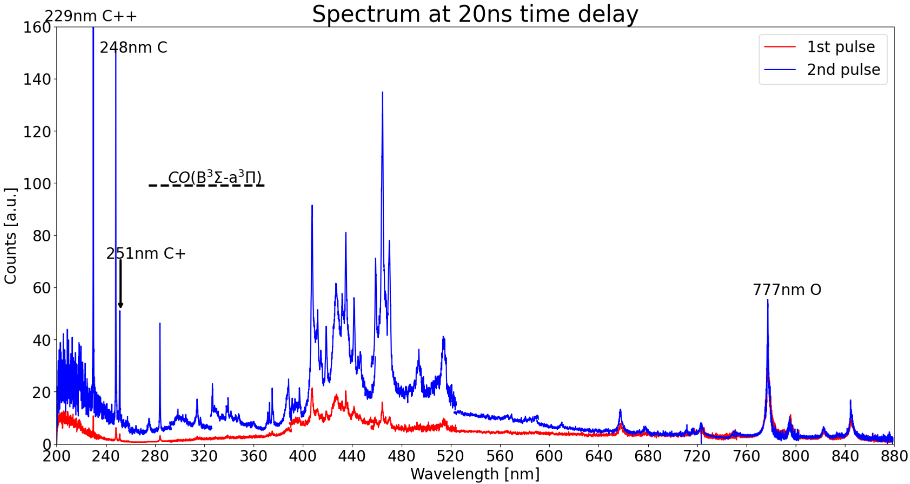
Comparison matched and unmatched line

- Species excitation greater for line unmatched due to current reflections
- O^+ excitation is still present for line unmatched



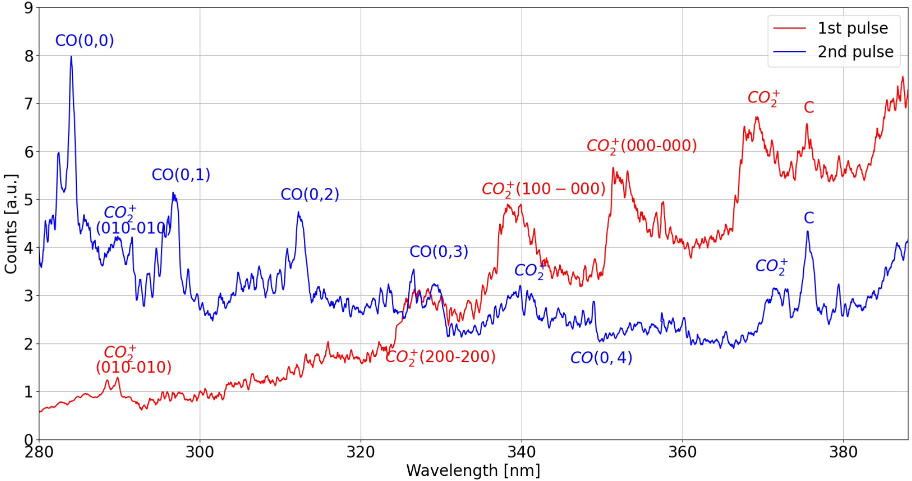
TR-OES: Line matched in impedance

- Remarkable increase in signal for the second pulse
- C^{++} emission stronger in the second pulse
- Different molecular emission features



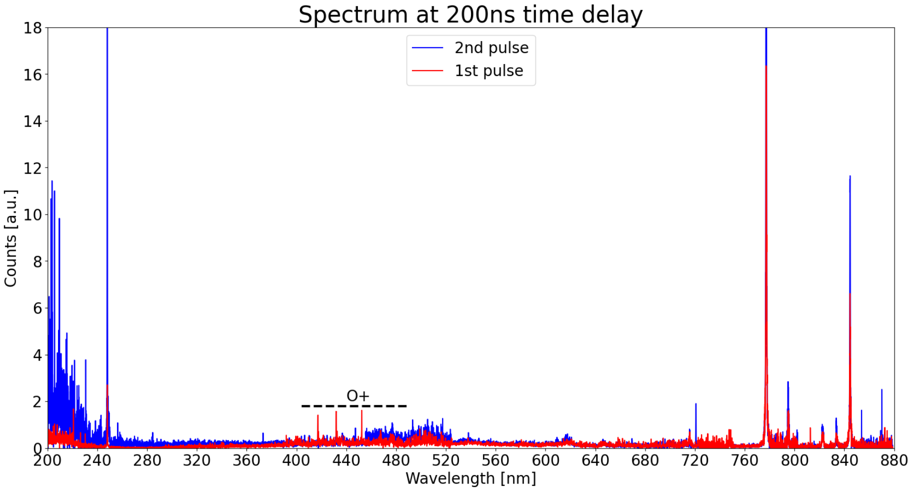
TR-OES: Molecular comparison first and second pulse

