Investigating the role of vibrational states, electronic states and surfaces in CO_2 plasma kinetics

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Laboratoire de Physique des Plasmas

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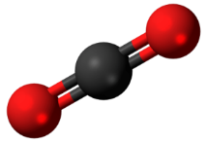
ANR
PIONEER PLASMA CATALYSIS CO_2 RECYCLING

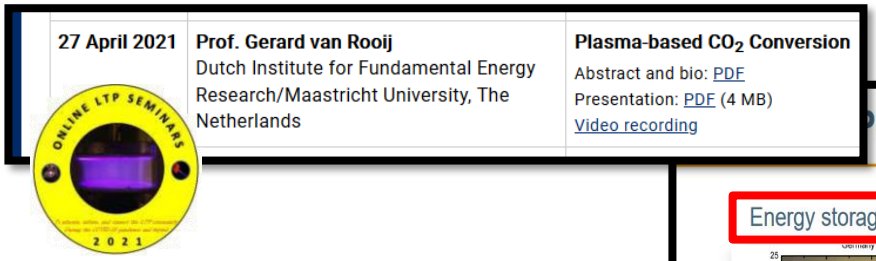
Why study CO_2 plasmas? 1. Climate issues

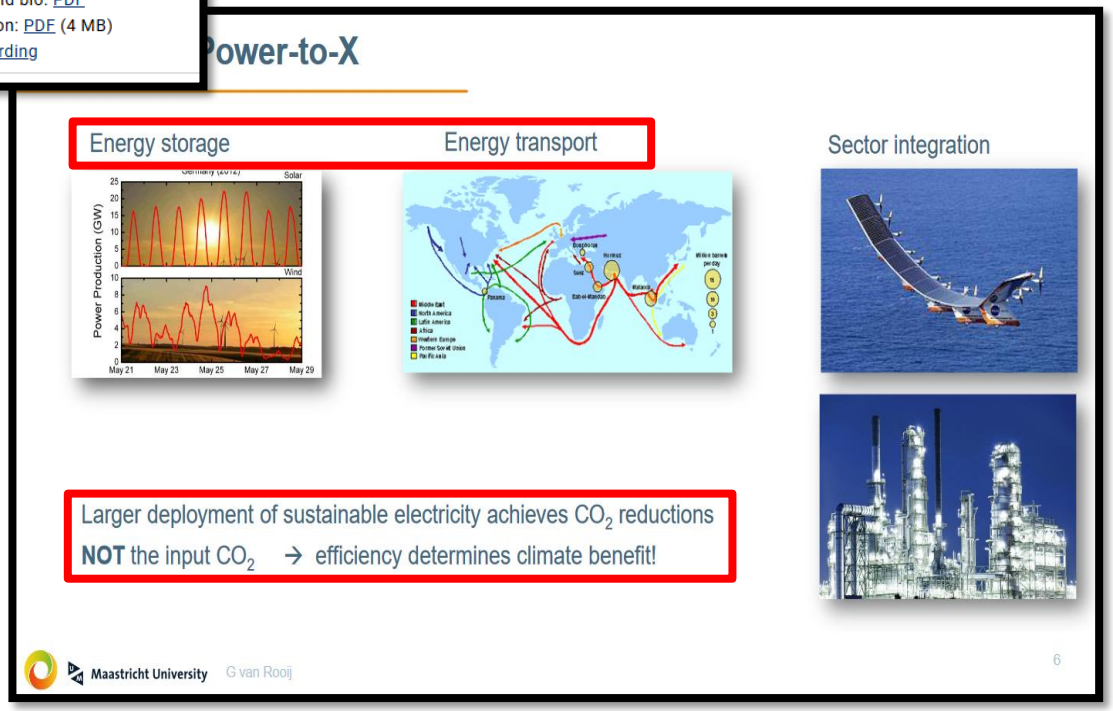
Motivations: **CO_2 = waste… or raw material ?**



- Solar fuels
- Platform molecules for organic chemistry

Challenge: To activate CO_2 chemical conversion via vibrational excitation





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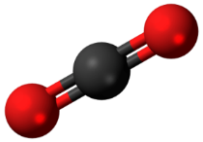

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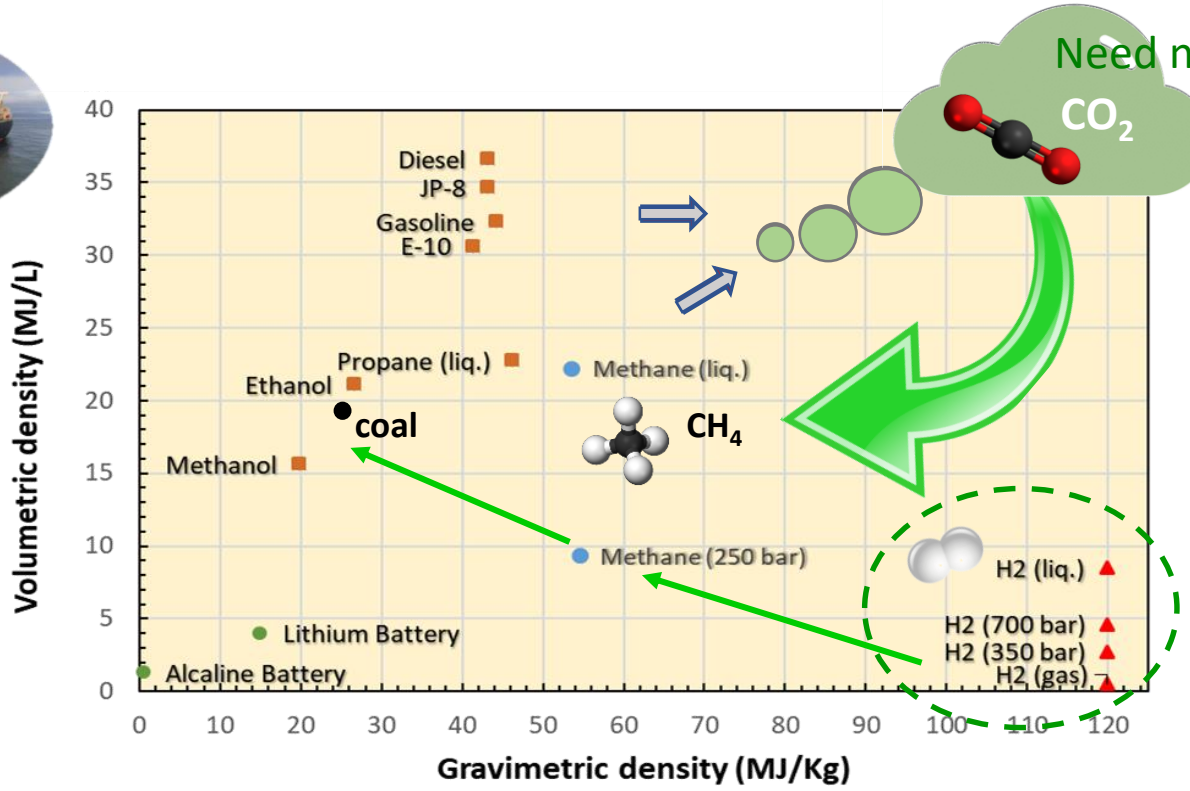

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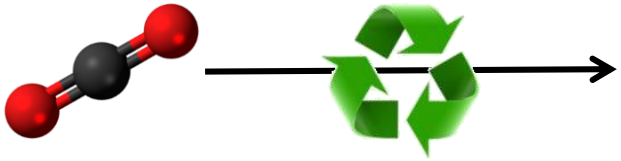

- Solar fuels
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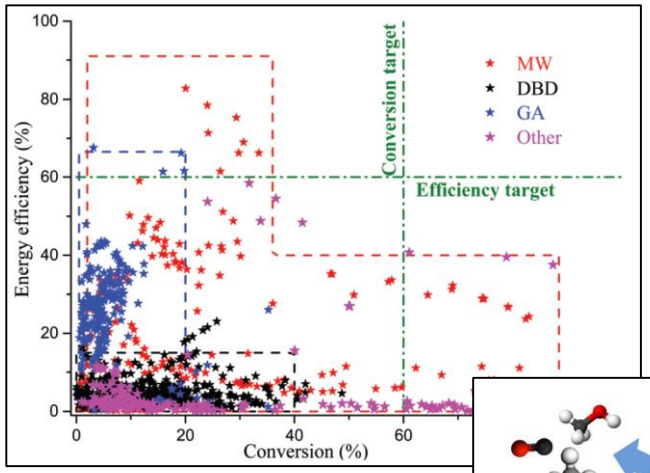
Challenge: To activate CO_2 chemical conversion via vibrational excitation

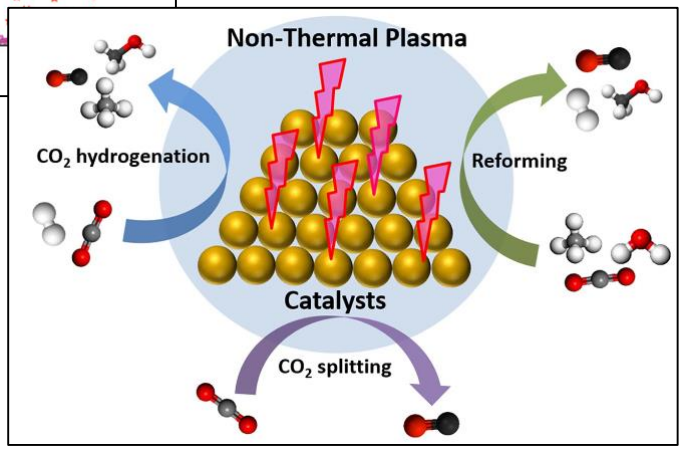
Plasma sources for efficient CO_2 conversion

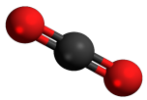
R. Snoeckx and A. Bogaerts, Chem. Soc. Rev., 2017, 46, 5805–5863



Plasma/Catalysis

Xu, Shanshan, et al Journal of Physics D: Applied Physics 54.23 (2021): 233001.





Need new technologies to recycle…

… CO_2, CO_2/N_2

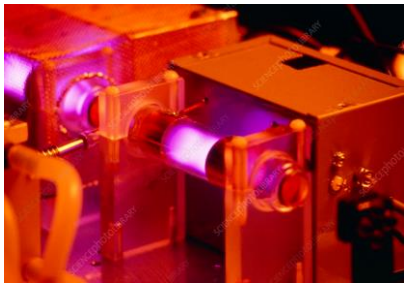
… CO_2+ H_2 (methanation)

… CO_2+ CH_4 (Dry gas reforming)

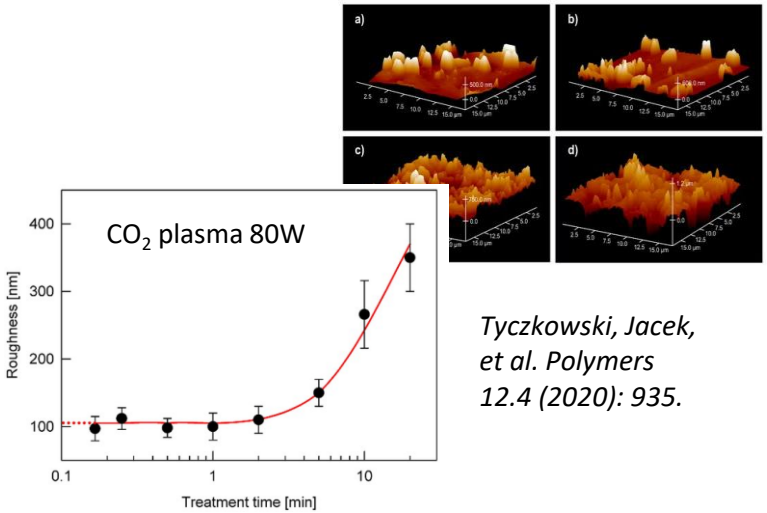
Why study CO_2 plasmas? 2. other applications

Other applications of CO2 plasmas:

CO_2 lasers
(surgery, metal cutting, etc…)

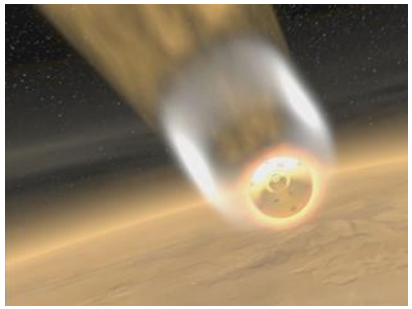


Surface treatments
(polymers functionalization)



Tyczkowski, Jacek, et al. Polymers 12.4 (2020): 935.

Spacecraft shield
(Mars, Venus, Earth atmosphere entry)

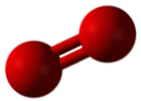


O_2 production on Mars
(ISRU fuel production)

CO_2 plasmas are studied for a long time… → gives basis to study them!

Why study CO_2 plasmas? 3. because a lot is unkown!

Reminder about **O_2 plasmas**…



25 May 2021	**Dr. Jean-Paul Booth** Laboratoire de Physique des Plasmas, École Polytechnique, France	**Laser Cavity Ringdown Spectroscopy of Oxygen Plasmas: Direct Measurement of the Densities of Oxygen Atoms, Ozone and Negative Ions and Gas Temperature** Abstract and bio: PDF Presentation: PDF (4 MB) Video recording

Outstanding questions about O_2 plasmas

Electron impact dissociation
cross-section low energy/ rate constant at low E/N

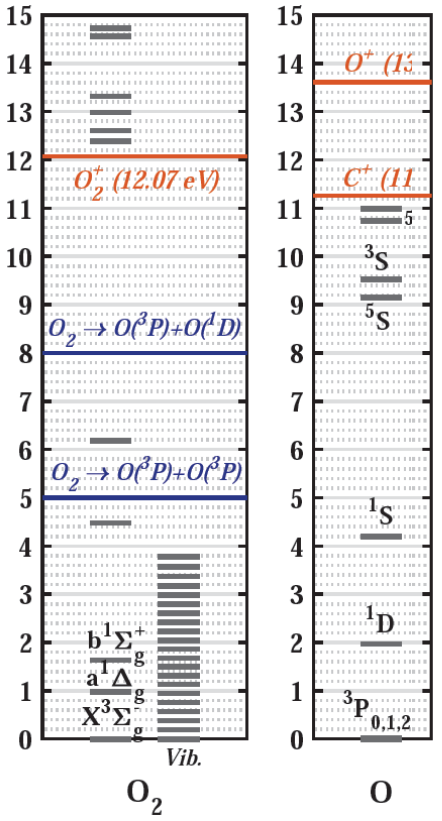
O atom surface recombination, γ :
Universal law for γ?
Effect of ion bombardment?

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

Kinetics : quenching - surface and gas phase

Electronegativity
negative ion creation and loss mechanisms

Temperature
Gas heating mechanisms
Surface thermal accommodation
} predictive models immature



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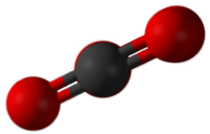
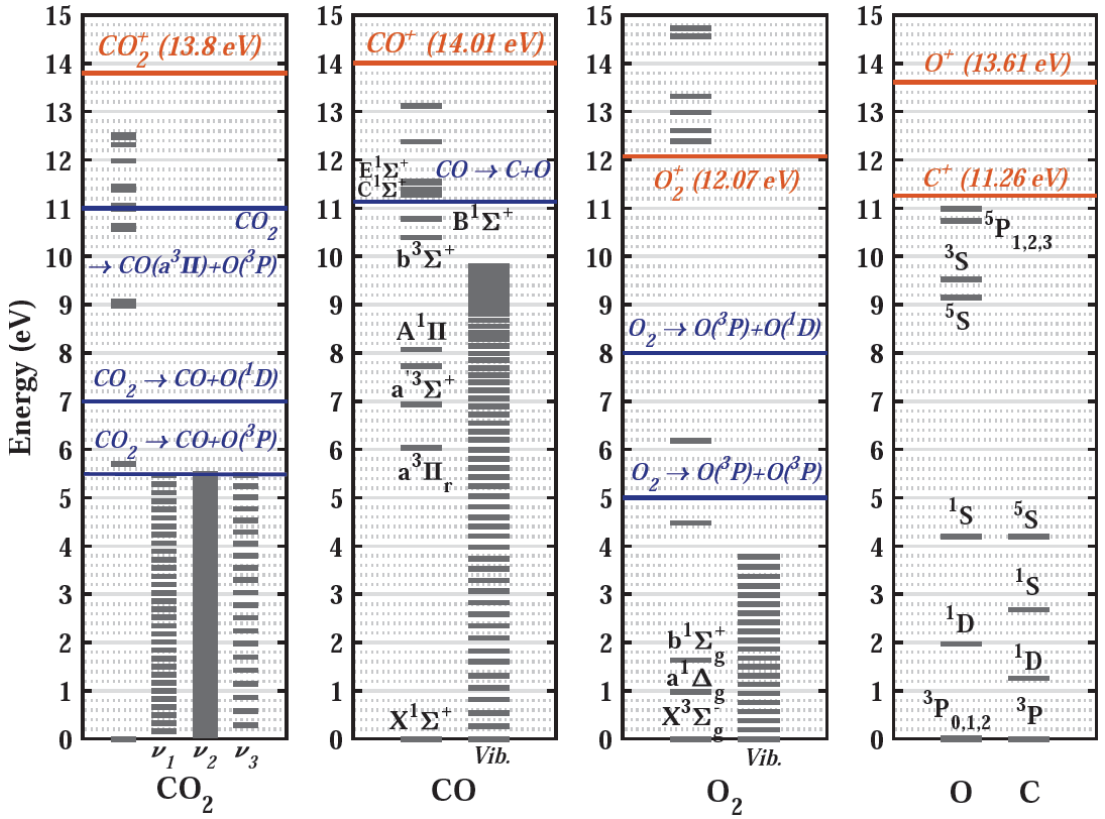
Even more unknowns in **CO_2 plasmas**…

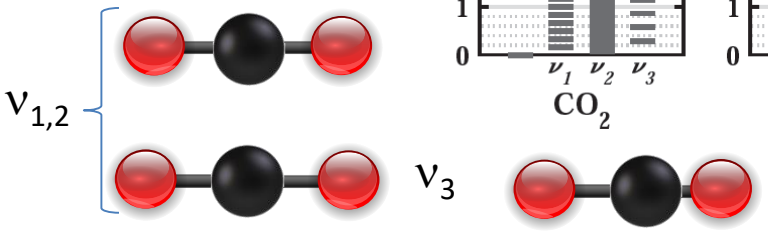


! strong lack of fundamental data

Capitelli et al (2017) Plasma Sources Sci. Technol. 26 055009

- Accuracy of state to state description vibrational kinetics CO_2 and CO
- Taking into account properly V-T, especially with O
- e impact dissociation cross section of CO_2
- role in chemistry of vibrationally excited molecules and electronic states (CO_2(10,5eV), O(^{1}D), CO($a^3\Pi$), etc…)
- Take into account time evolution of T_{gas}





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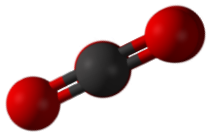

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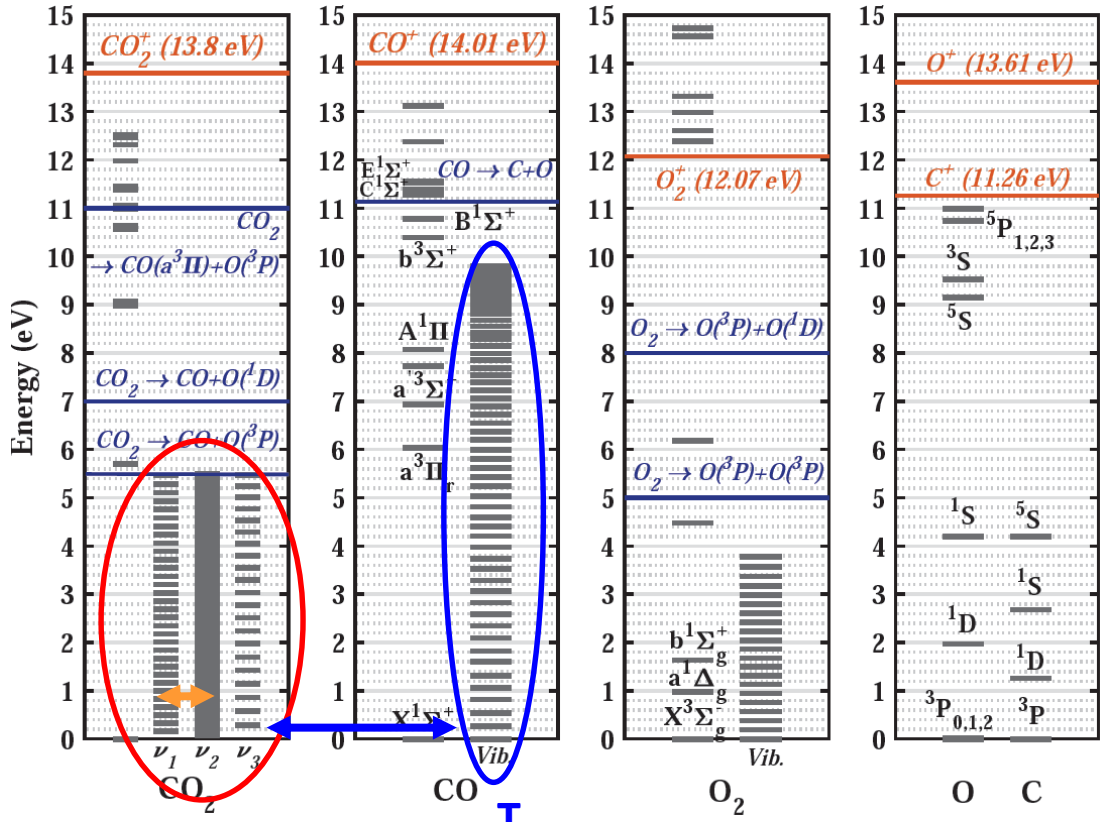

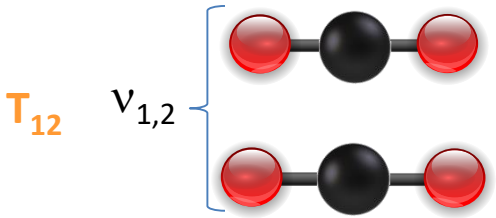

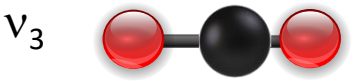

T_3

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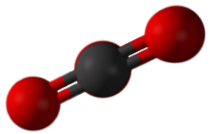
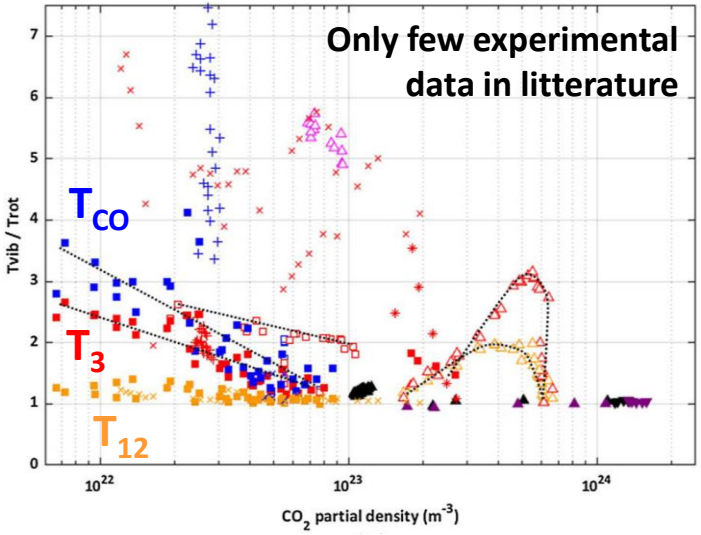
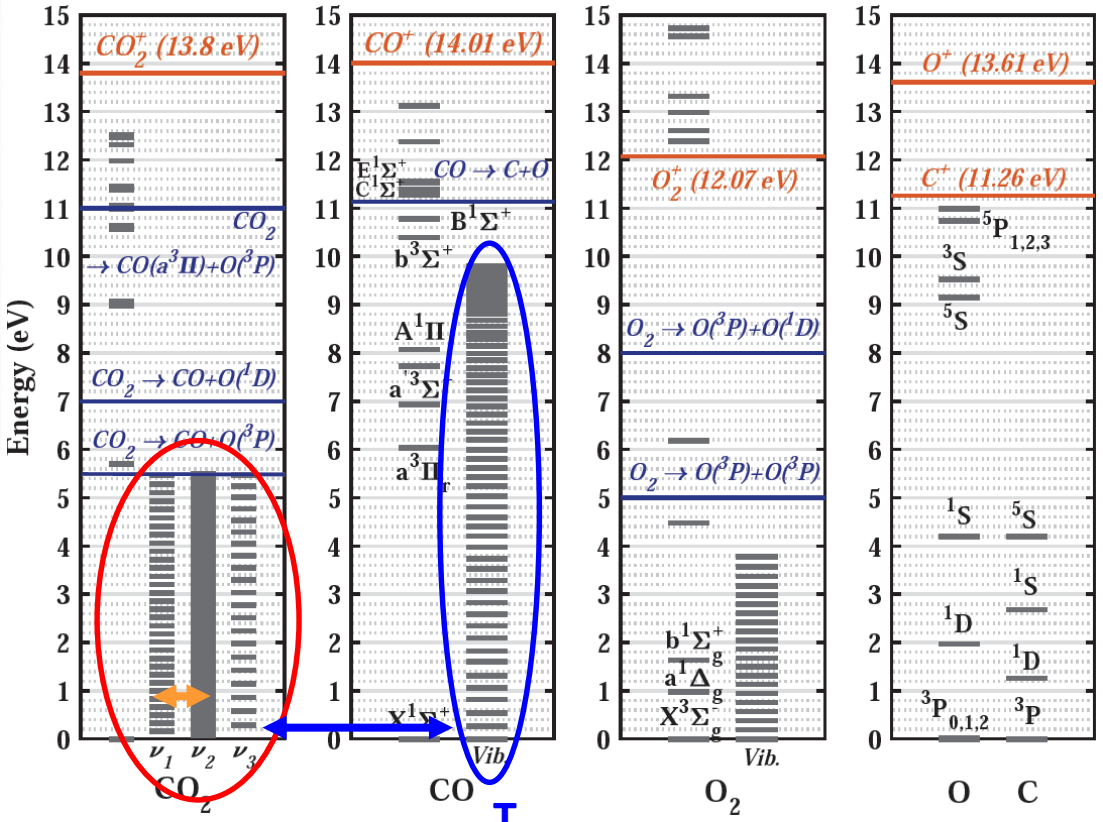
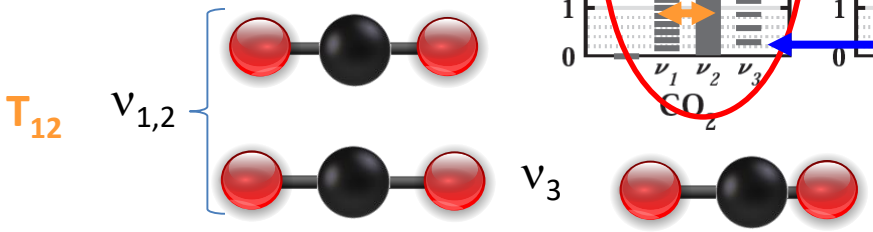




Pietanza et al (2021) accepted Eur. Phys. J. D, 10.1140/epjd/s10053-021-00226-0





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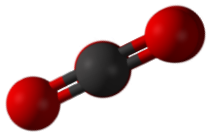
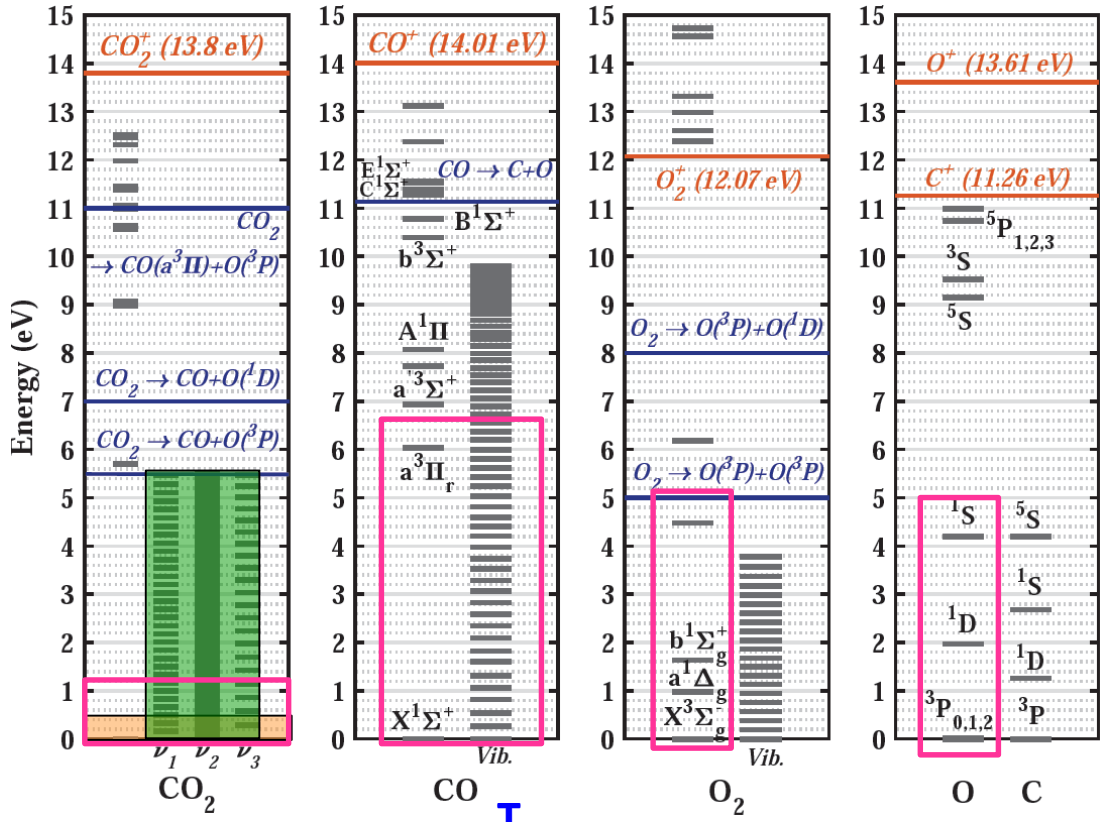


strong lack of fundamental data

And from modelling point of view:

- CO2 laser
- Spacecraft shield (full STS, but no electrons)
- Recent developpement of 0D kinetics models
- 2D, 3D fluid model with simplified kin. scheme

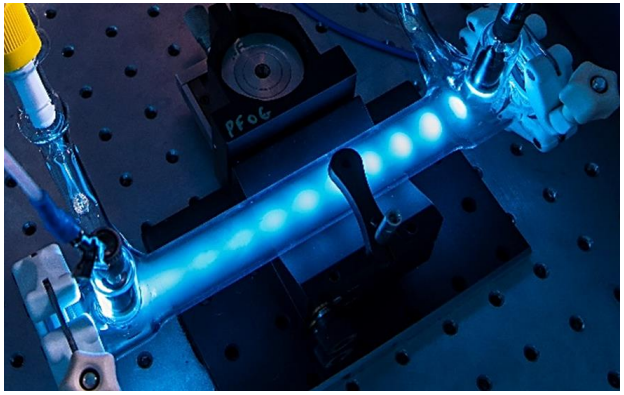
Pietanza et al (2021) accepted Eur. Phys. J. D, 10.1140/epjd/s10053-021-00226-0

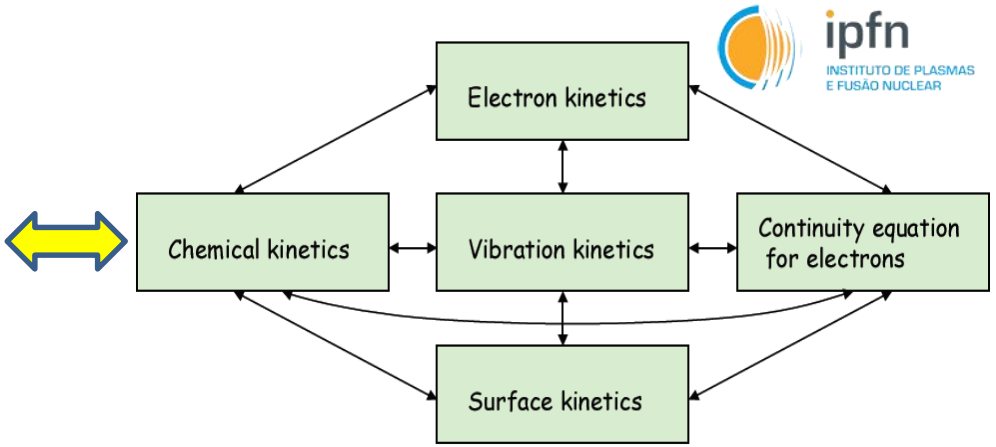


T_{12} $\nu_{1,2}$ ν_3 T_3 T_{CO}

Glow discharge as a benchmark for kinetic models

DC glow discharge (also RF discharge…)





Combining a simple discharge and multiple diagnostics to provide constraints for a step-by-step validation of models

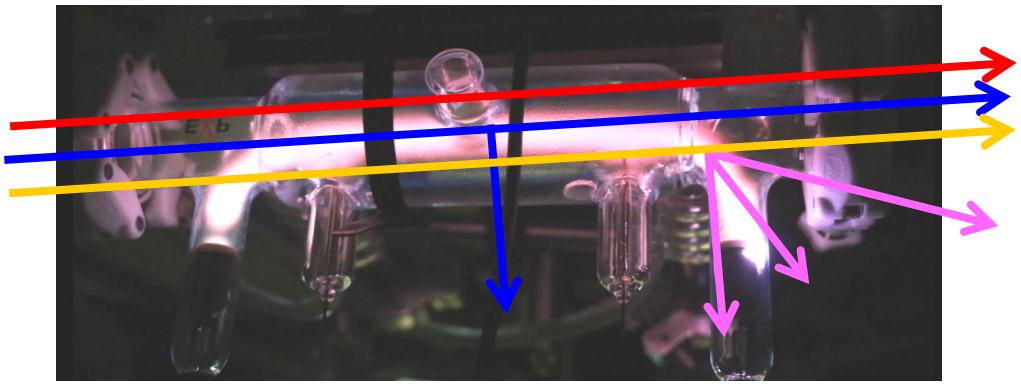
Final goal:

Coupling full chemistry with electron/vibration kinetics and surface processes

Advantages of glow discharge for diagnostics

Pyrex tube, diam = 2cm, L = 23 cm

Controlled T_{wall}= 323 K, E_{field} measured



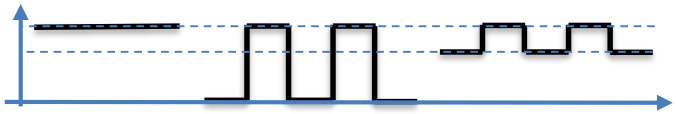
***In situ* time resolved FTIR**

HR-TALIF

CRDS

Modulated actinometry

→ Continuous, Pulsed, modulated discharge



→ With Gas flow or « static » conditions

Diagnostics :

- IR absorption spectroscopy (CO2*v, CO*v, Tg, [M])
- CRDS (Tg, [O], γ_o)
- Raman scattering (CO_2, CO, O_2,Tg, Tvib)
- High Resolution TALIF (Tg, [O])
- Actinometry ([O], γ_o)

Line of sight measurements

Spatially resolved

Also important to cross check diagnostics!

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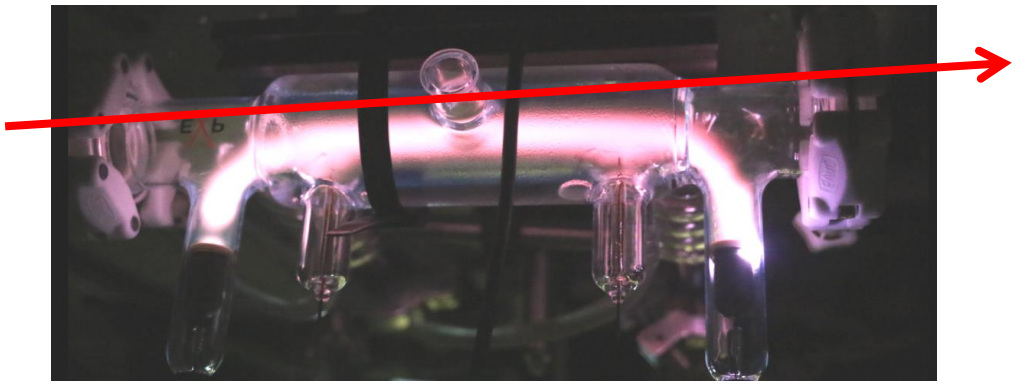
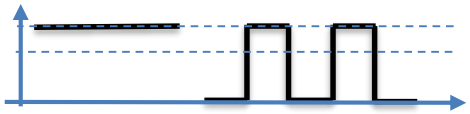


***In situ* time resolved FTIR**

→ Continuous, Pulsed



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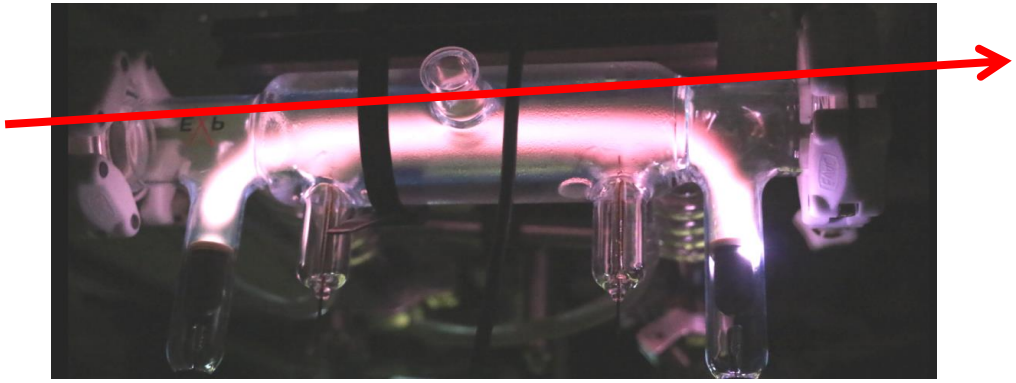
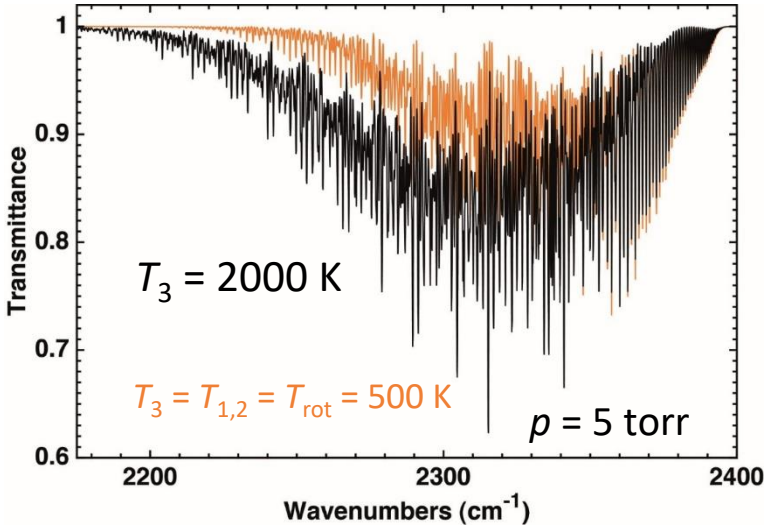
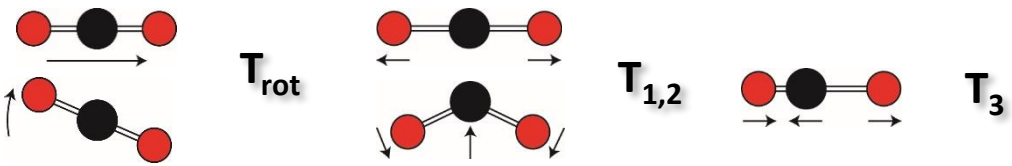


***In situ* time resolved FTIR**

normal, rapid scan, step scan





B L M Klarenaar et al (2017) Plasma Sources Sci. Technol. 26 115008

Diagnostics :

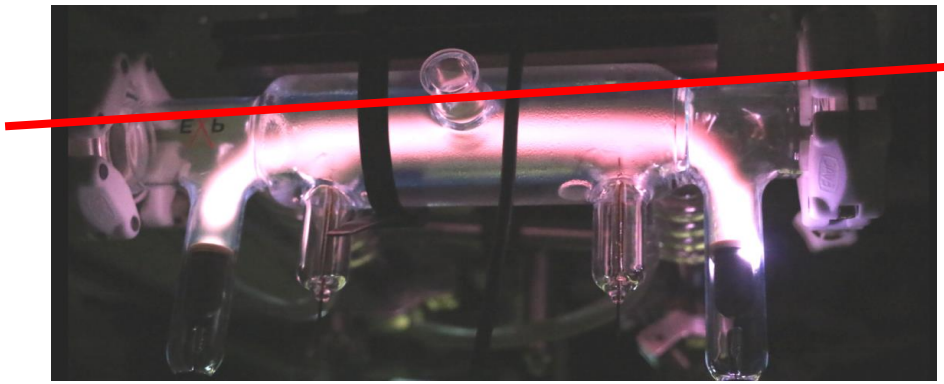
- IR absorption spectroscopy (CO2*v, CO*v, [M])