- CO emission features in the second pulse
- Just CO_2 ionization in the first pulse



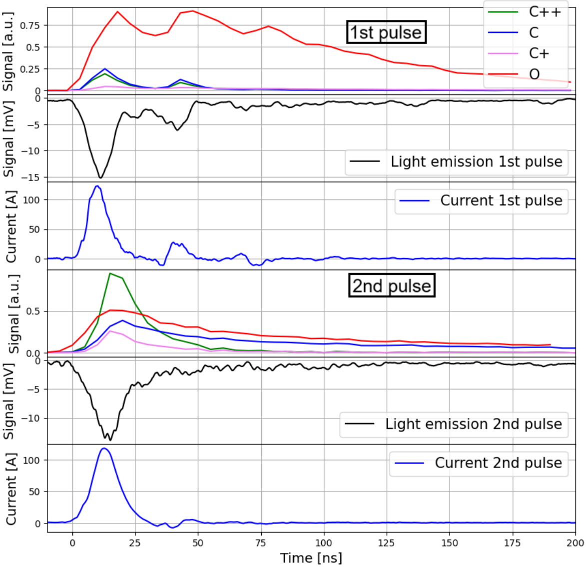
TR-OES: Line matched in impedance

- O^+ emission in the first pulse due to current reflections



TR-OES: Line matched in impedance

- Three emission signal peaks for the first pulse
- Just one emission signal peak for the second pulse
- C^{++} emission is the most prominent up to 30 ns



Conclusions

- Emission analysis at the cathode revealed a different temporal evolution of the formed species.

Conclusions

- Emission analysis at the cathode revealed a different temporal evolution of the formed species.
- Successful current rebounds suppression by impedance matching and burst mode.

Conclusions

- Emission analysis at the cathode revealed a different temporal evolution of the formed species.
- Successful current rebounds suppression by impedance matching and burst mode.
- Single emission profile of the atomic lines in the second pulse.

Conclusions

- Emission analysis at the cathode revealed a different temporal evolution of the formed species.
- Successful current rebounds suppression by impedance matching and burst mode.
- Single emission profile of the atomic lines in the second pulse.
- Clear dissociation of CO_2 in the second pulse of the line matched in impedance.

Future perspectives

- Temporal evolution of other relevant emissions(e.g. O^+)

Future perspectives

- Temporal evolution of other relevant emissions(e.g. O^+)
- Electron density through Stark broadening

Future perspectives

- Temporal evolution of other relevant emissions(e.g. O^+)
- Electron density through Stark broadening
- Electron temperature from the intensity of atomic and ionic emission lines

Future perspectives

- Temporal evolution of other relevant emissions(e.g. O^+)
- Electron density through Stark broadening
- Electron temperature from the intensity of atomic and ionic emission lines
- Gas temperature adding a small quantity of N_2.

Thank you for your attention

CO_2 dissociation

- Direct electron impact dissociation:

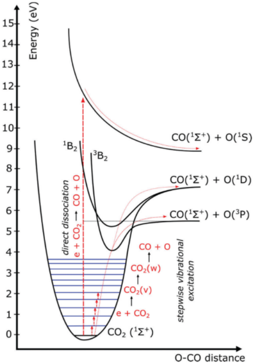
$$e^{-} + CO_2(v = 0) \rightarrow CO + O + e^{-} \tag{1}$$

- Electron impact dissociation from vibrationally excited levels:

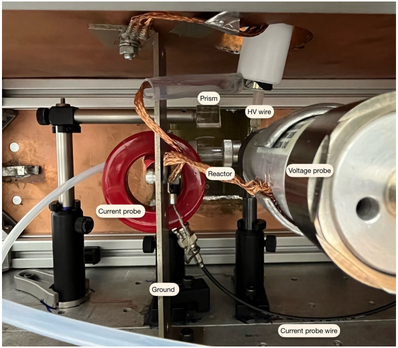
$$e^{-} + CO_2(v > 0) \rightarrow CO + O + e^{-} \tag{2}$$

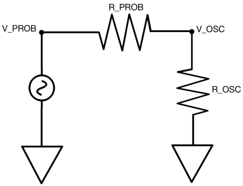
- Vibrational excitation (vibrational ladder climbing):