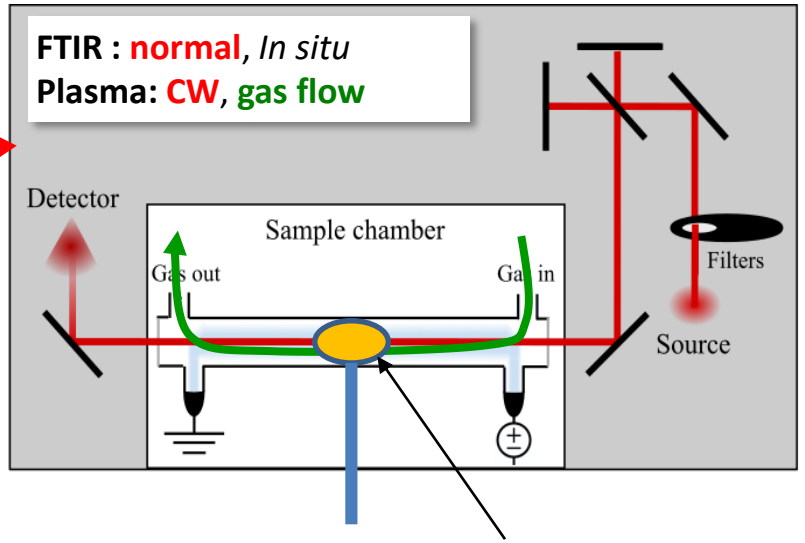
$T_3 = T_{1,2} = T_{rot}$ = 300 K

$$(\nu_1, \nu_2^{l_2}, \nu_3) \rightarrow (\nu_1, \nu_2^{l_2}, \nu_3 + 1)$$

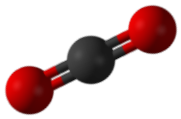
Database: HITEMP-2010 – ~300 vibrational transitions

Step by step investigation of CO_2 kinetics

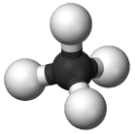




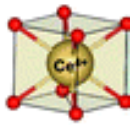
1. Vibrational kinetics in pure CO_2
2. Neutrals chemistry in pure CO_2



3. Vibrational quenching in CO_2/CH_4
4. First insights about CO_2/CH_4 chemistry



5. Towards plasma/catalyst study in CO_2/CH_4



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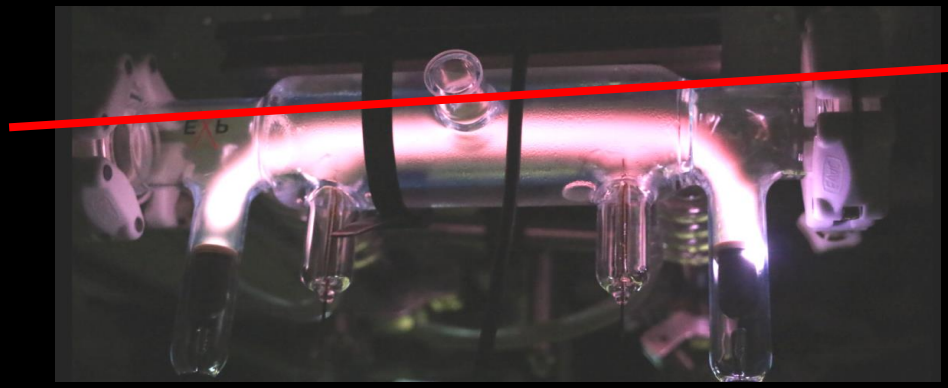

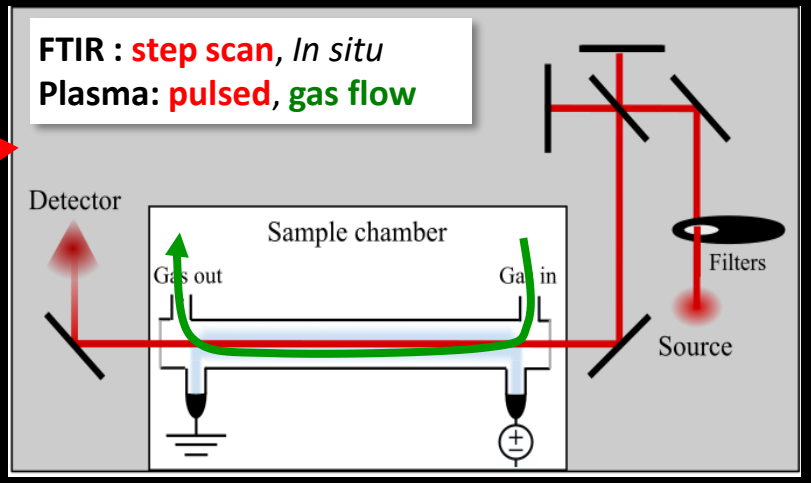

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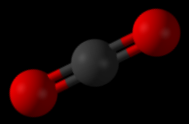

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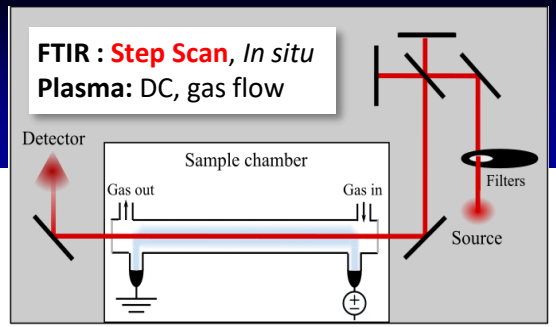
FTIR – step scan for time resolved measurements



$$(\nu_1, \nu_2^{l_2}, \nu_3) \rightarrow (\nu_1, \nu_2^{l_2}, \nu_3 + 1)$$

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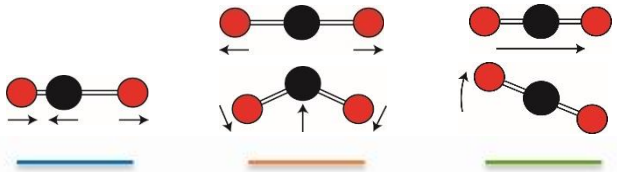
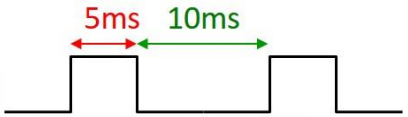
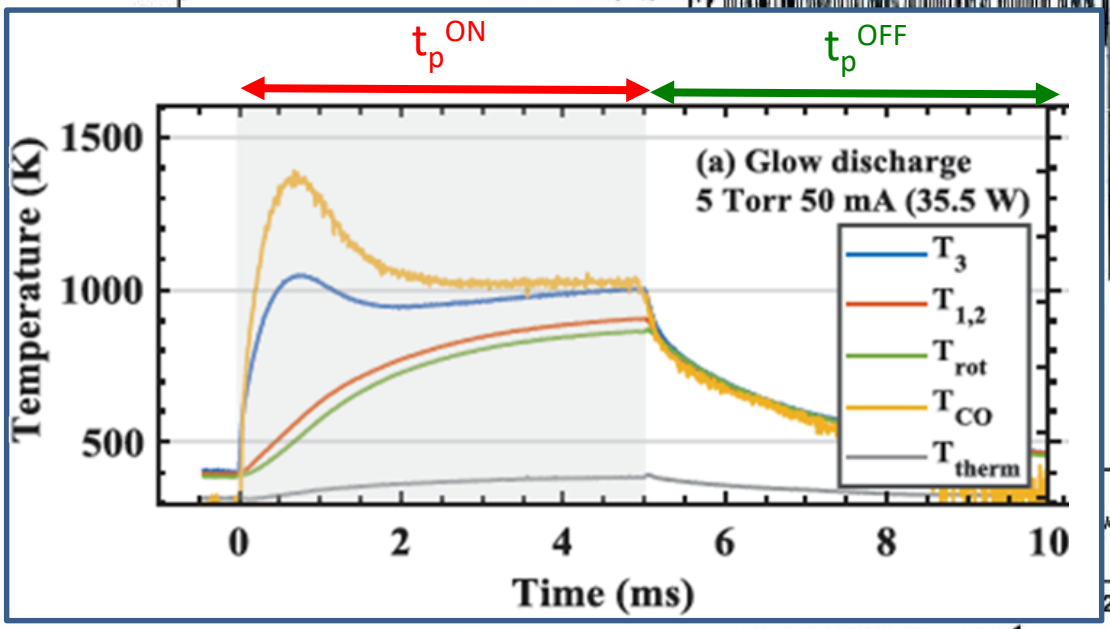
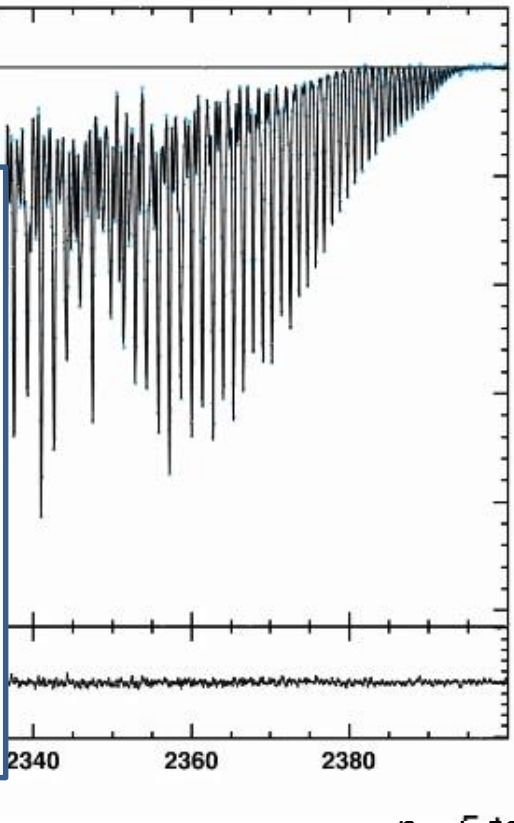


Pulse: 5ms ON. 10ms OFF



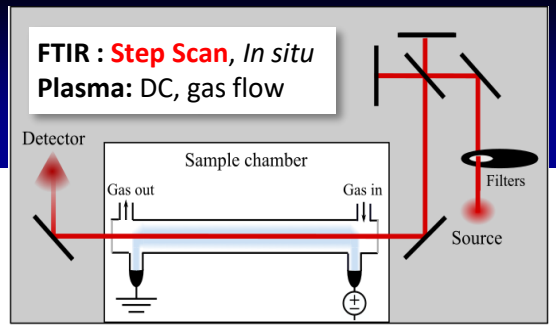




p = 5 torr

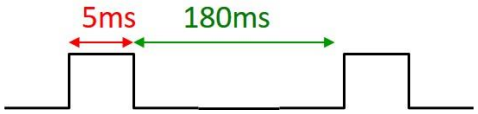
B L M Klarenaar et al (2017) Plasma Sources Sci. Technol. 26 115008

FTIR – step scan: CO_2 vibrational kinetics ONLY



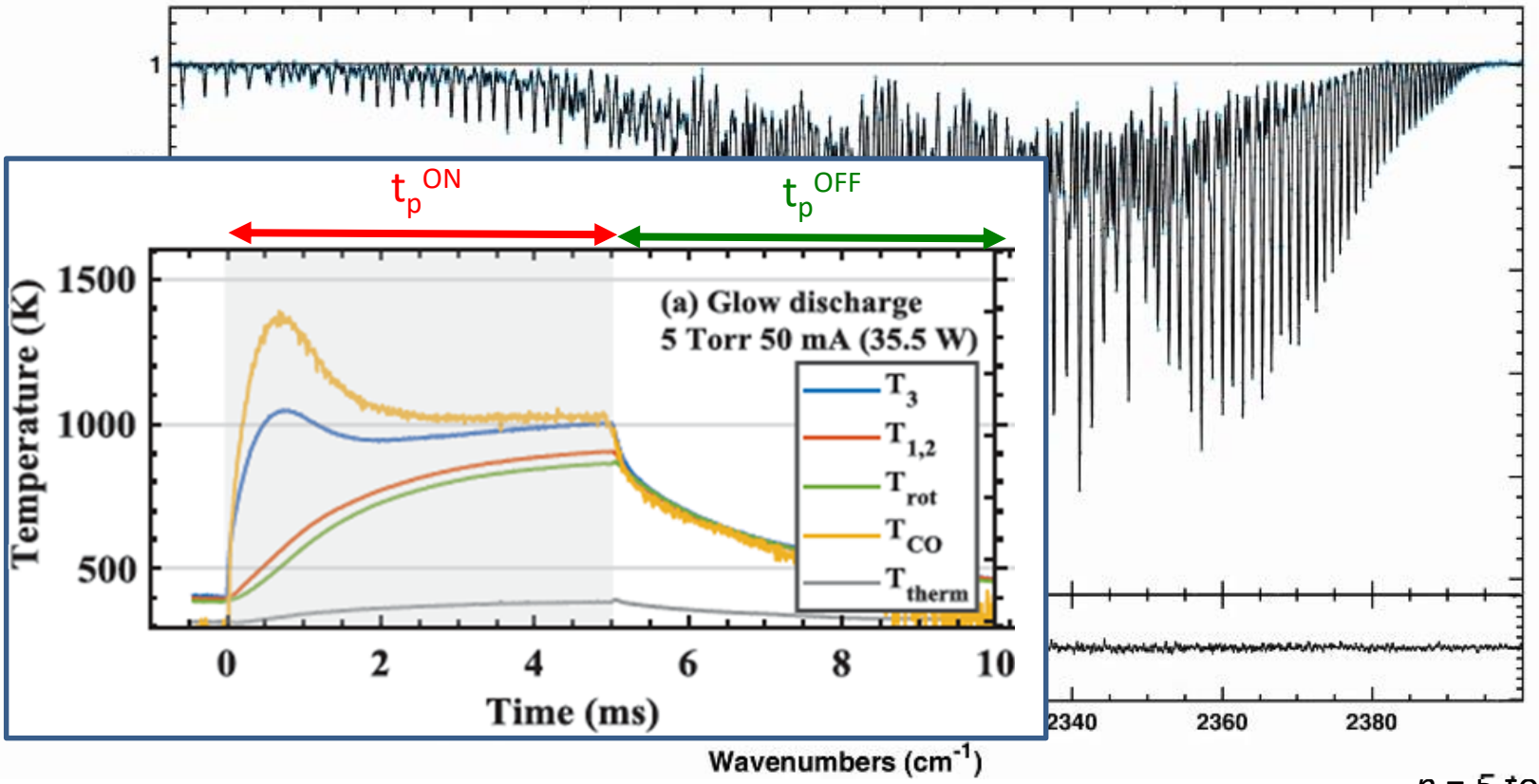
$\tau_{res} < T_{pulse}$ (5 ms ON – ~180 ms OFF)

→ Gas fully renewed between 2 pulses



No CO, O_2 left at the begining of the pulse → e-V, V-V and V-T in pure CO_2

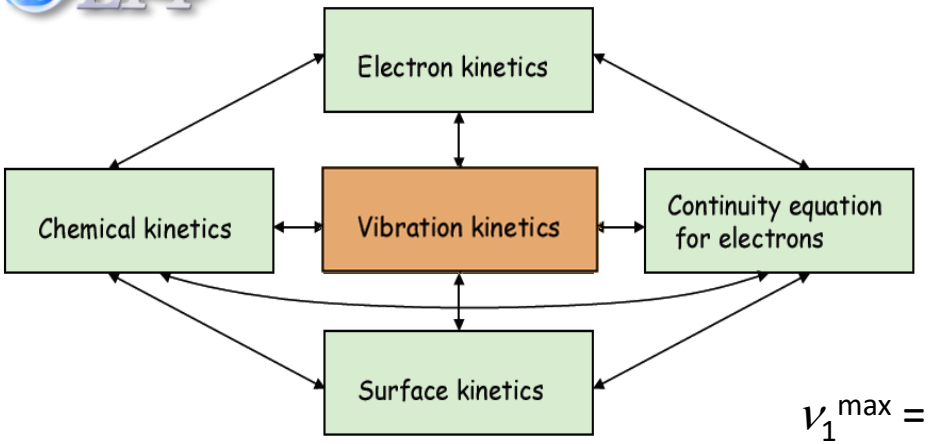
Fit of individual vibrational level densities

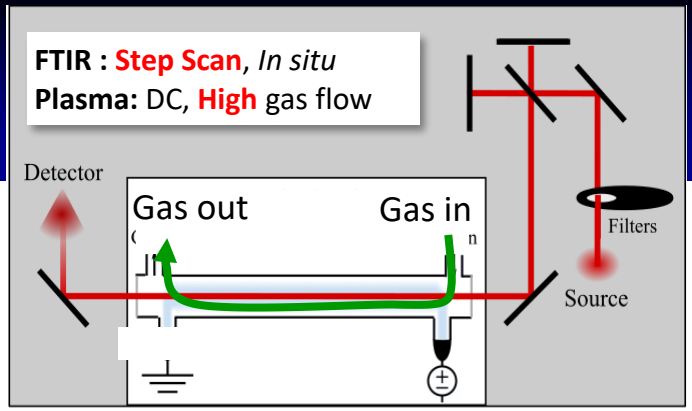


p = 5 torr

B L M Klarenaar et al (2017) Plasma Sources Sci. Technol. 26 115008

FTIR – step scan: CO_2 vibrational kinetics ONLY

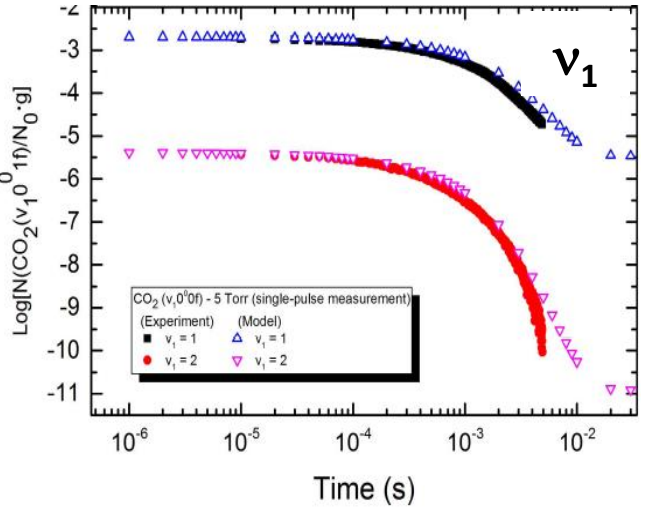


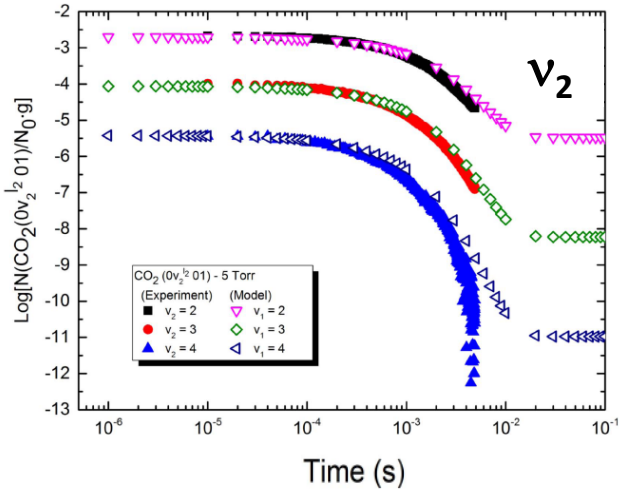


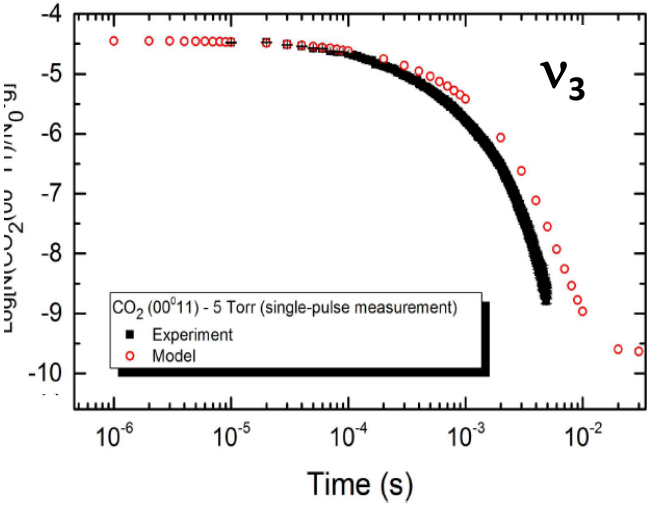
$\nu_1^{max} = 2$, $\nu_2^{max} = 5$, $\nu_3^{max} = 5$ → 72 vibrational levels

Temporal post-discharge ✓

Scaling law for V-V, V-T ✓ $T_1 = T_2$ ✓ e-V ✓

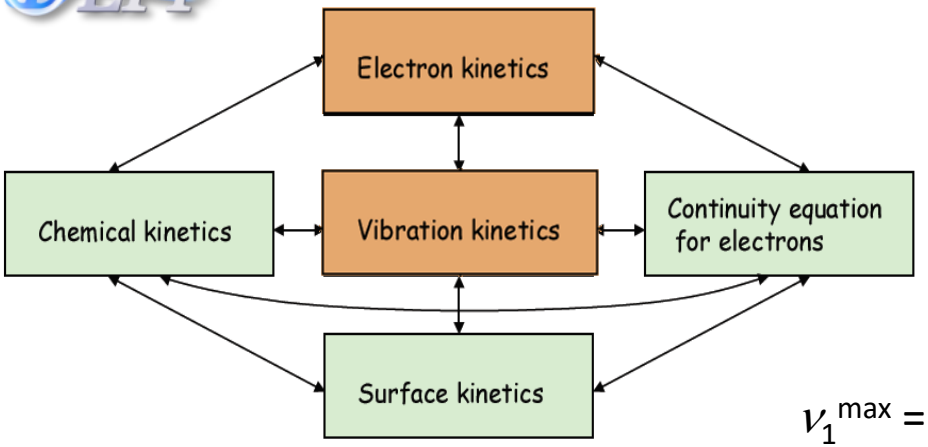


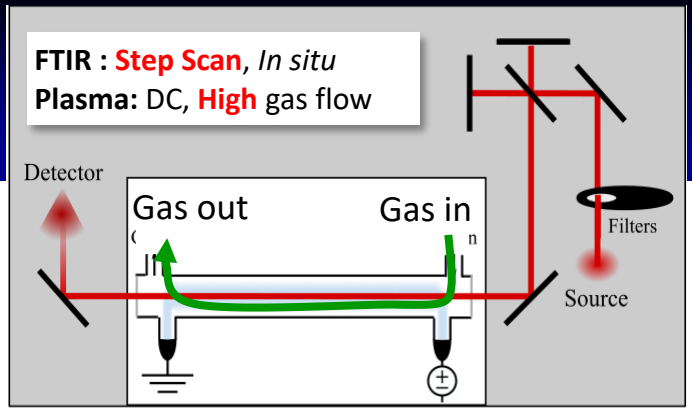




Grofulović, M., et al. Plasma Sources Science and Technology 27.11 (2018): 115009

FTIR – step scan: CO_2 vibrational kinetics ONLY

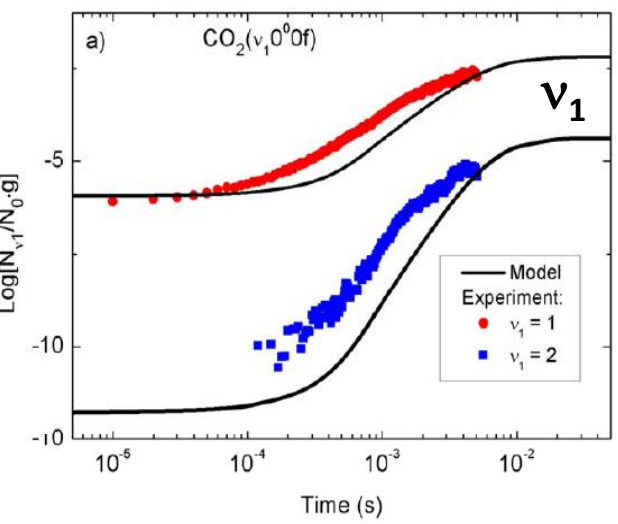


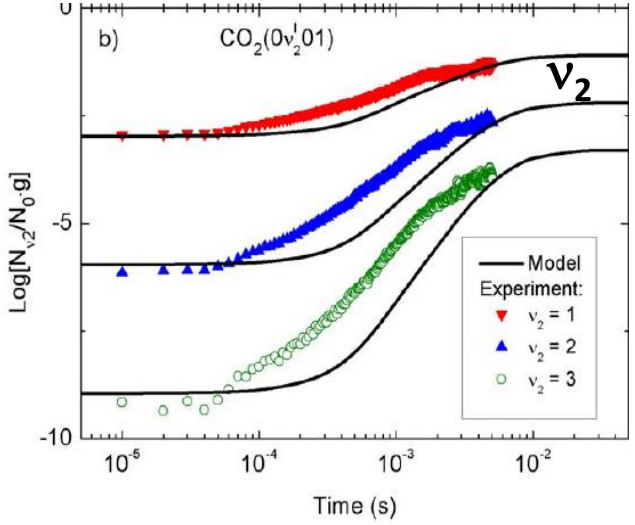


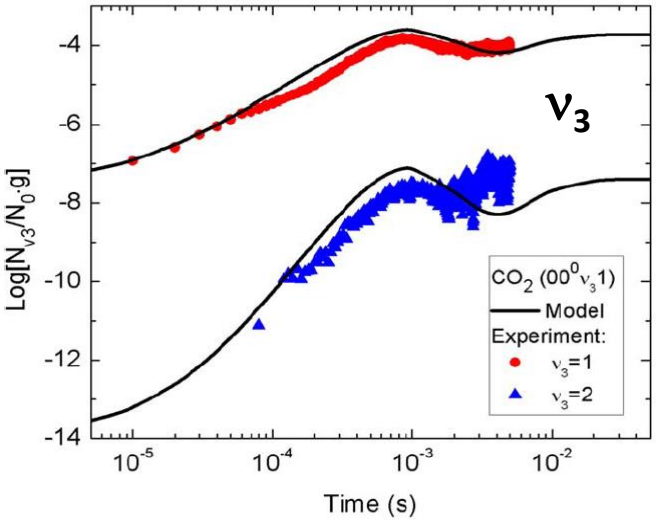
$\nu_1^{max} = 2$, $\nu_2^{max} = 5$, $\nu_3^{max} = 5$ → 72 vibrational levels

During the plasma pulse ✓

Scaling law for V-V, V-T ✓ $T_1 = T_2$ ✓ e-V ✓



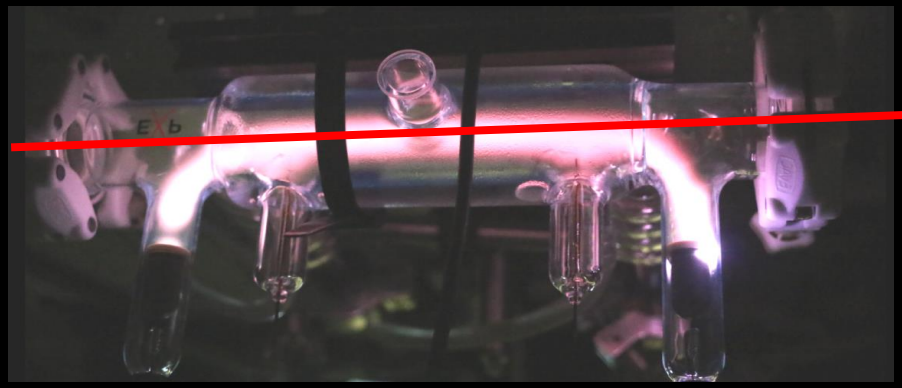


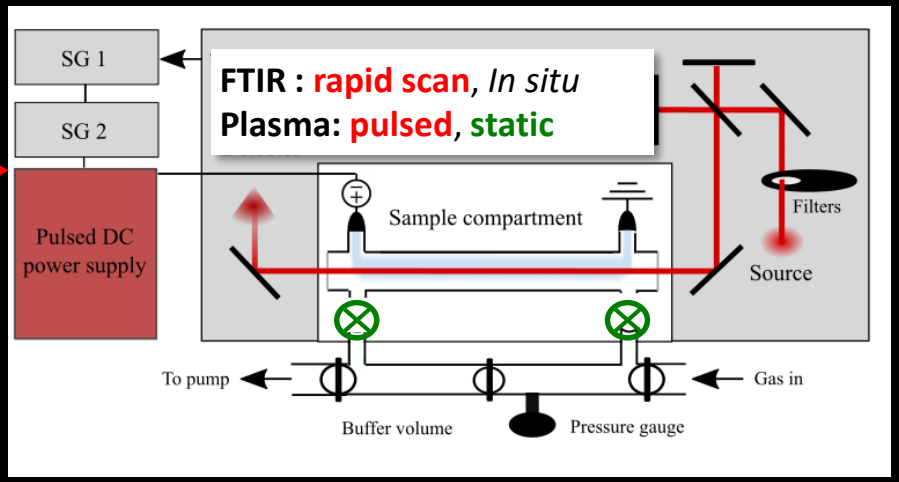


Grofulović, M., et al. Plasma Sources Science and Technology 27.11 (2018): 115009

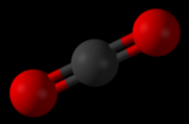
Silva, T., et al. Journal of Physics D: Applied Physics 51.46 (2018): 464001

Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics





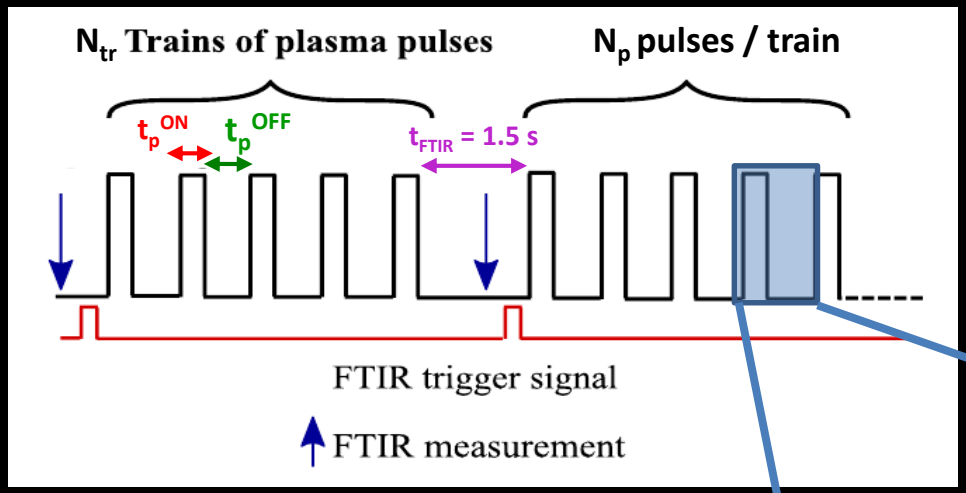
1. Vibrational kinetics in pure CO_2
2. **Neutrals chemistry in pure CO_2**

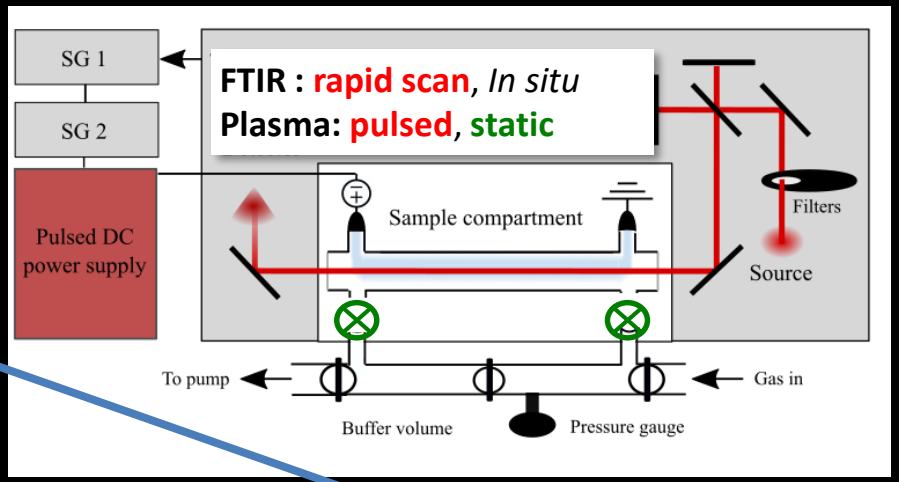


3. Vibrational quenching in CO_2/CH_4
4. First insights about CO_2/CH_4 chemistry

5. Towards plasma/catalyst study in CO_2/CH_4

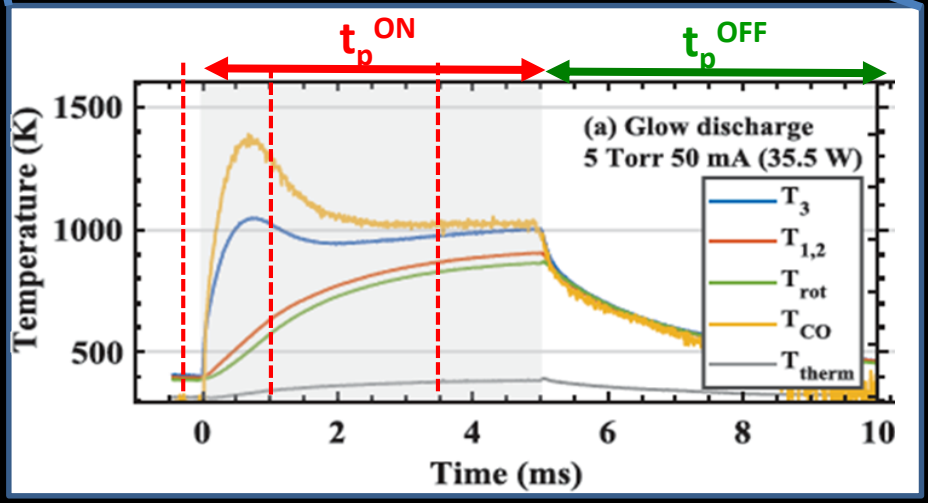
Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics



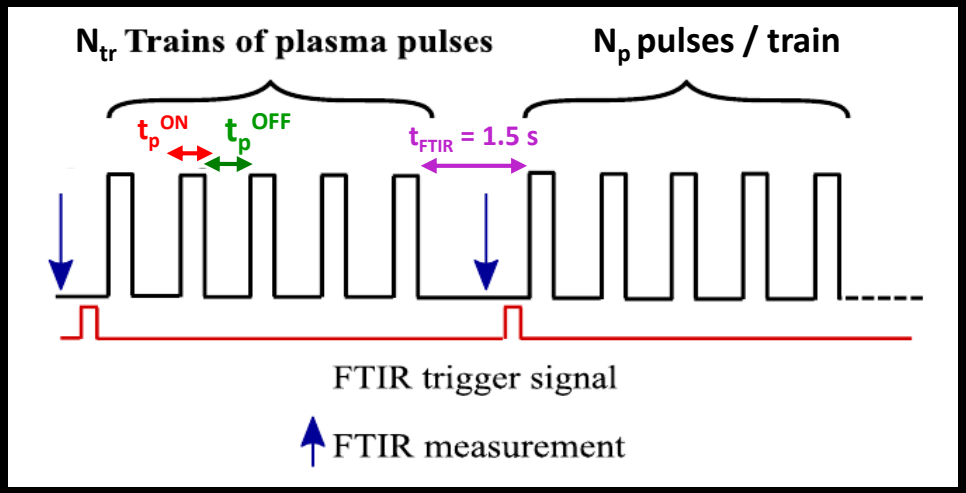


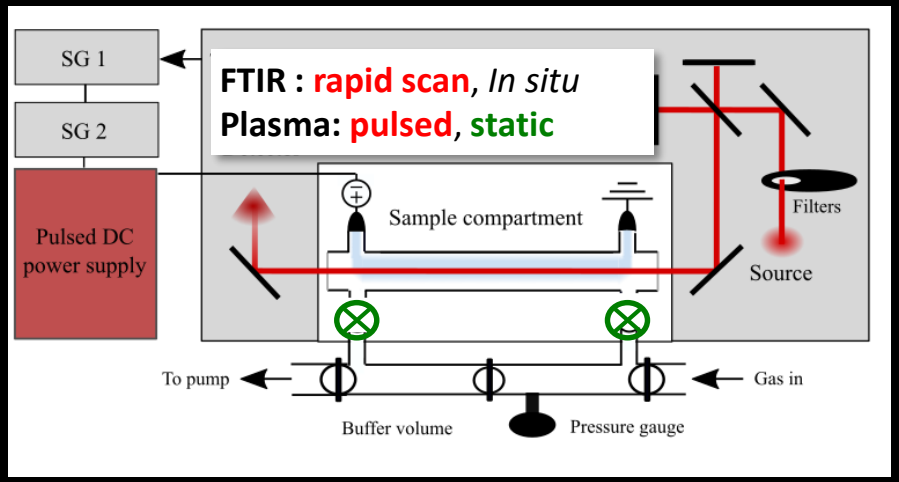
0.5ms < t_p^{ON} < 10ms

0.5ms < t_p^{OFF} < 50ms



Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics





0.5ms < t_p^{ON} < 10ms

0.5ms < t_p^{OFF} < 50ms

$$t_{tr}^{ON} = \Sigma(t_p^{ON}) = N_p \times t_p^{ON}$$

$$T^{ON} = \Sigma(t_{tr}^{ON}) = N_{tr} \times t_{tr}^{ON}$$

$T^{ON} = \Sigma(t_p^{ON})$ → total plasma ON time

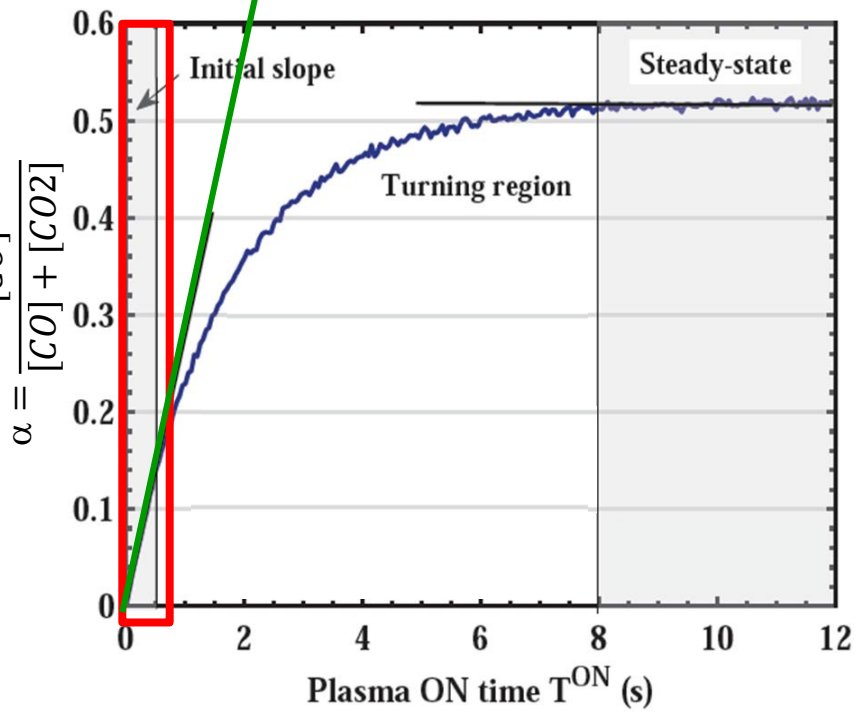
Typical measurement in “static” conditions

$$R = n_e \cdot K_{diss} \cdot [CO_2] \cdot t$$

Pure CO_2 → Balance between :