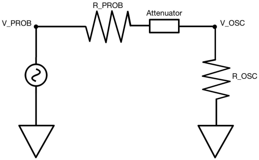
$$CO_2(v > 0) + CO_2(w > v) \rightarrow CO_2(v - 1) + CO_2(w + 1) + \Delta\epsilon_{vw} \rightarrow CO + O + CO_2 \tag{3}$$



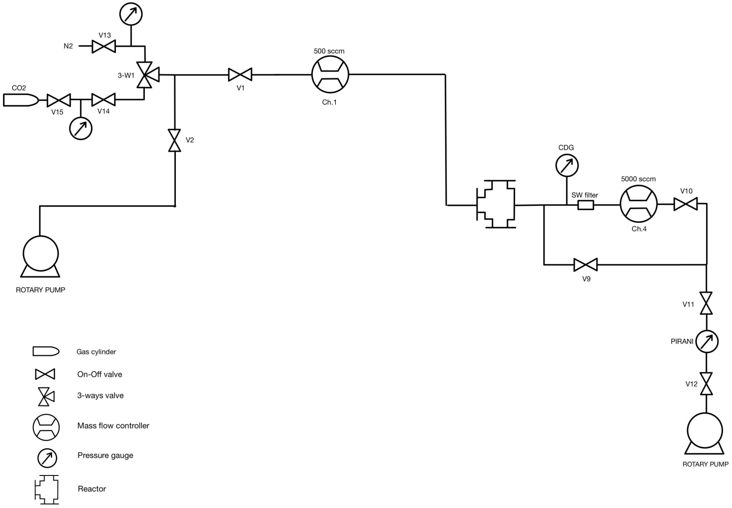
Experimental Setup: Electrical diagnostics