CO_2 dissociation → CO

CO + O back reaction mechanism → CO_2

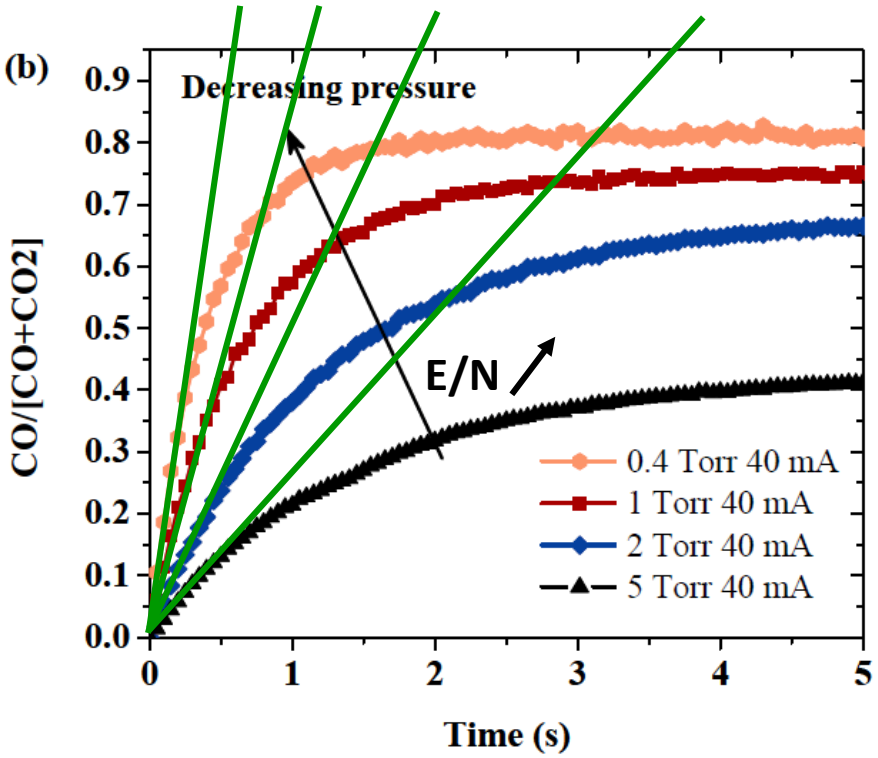


$$T^{ON} = \Sigma(t_p{}^{ON})$$

Electron impact dissociation rate

Initial conversion → direct electron impact dissociation

$$\alpha = \frac{[CO]}{[CO] + [CO2]} \qquad R = n_e \cdot K_{diss} \cdot [CO_2] \cdot t$$



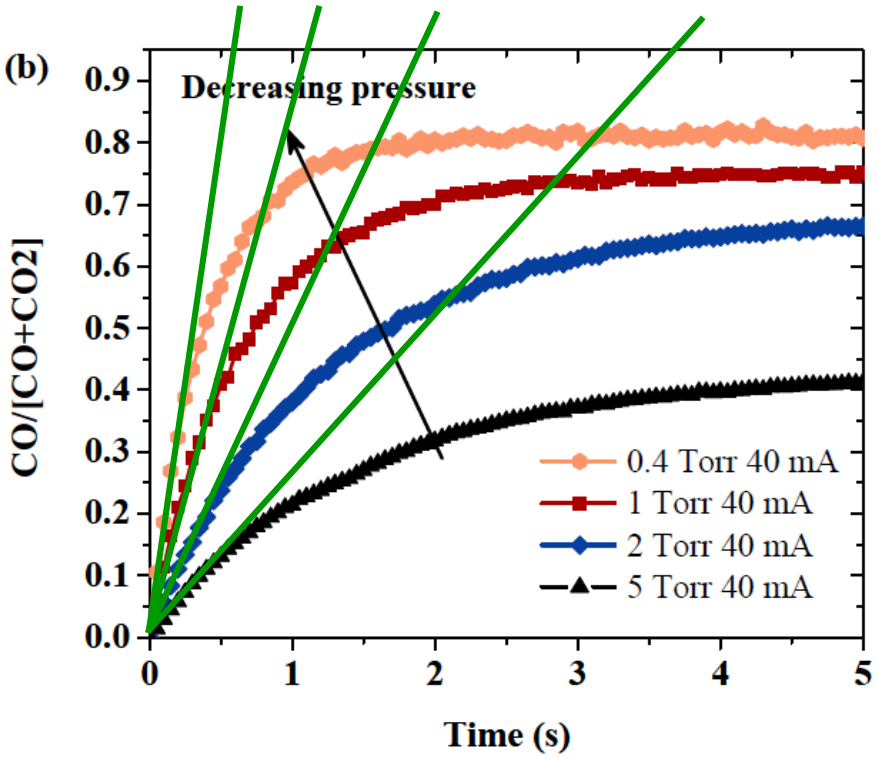
- Variation of E/N (via pressure and current)
- Variation of $t_p^{ON/OFF}$ → no influence of T_{vib} or T_{rot}
- Comparison with 0D model from IST Lisbon

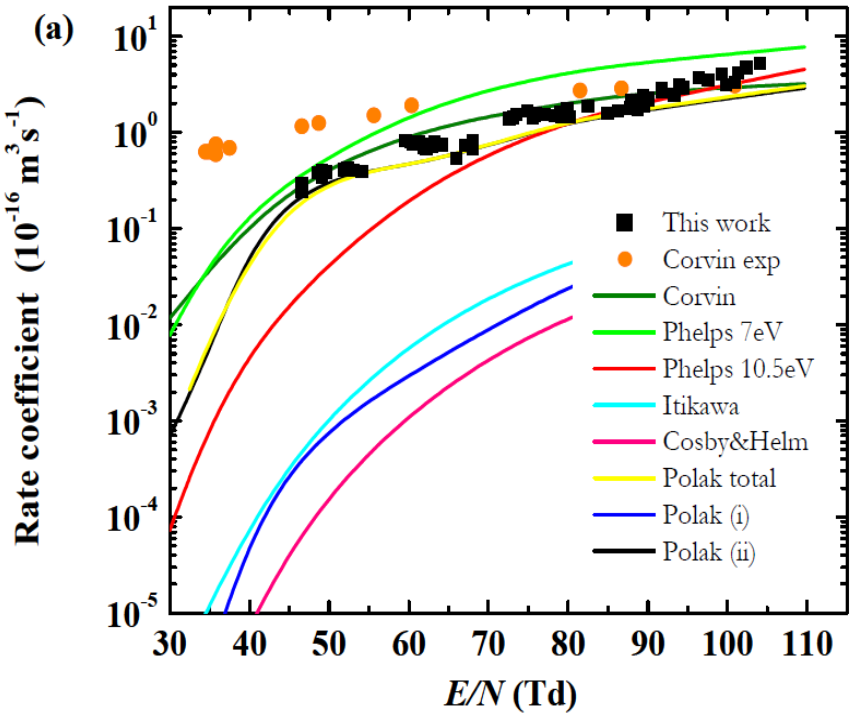
$$T^{ON} = \Sigma(t_p^{ON})$$

Electron impact dissociation rate

Initial conversion → direct electron impact dissociation

$$\alpha = \frac{[CO]}{[CO] + [CO2]} \qquad R = n_e \cdot K_{diss} \cdot [CO_2] \cdot t$$





→ Good agreement with e- impact cross section from *Polak et al* for E/N ∈ [40-105 Td]

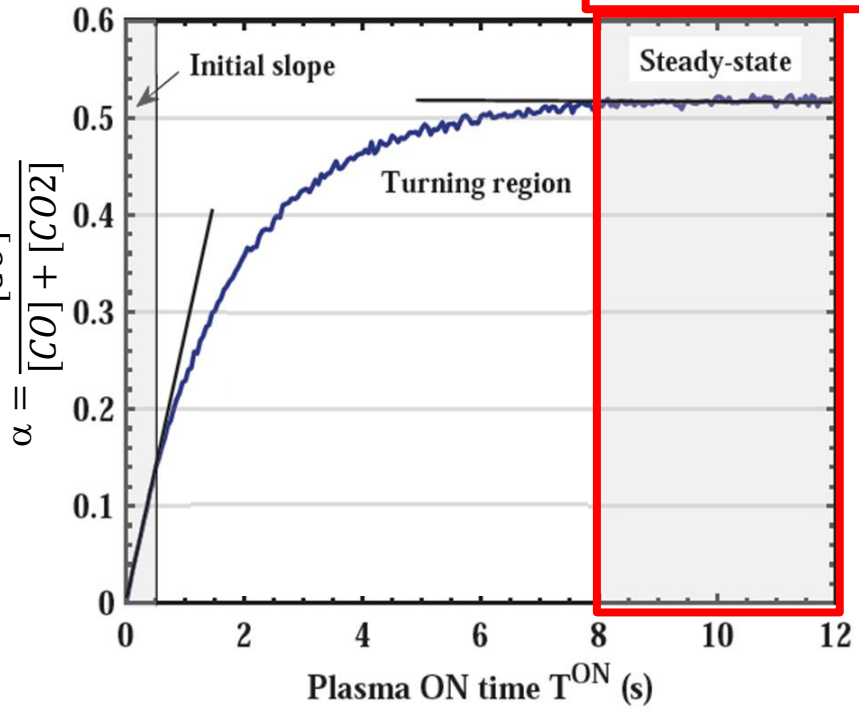
→ Phelps more appropriate for E/N > 105 Td ?

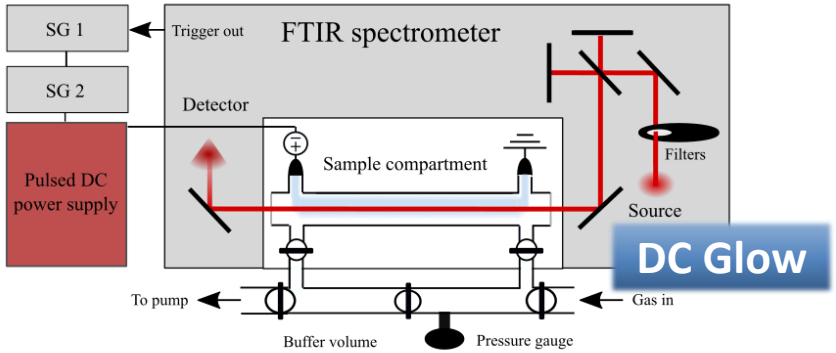
A.S. Morillo-Candas, et al, PSST. 29 (2020) 01LT01
Polak L S and Slovetsky D I 1976 Int. J. Radiat. Phys. Chem. 8 257

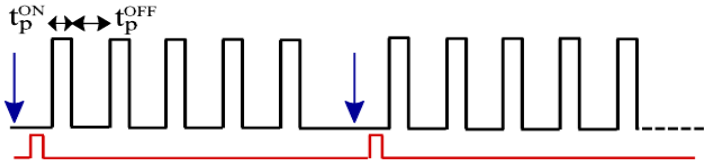
N. Yu Babaeva and G. V. Naidis, PSST 30 (2021) 03LT03

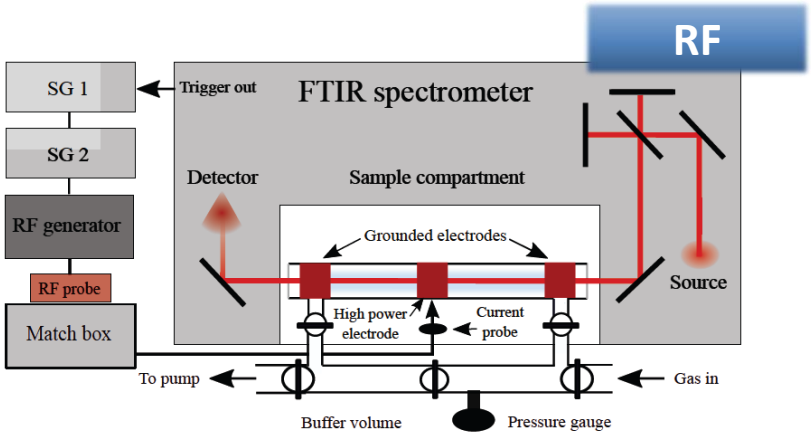
Parametric study on “back reaction” mechanisms

Pure CO_2 → Balance between : CO_2 dissociation → CO
CO + O « back reaction » mechanism → CO_2

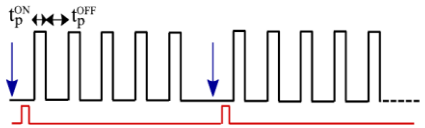


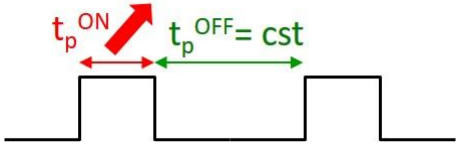




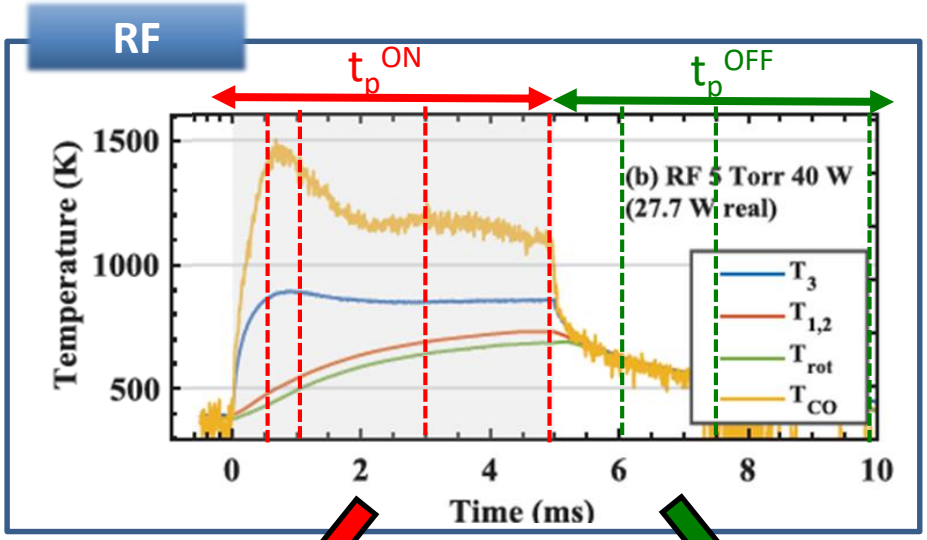


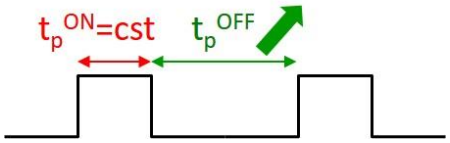
Dissociation fraction for different pulse durations



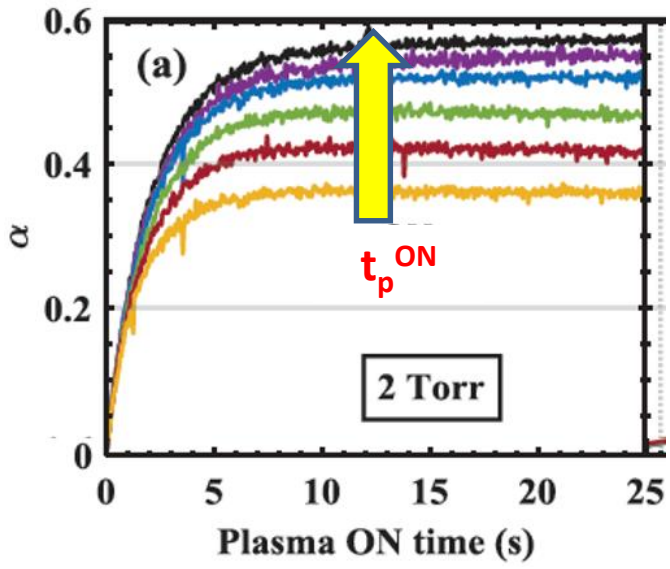


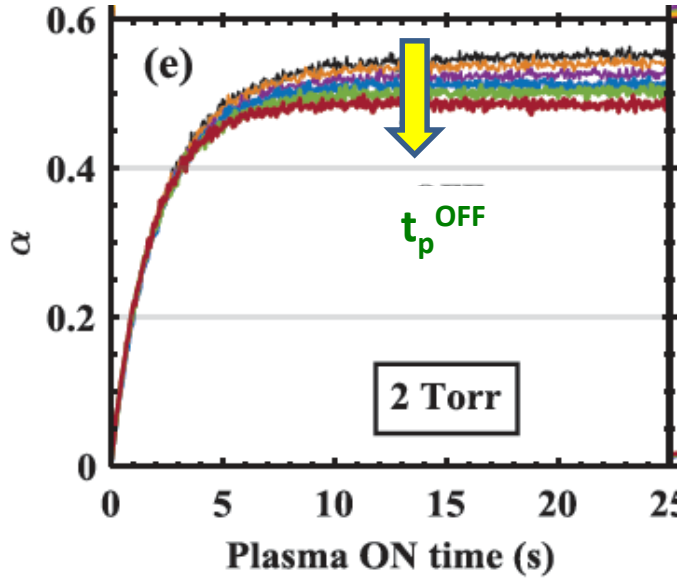
0.5ms < t_p^{ON}< 10ms



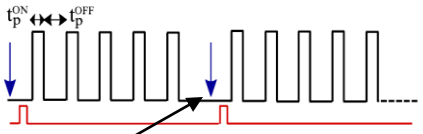


0.5ms < t_p^{OFF} < 50ms

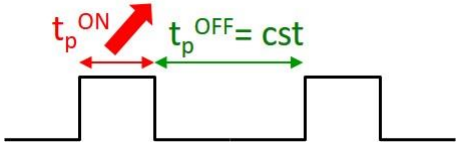




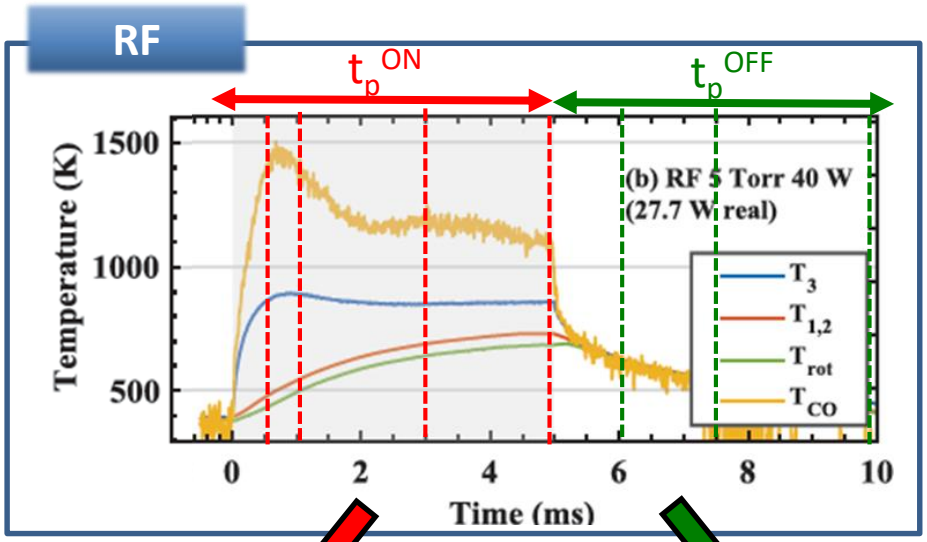
Dissociation fraction for different pulse durations

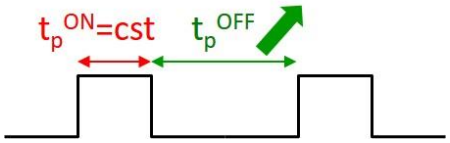


O atoms are lost in between trains of pulses…

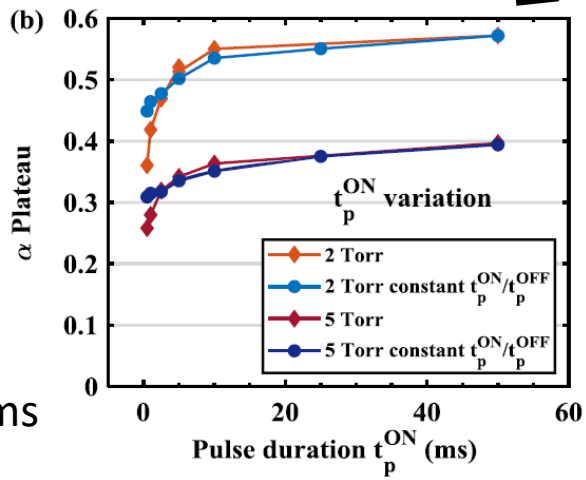


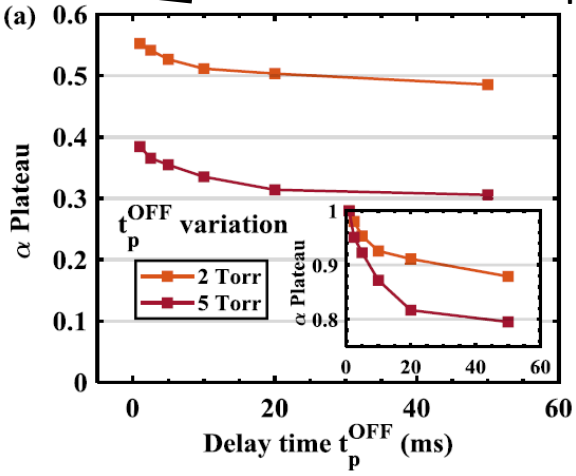
0.5ms < t_p^{ON}< 10ms





0.5ms < t_p^{OFF} < 50ms





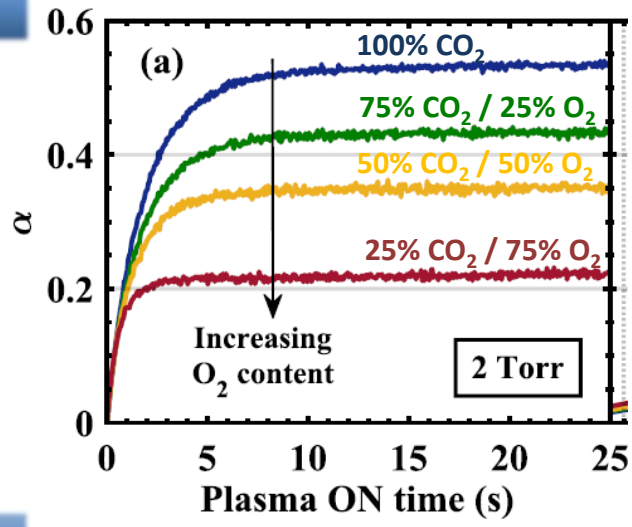
τ_{max_Tvib} ~ 1ms
$\tau_{heating}$ ~ 5ms
τ_{O_losses} ~ 100ms

$$CO(X^1\Sigma_g^+) + O(^3P) + M \rightarrow CO_2(X^1\Sigma^+) + M$$

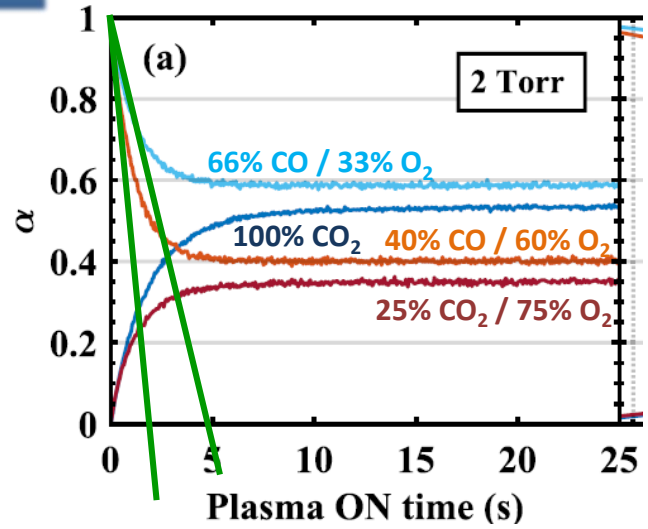
Which other back reaction ?
Role of O_2?

Importance of CO(a3Pi) on « back reaction » mechanisms

CO_2/O_2



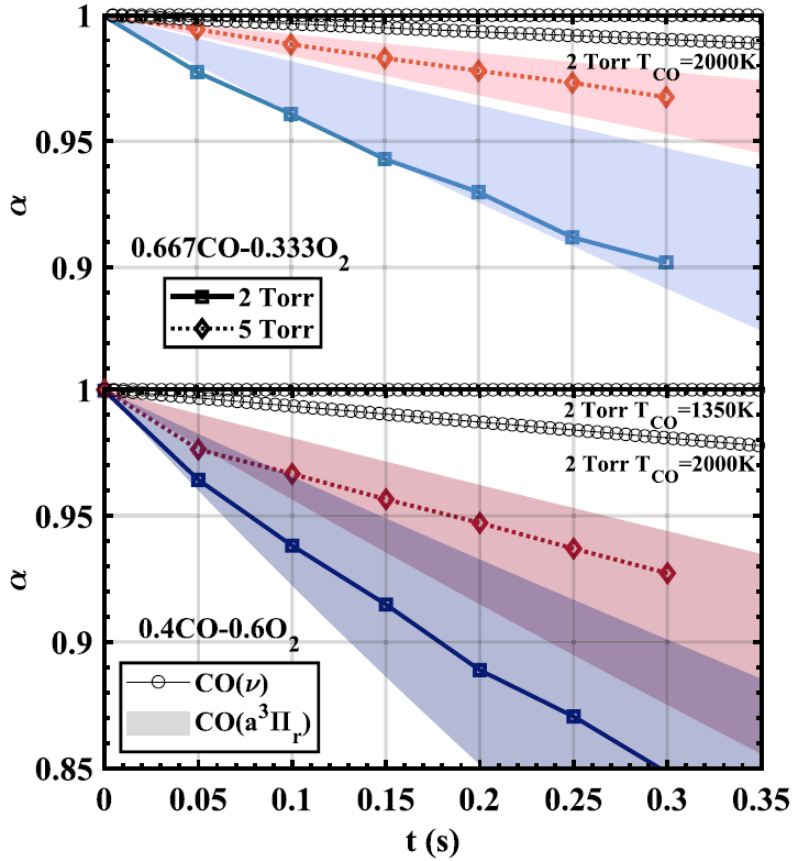
CO/O_2



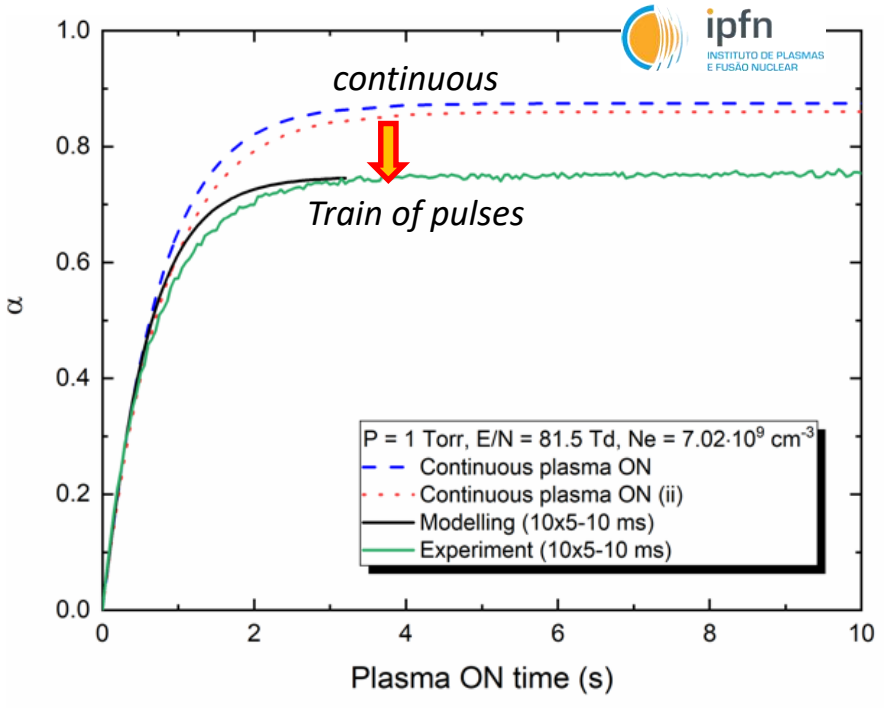
Vibrations? $CO(\nu) + O_2 \rightarrow CO_2 + O$

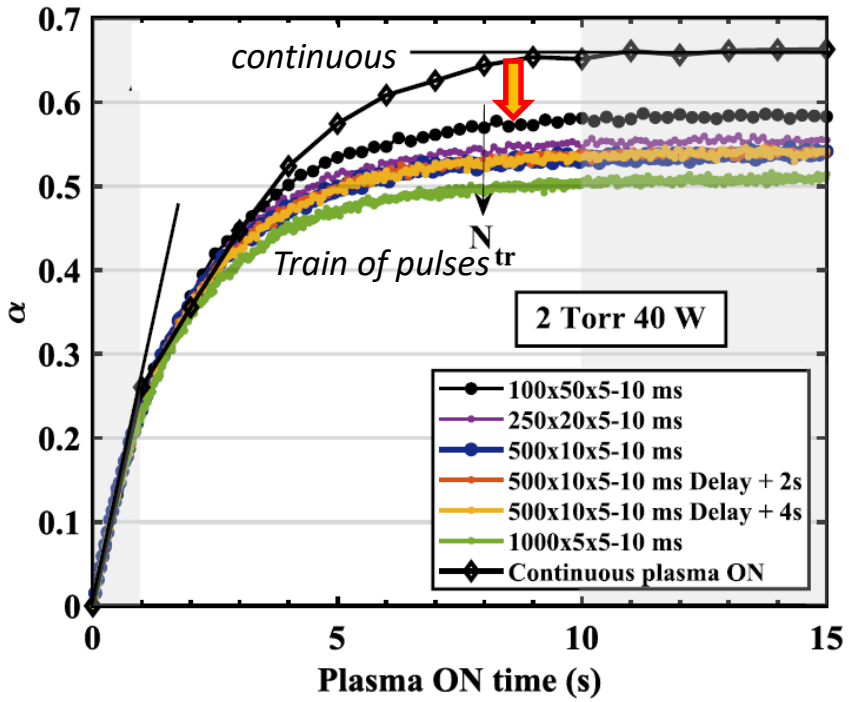
Metastables? $CO(a^3\Pi_r) + O_2 \rightarrow CO_2 + O$

$CO(a^3\Pi_r) + CO \rightarrow CO_2 + C$



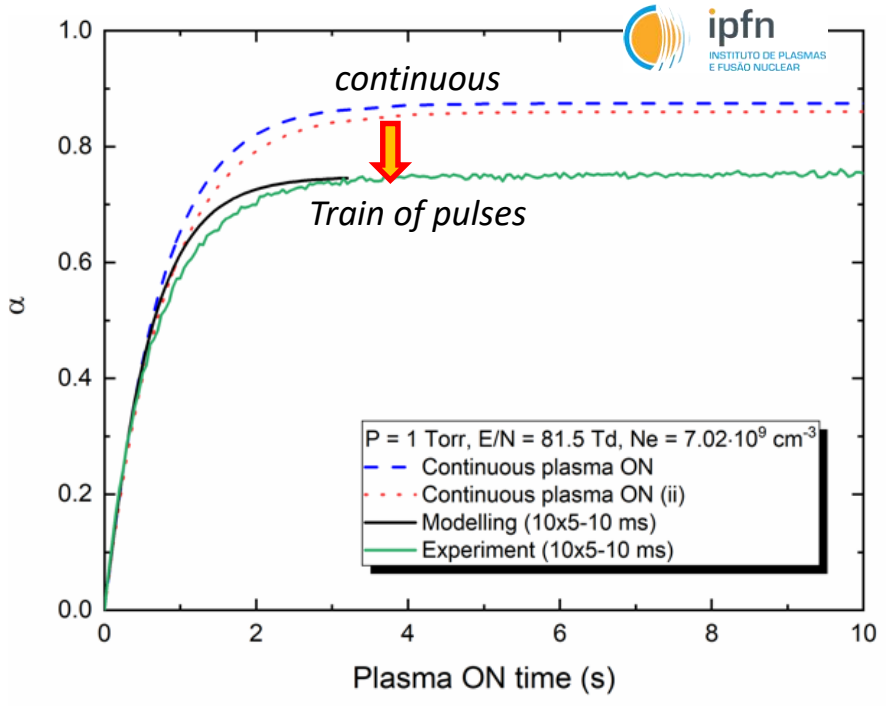
Importance of CO(a3Pi) on « back reaction » mechanisms

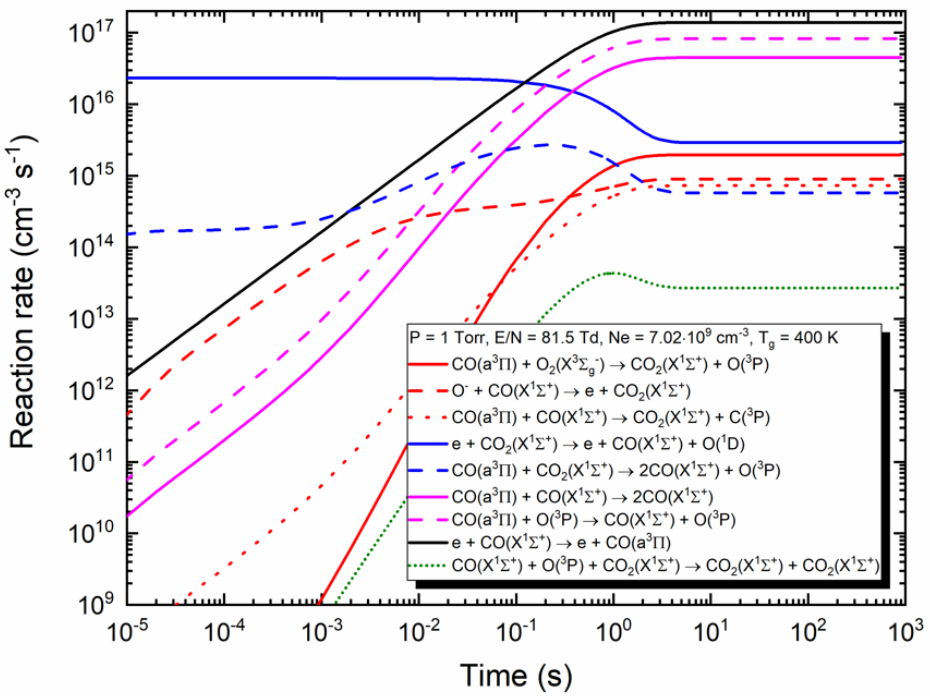




→ 0D model capture well the effect of t_p^{OFF}

Importance of CO(a3Pi) on « back reaction » mechanisms





→ 0D model capture well the effect of t_p^{OFF}

→ Need to include CO(a3Pi) and O^- reactions

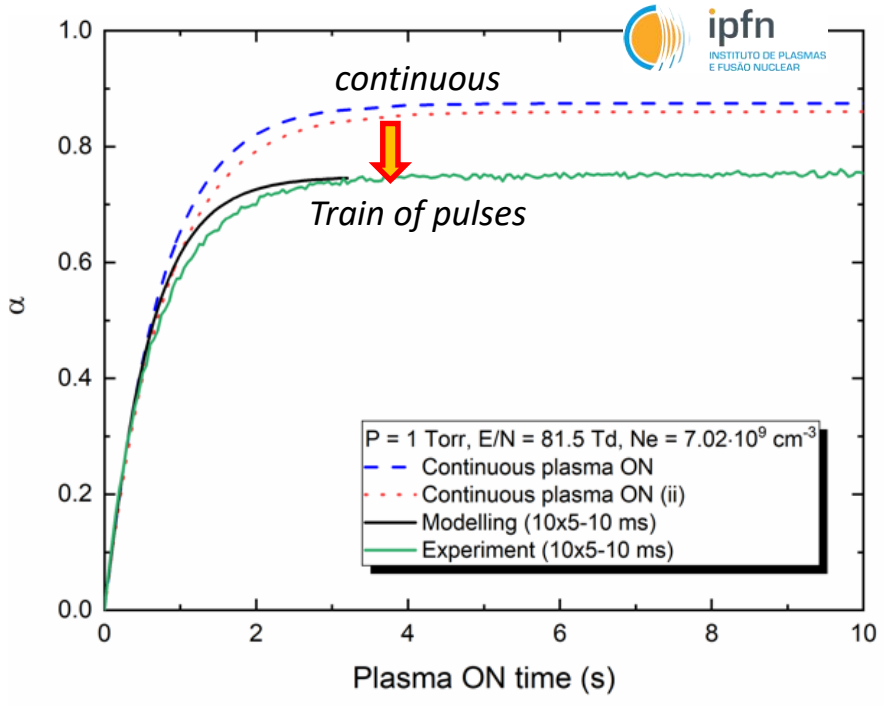
$CO(a^3\Pi) + CO_2(X^1\Sigma^+) \rightarrow 2CO(X^1\Sigma^+) + O(^3P)$

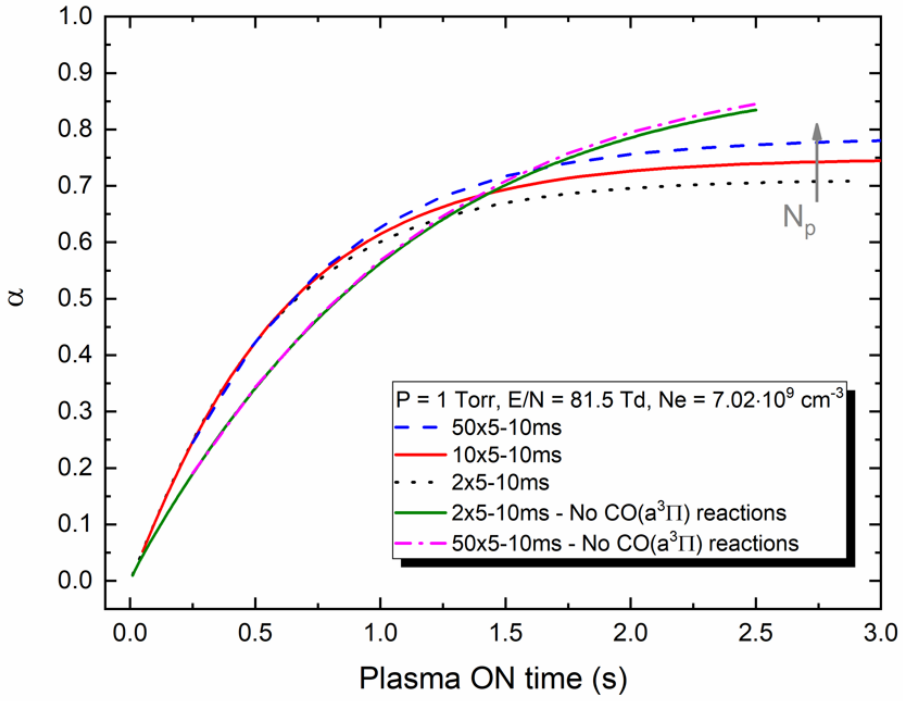
$$CO(a^3\Pi) + O_2(X) \rightarrow CO_2(X) + O(^3P)$$

$$CO(a^3\Pi) + CO(X^1\Sigma_g^+) \rightarrow CO_2(X) + C(^3P)$$

$$O^- + CO(X^1\Sigma_g^+) \rightarrow e + CO_2(X^1\Sigma^+)$$

Importance of CO(a3Pi) on « back reaction » mechanisms





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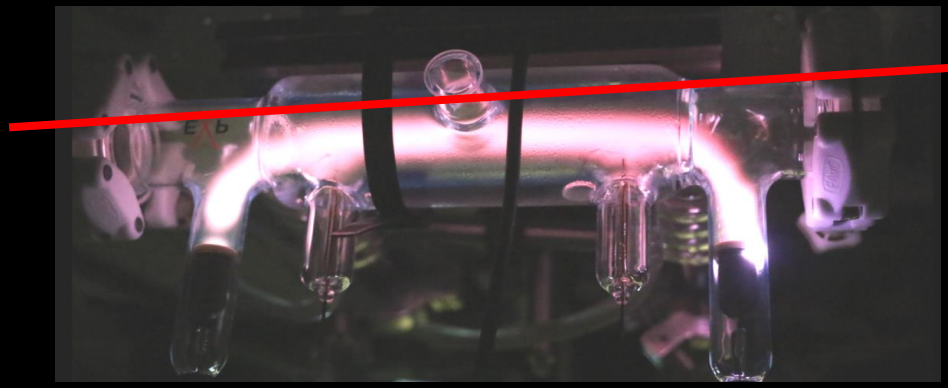
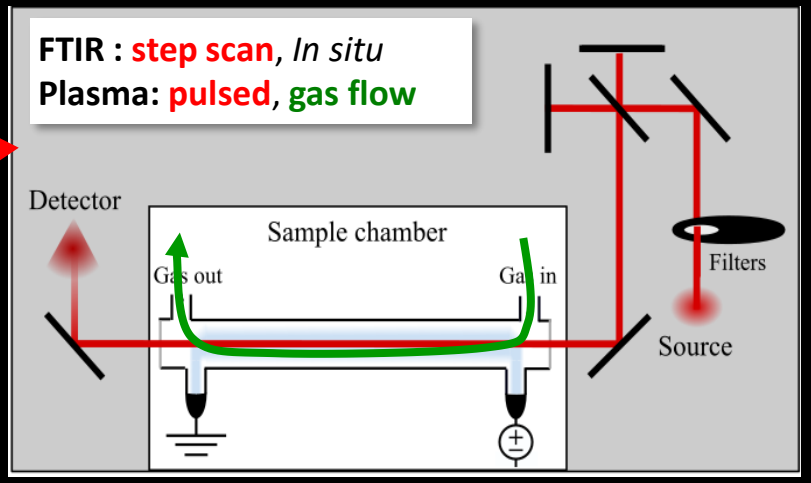
Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics





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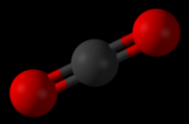

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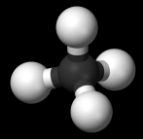
4. First insights about CO_2/CH_4 chemistry

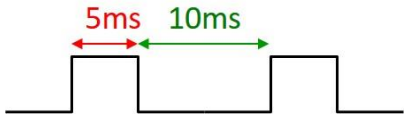


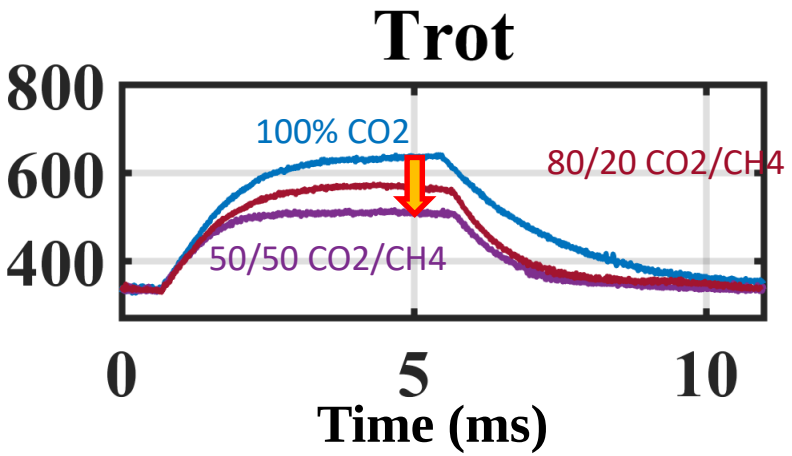
5. Towards plasma/catalyst study in CO_2/CH_4

Effect of CH_4 on T_{rot}

CO_2/CH_4

DC Glow flow
2Torr, 50 mA



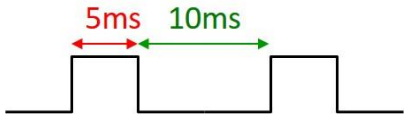


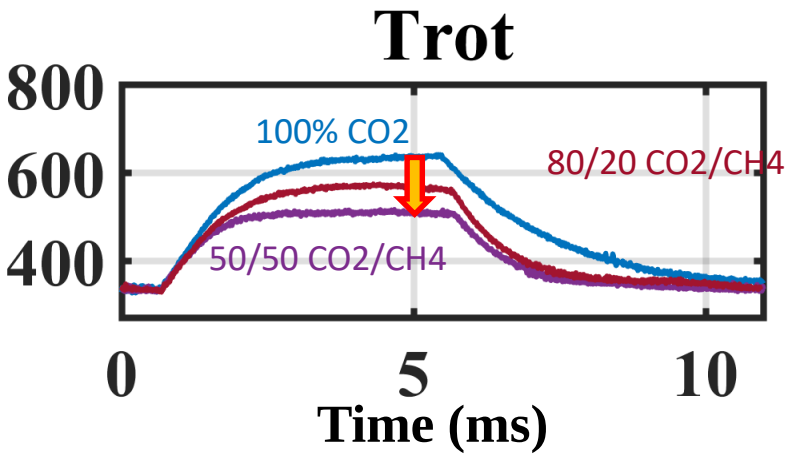
Main heat loss at the wall
→ Increase of thermal conductivity with CH_4?