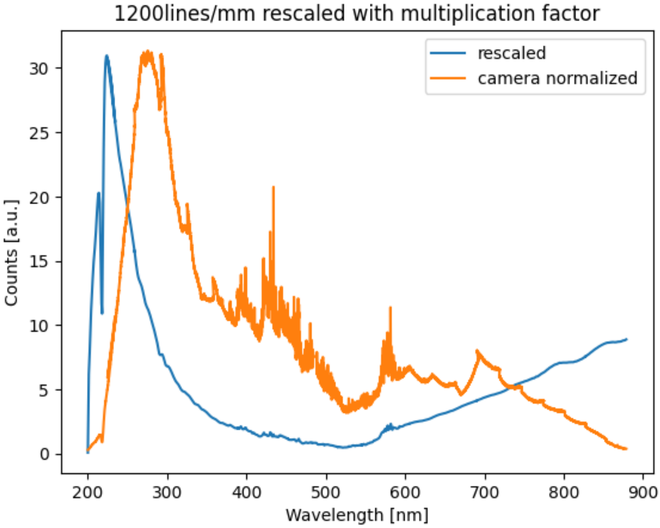




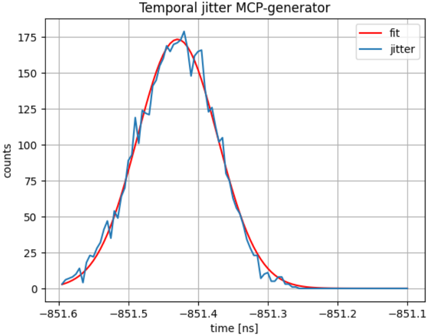
Experimental Setup: Gas Handling

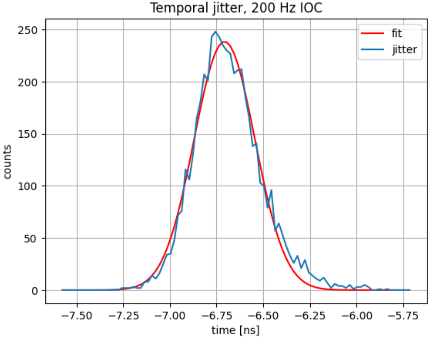


Preliminary steps: Spectrum calibration

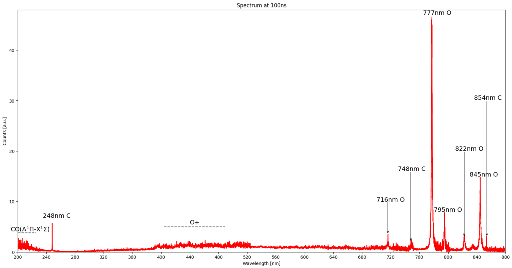


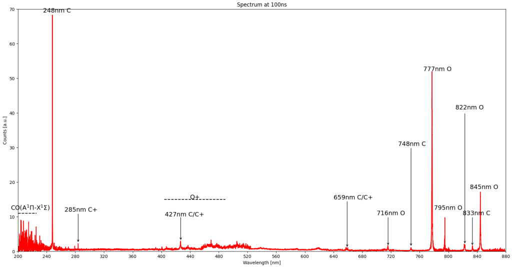
Preliminary steps: Temporal jitter



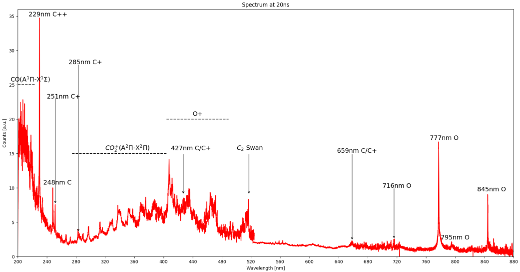


TR-OES: 4


Spectrum at 100ns
Counts [a.u.]
Wavelength [nm]
777nm O
854nm C
822nm O
748nm C
845nm O
716nm O
795nm O
248nm C
O+
CO(A¹Π-X¹Σ)

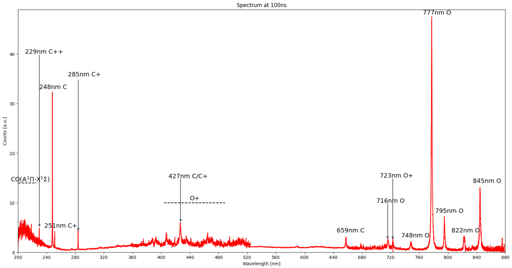

Spectrum at 100ns
Counts [a.u.]
Wavelength [nm]
248nm C
777nm O
822nm O
748nm C
845nm O
659nm C/C+
O+
CO(A¹Π-X¹Σ)
285nm C+
427nm C/C+
716nm O
795nm O
833nm C

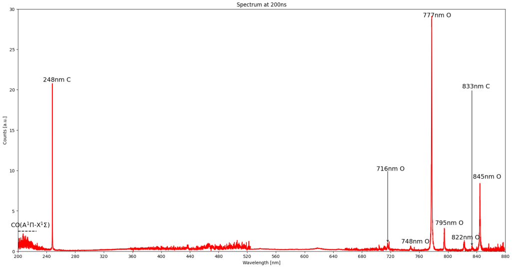
TR-OES: 1


Spectrum at 20ns
229nm C++
285nm C+
CO(A¹Π-X¹Σ)
251nm C+
O+
CO_2^+(A²Π-X²Π)
427nm C/C+
C_2 Swan
659nm C/C+
777nm O
248nm C
716nm O
845nm O
795nm O
Counts [a.u.]
Wavelength [nm]

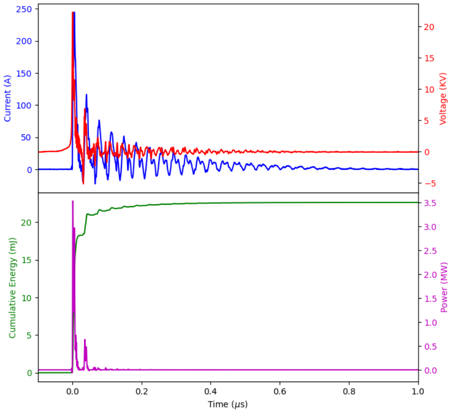

367nm
CO_2^+(A²Π-X²Π)
(000-000)
351nm
(100-000)
337nm
(200-000)
325nm
C:375.5nm
CO
CO_2^+(B²Σ-X²Π): 288nm, 289nm
(010-010)
313nm
Counts [a.u.]
Wavelength [nm]

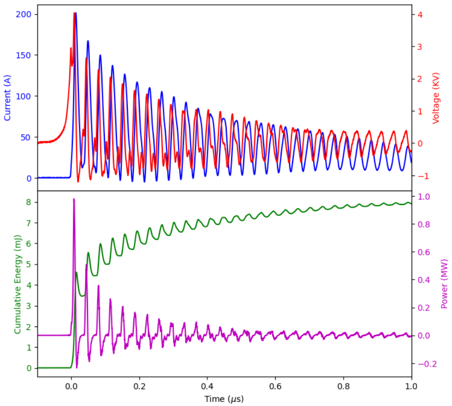
TR-OES: 1


Spectrum at 100ns
777nm O
229nm C++
285nm C+
248nm C
CO(A1Π-X1Σ)
427nm C/C+
723nm O+
845nm O
O+
716nm O
795nm O
251nm C+
659nm C
822nm O
748nm O
Counts [a.u.]
Wavelength [nm]