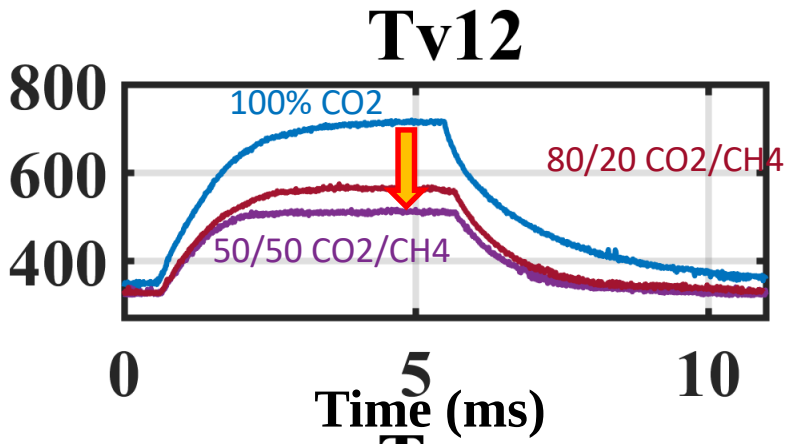
Effect of CH_4 on vibrational temperatures

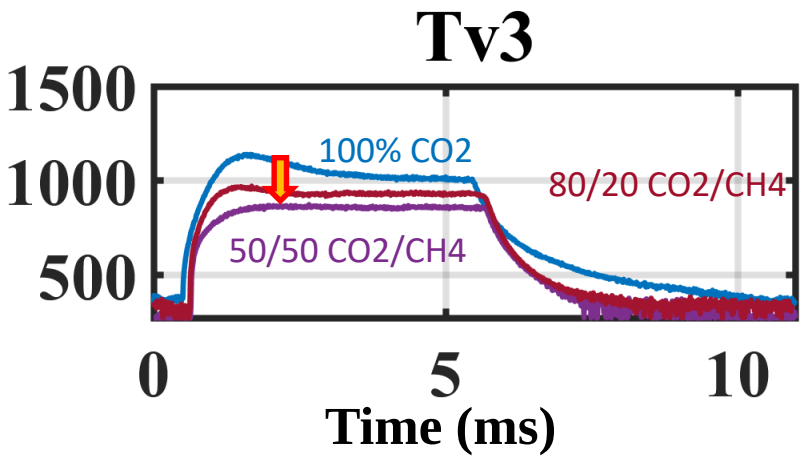
CO_2/CH_4

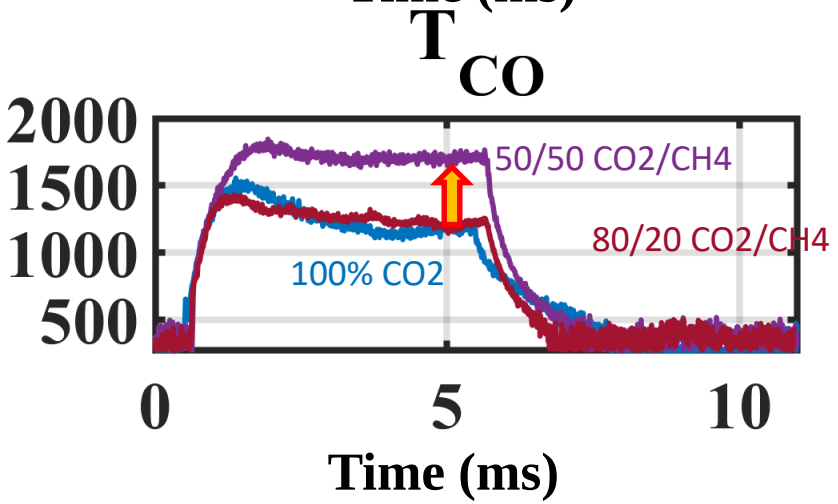
DC Glow flow
2Torr, 50 mA









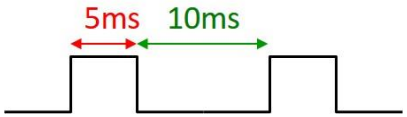


Important drop in CO_2 vibrational temperatures
Large increase in CO vibrational temperature

➡ Role of quenchers?

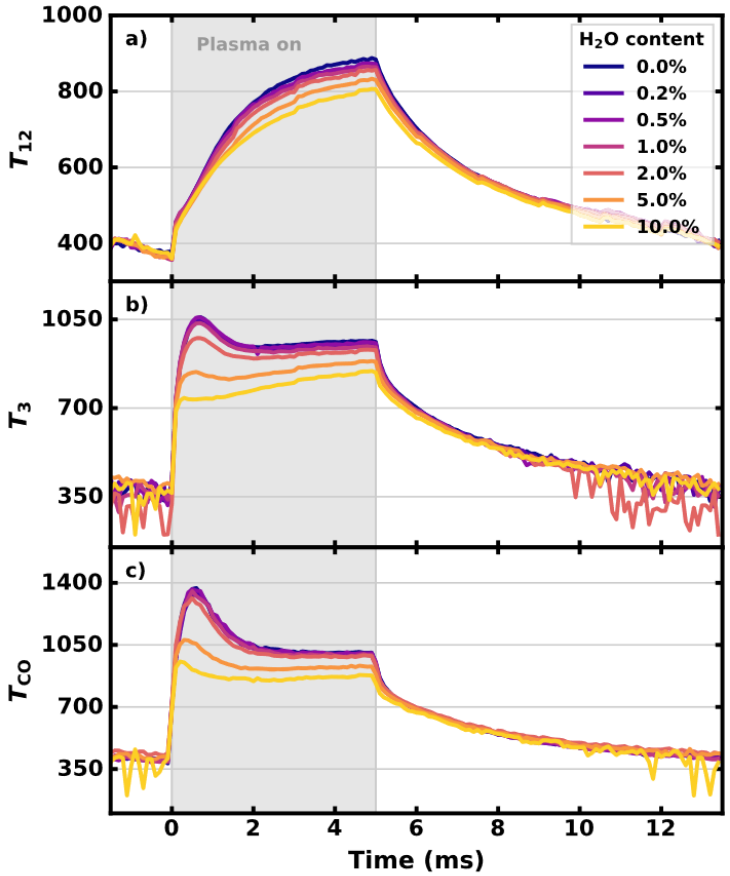
Quenching of CO_2 and CO vib. by H_2O ?

DC Glow flow
2Torr, 50 mA



H_2O often mentioned as very efficient quencher

Measurement with QCL in the same plasma reactor at TU/e



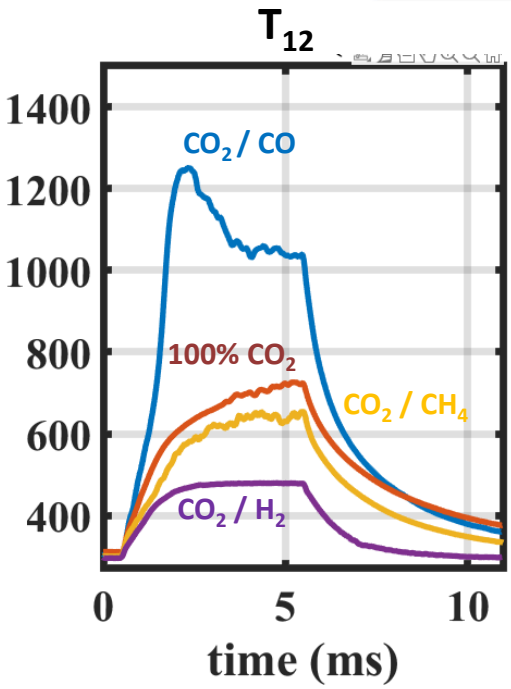
Damen, M. A., et al Plasma Sources Science and Technology 29.9 (2020): 095017.

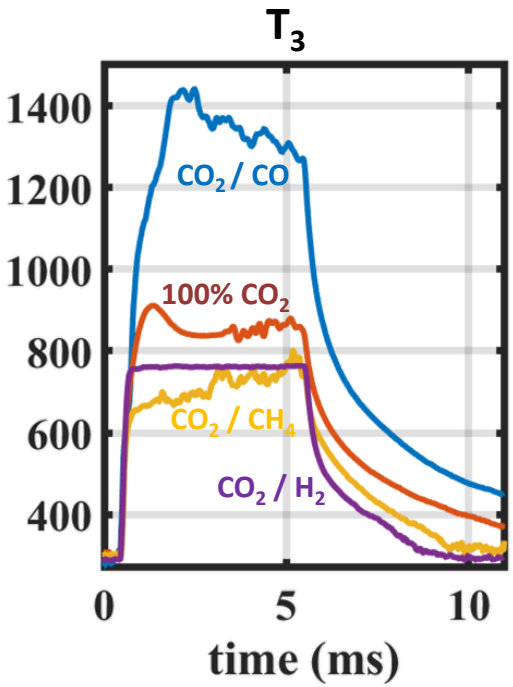
quenching of CO_2 and CO vib. by CO, CH_4, H_2

DC Glow flow
2Torr, 50 mA

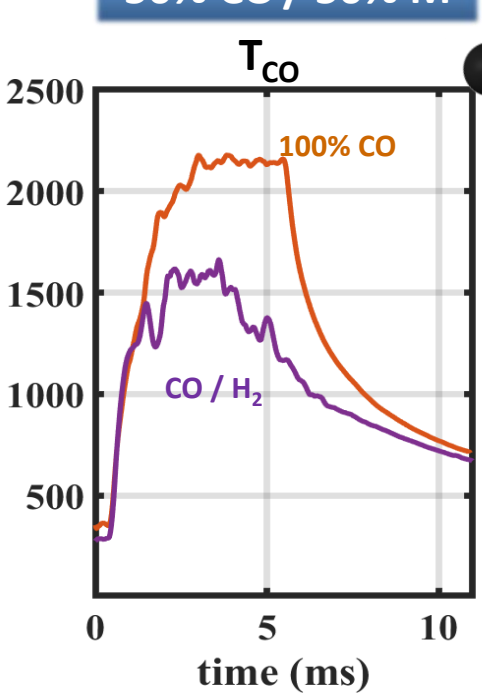
Gas fully renewed between 2 pulses

50% CO_2 / 50% M



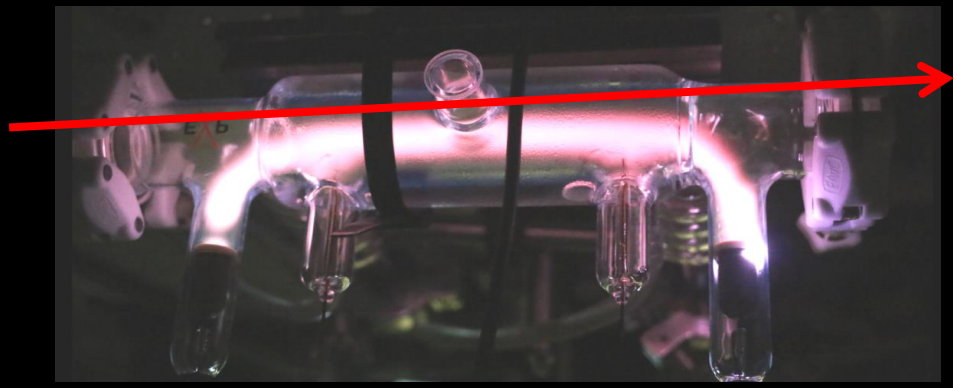


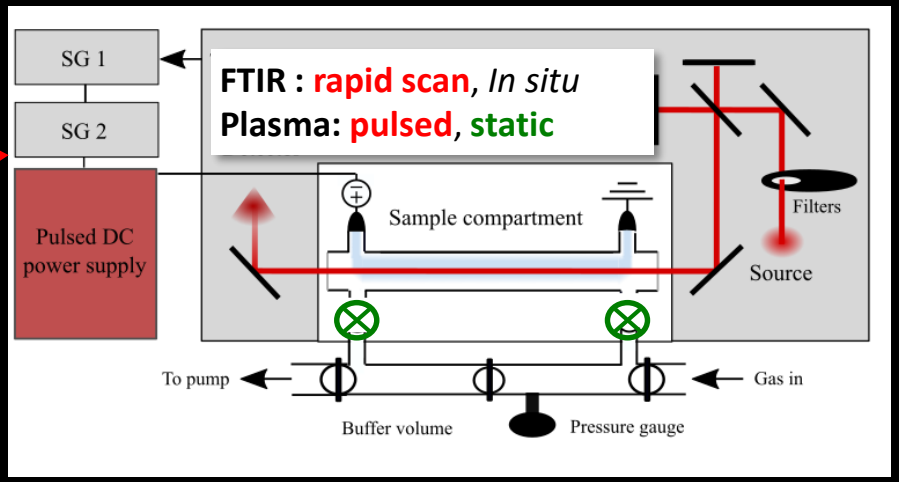
50% CO / 50% M



→ H2 is the most efficient quencher of CO2… less obvious for CO
→ 0D model in progress to describe V-V' and V-T processes and constraint quenching rates

Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics





1. Vibrational kinetics in pure CO_2
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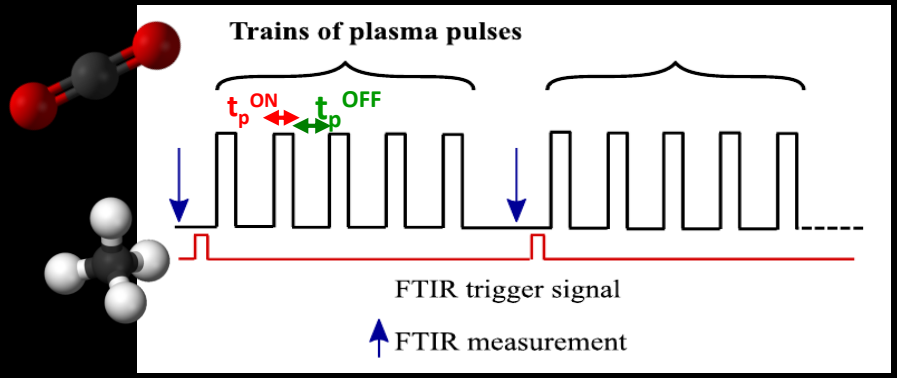
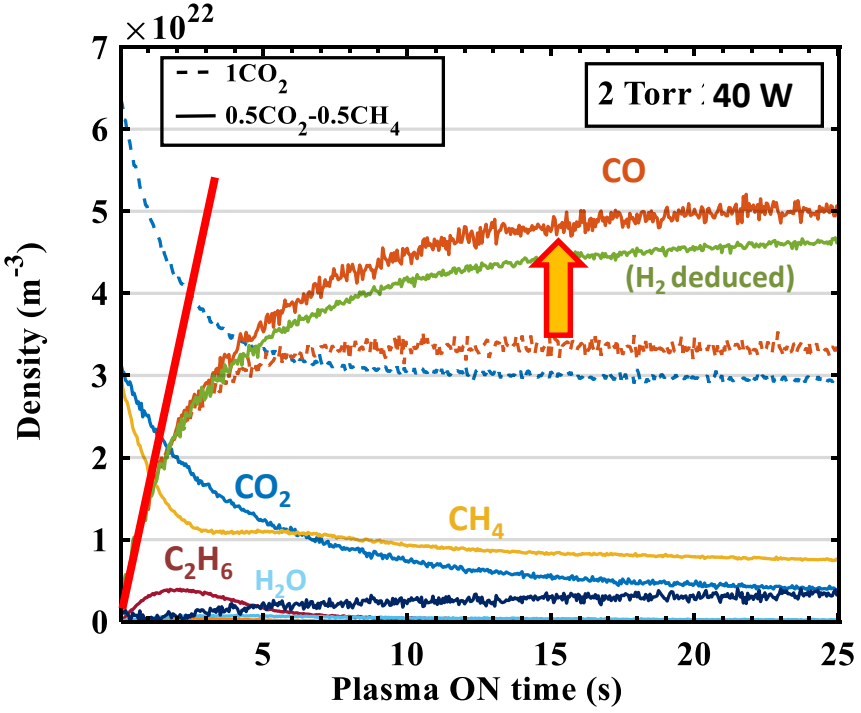
3. Vibrational quenching in CO_2/CH_4
4. **First insights about CO_2/CH_4 chemistry**

5. Towards plasma/catalyst study in CO_2/CH_4

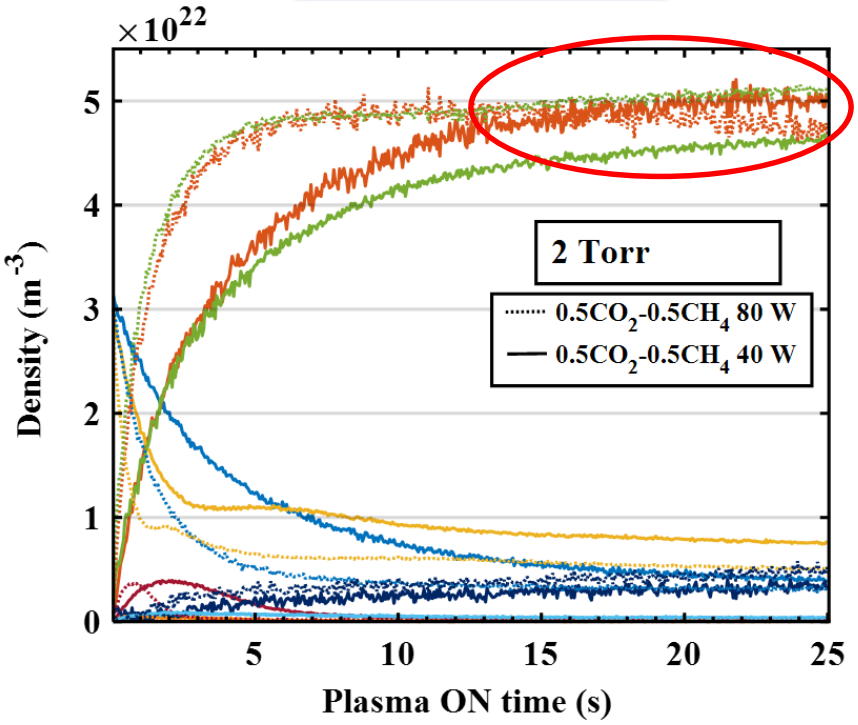


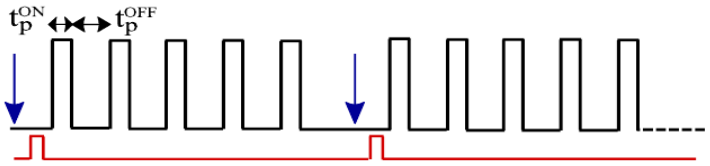
Neutrals chemistry in CO_2/CH_4 in closed reactor