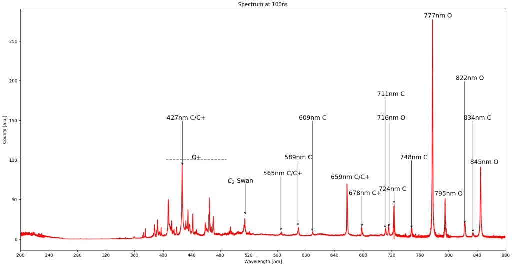

Spectrum at 200ns
777nm O
248nm C
833nm C
716nm O
845nm O
CO(A1Π-X1Σ)
795nm O
822nm O
748nm O
Counts [a.u.]
Wavelength [nm]

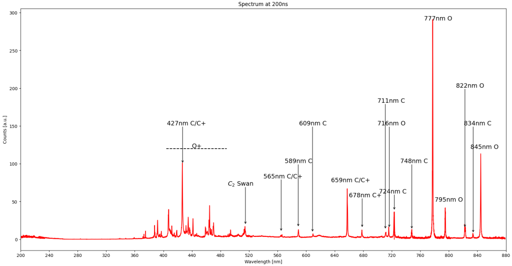
TR-OES: 3


Current (A)
Voltage (KV)
Cumulative Energy (mJ)
Power (MW)
Time (μs)


Current (A)
Voltage (KV)
Cumulative Energy (mJ)
Power (MW)
Time (μs)

TR-OES: 3

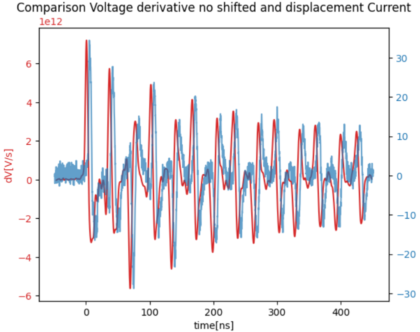

Spectrum at 100ns
Counts [a.u.]
Wavelength [nm]
777nm O
822nm O
711nm C
427nm C/C+
609nm C
716nm O
834nm C
O+
589nm C
748nm C
845nm O
C_2 Swan
565nm C/C+
659nm C/C+
678nm C+
724nm C
795nm O

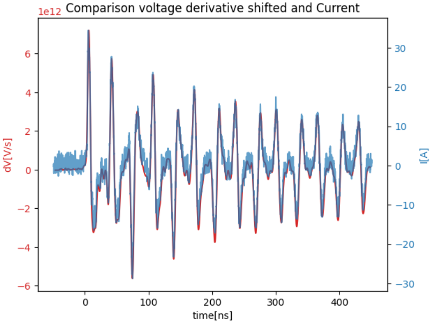

Spectrum at 200ns
Counts [a.u.]
Wavelength [nm]
777nm O
822nm O
711nm C
427nm C/C+
609nm C
716nm O
834nm C
O+
845nm O
589nm C
748nm C
565nm C/C+
C_2 Swan
659nm C/C+
678nm C+
724nm C
795nm O

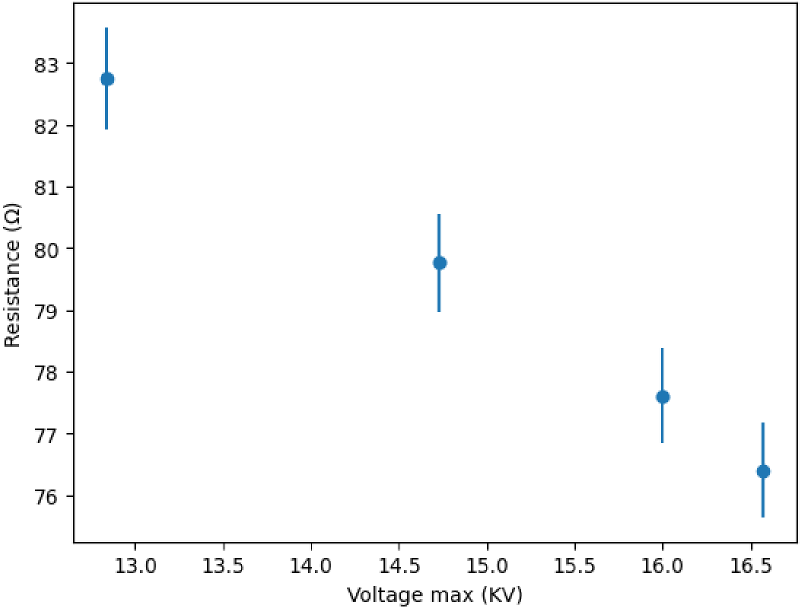
Preliminary steps: Delay and line capacitance calculation

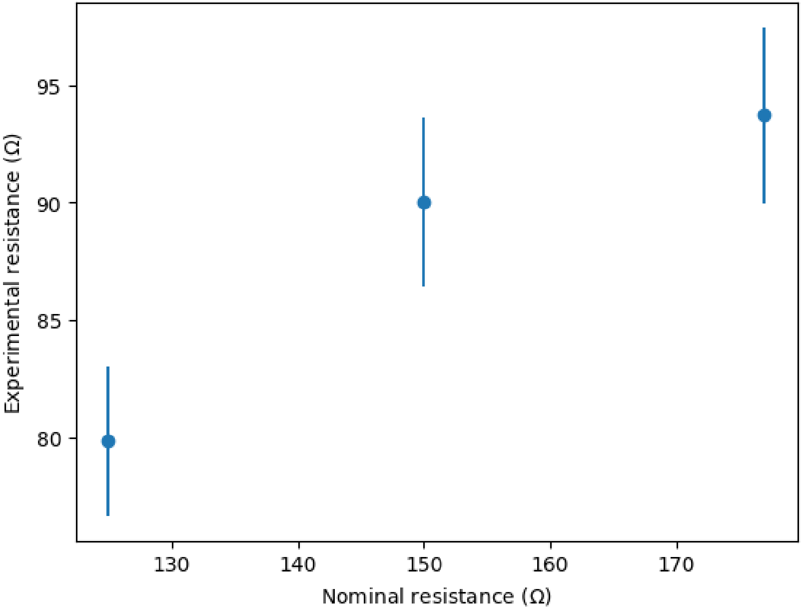
If there is no discharge, the current can be modeled as:

$$I_{\text{disp}}(t) = C\frac{dV(t)}{dt} \longrightarrow I_{\text{disp}}(t) = A\frac{dV(t+d)}{dt}$$

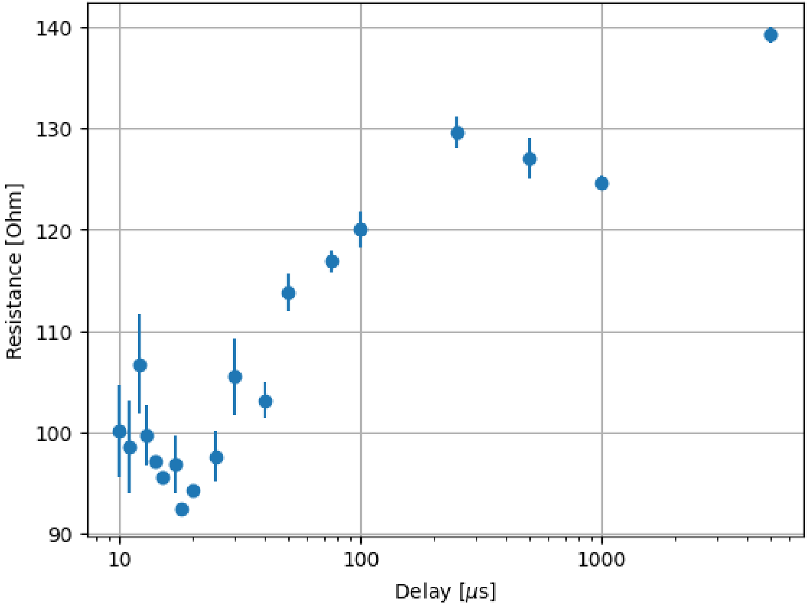





83
82
81
80
79
78
77
76
Resistance (Ω)
13.0
13.5
14.0
14.5
15.0
15.5
16.0
16.5
Voltage max (KV)



95
90
85
80
Experimental resistance (Ω)
130
140
150
160
170
Nominal resistance (Ω)



140
130
120
110
100
90
Resistance [Ohm]
10
100
1000
Delay [μs]