100% CO_2 | 50% CO_2 / 50% CH_4



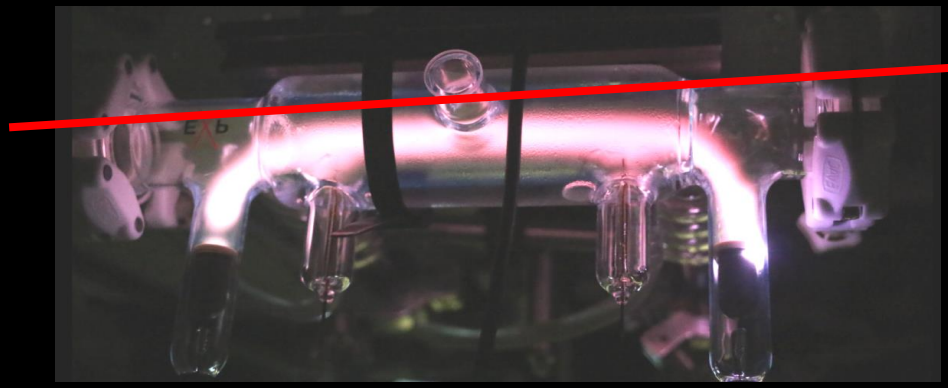
50% CO_2 / 50% CH_4

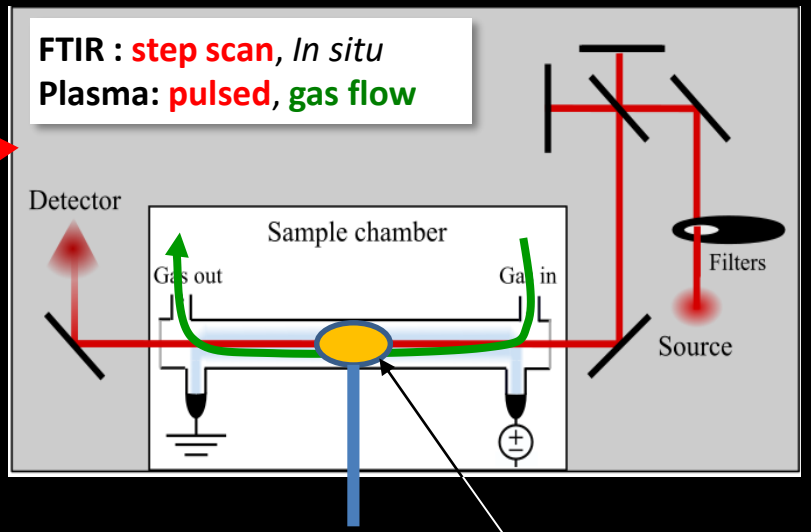




Same CO density at steady state…
→ back reaction to CO_2 removed?

Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics





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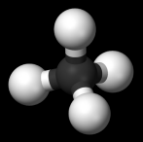
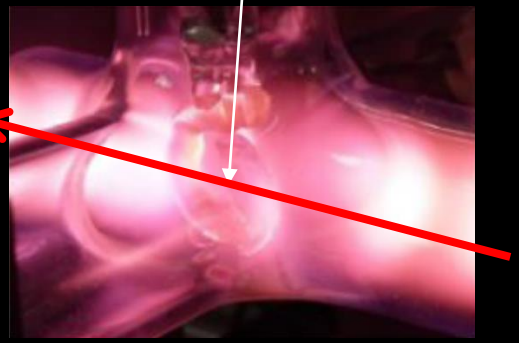


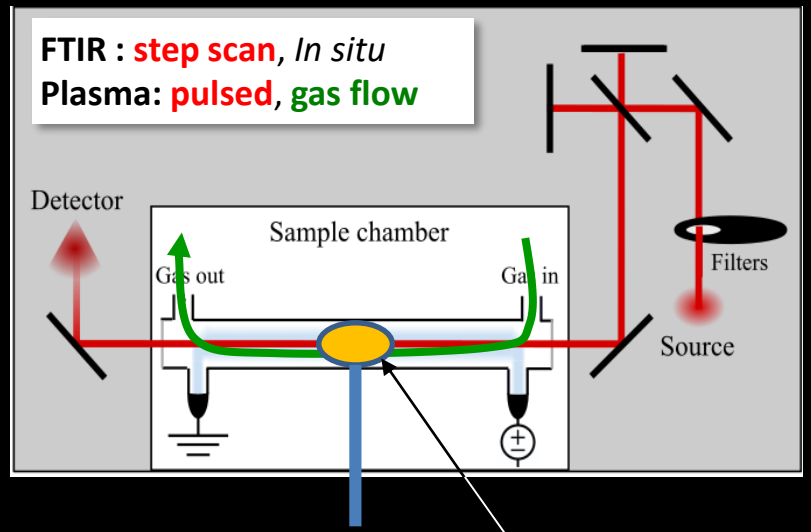
5. **Towards plasma/catalyst study in CO_2/CH_4**



Glow discharge as a benchmark for kinetic models
Step by step validation of CO_2 kinetics

Steps

1. Clean surface of the material with O_2 plasma for around 40 min
2. Send CO_2 or CO_2/CH_4 gas flow (adsorption)
3. Ignite plasma at 10mA then 50mA
4. Ignite plasma at 50mA
5. Send O_2 gas to observe which bands remain on the spectrum
6. Ignite O_2 plasma



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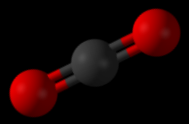

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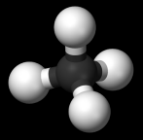

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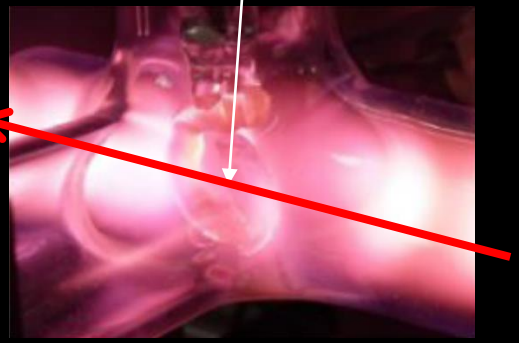
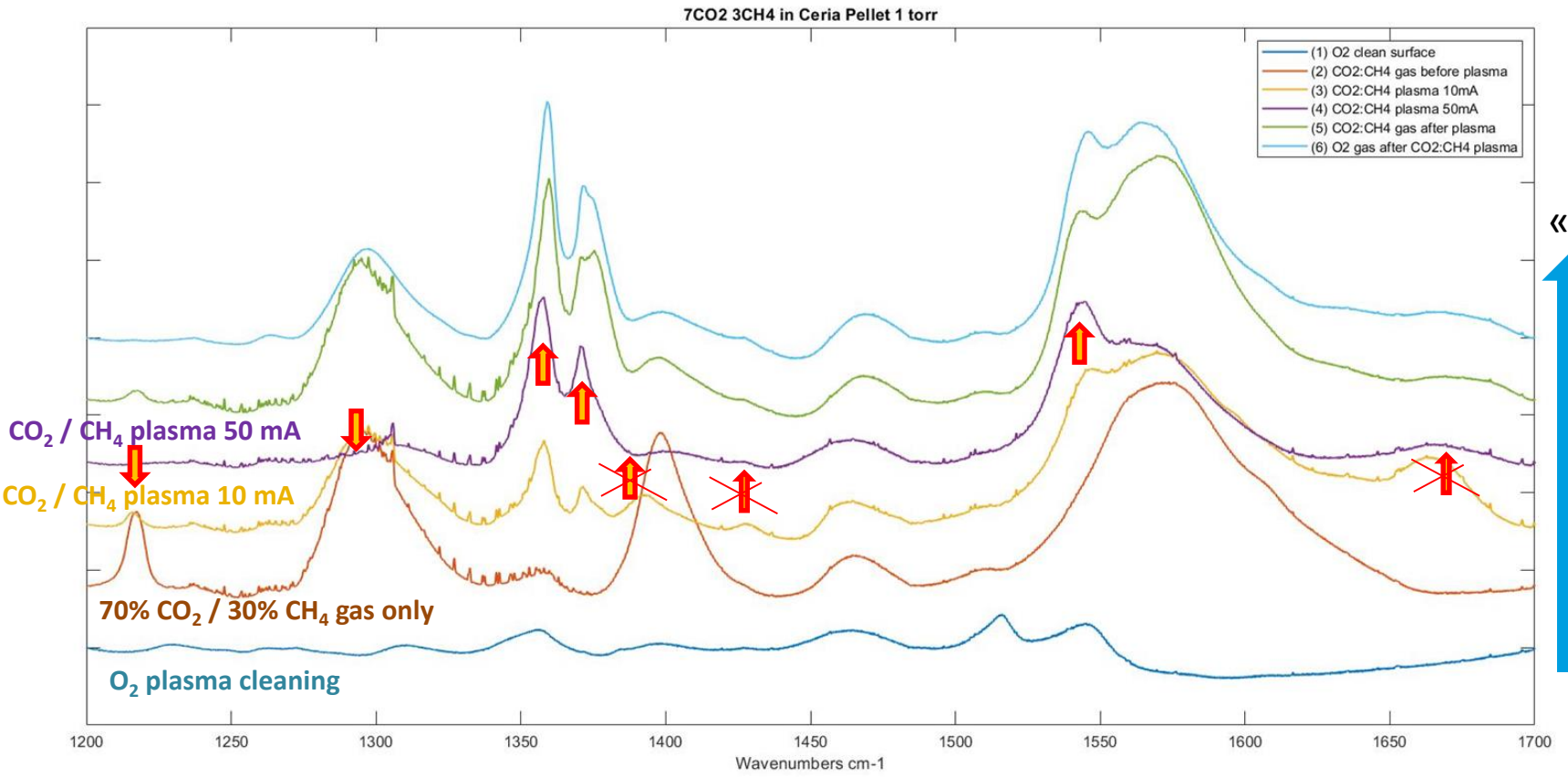


Example of spectra evolution during the 6 steps of the procedure



« 6 steps »

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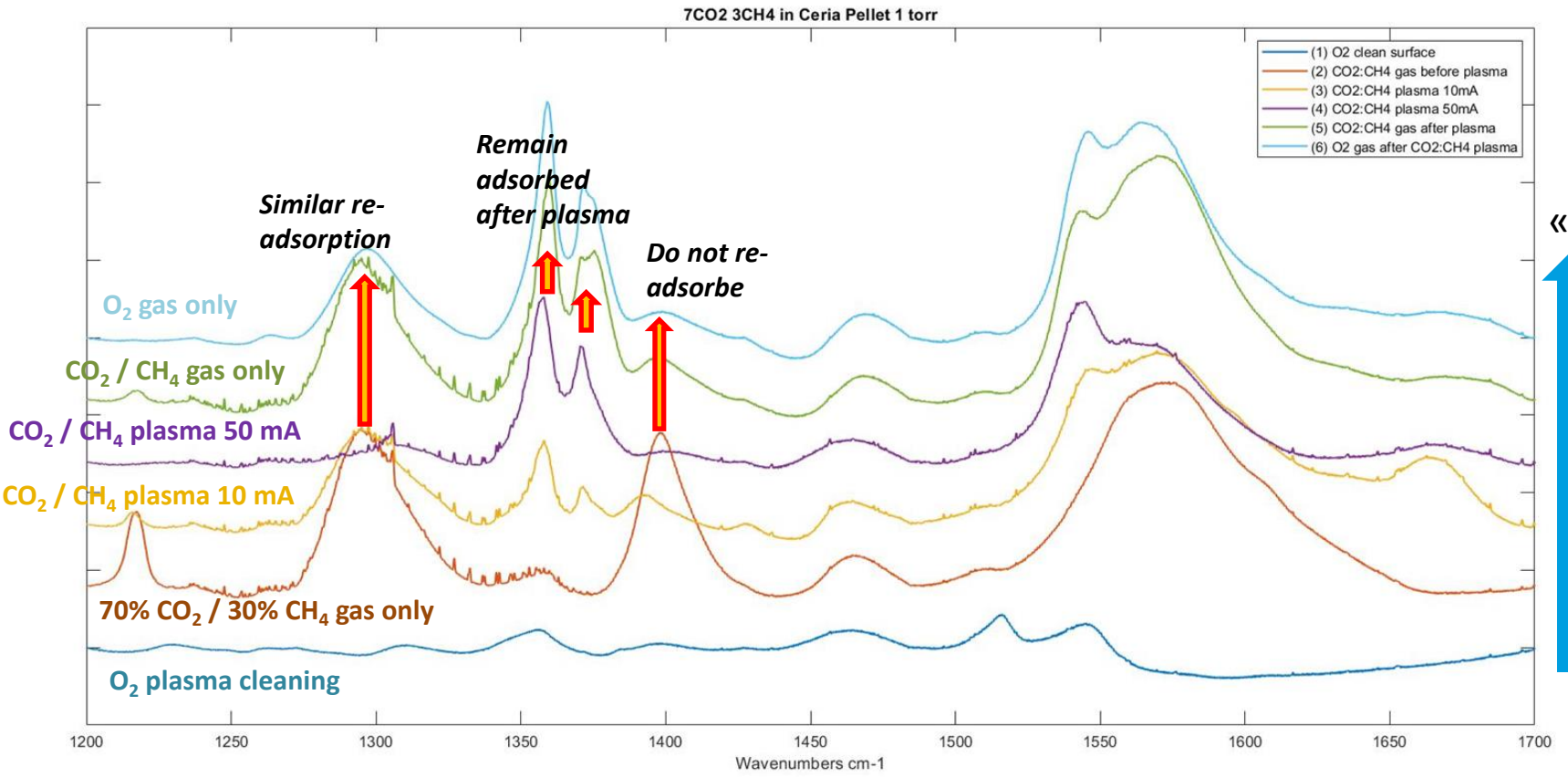
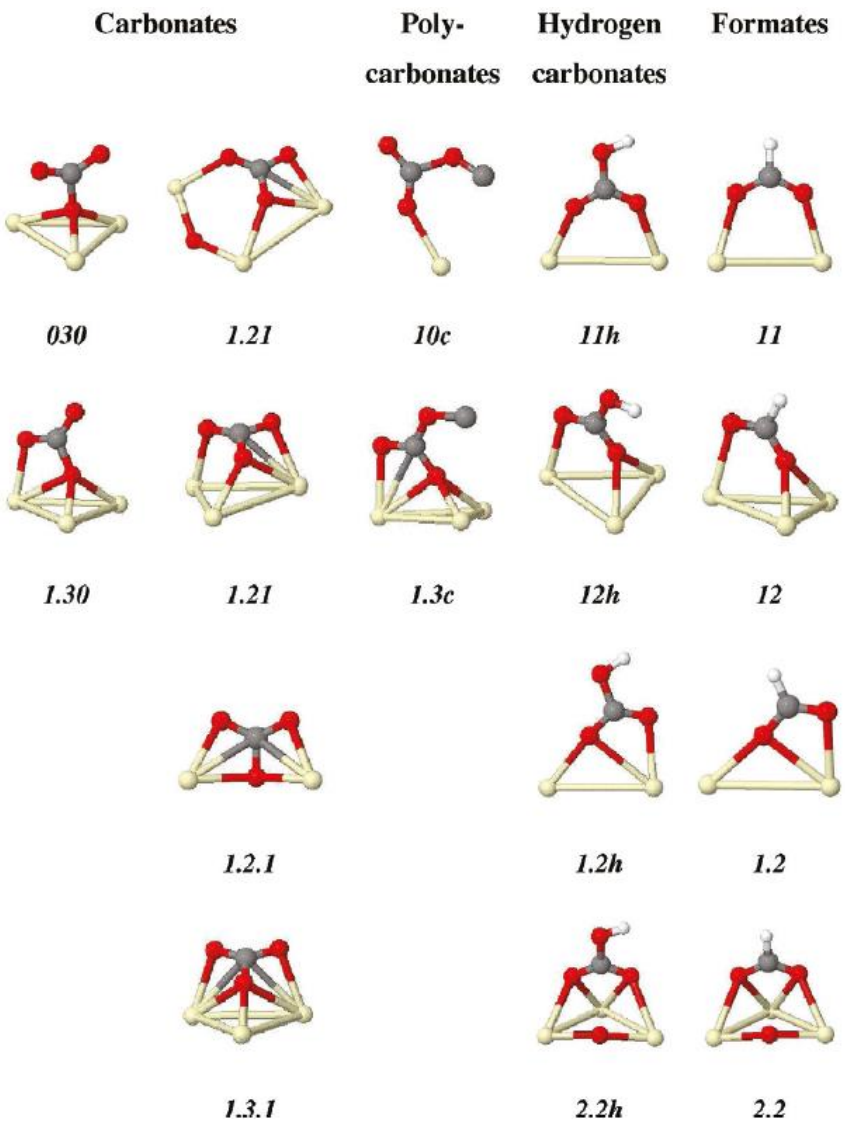


« 6 steps »

Identification of bands on surface

Vayssilov, Georgi N., et al. The Journal of Physical Chemistry C 115.47 (2011): 23435-23454



The Journal of Physical Chemistry C

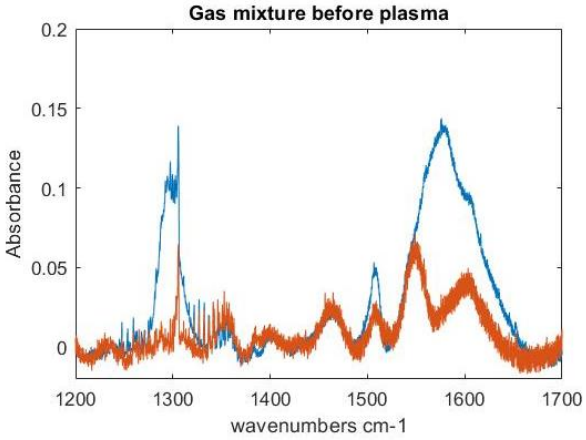
Table 3. Experimental Vibrational Frequencies (in cm^{-1}) and Their Assignment to Various Surface Oxo-Carbonat Ceria According to the Intervals of the Calculated Vibrational Frequencies

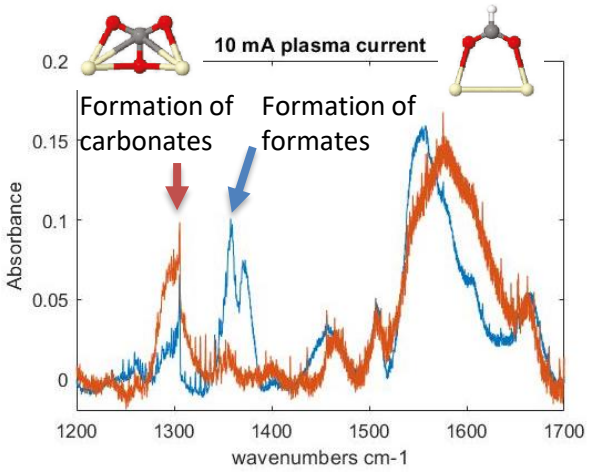
frequencies				treatment	figure	assignment
ν(CO)	ν(CO)	ν(CO)	comb.			Carbonates
1451	1377	1065		CO on activated CeO_2	Figure 7	tridentate, 1.21, 1.2.1
1458	1362	1045		CO_2 on activated CeO_2	Figure 5	tridentate, 1.21, 1.2.1
1463	1358	1065		CO_2 on activated CeO_2	Figure 5	tridentate, 1.21, 1.2.1
1473	1380	1044	~2876[b]	CO on activated CeO_2	Figure 7	tridentate, 1.21, 1.2.1
1490	1380	1085		CO on hydroxylated CeO_2	Figure 9	tridentate, 1.21, 1.2.1, in vicinity of Ce^{3+}
1500	1342[a]	1038		CO_2 on activated CeO_2	Figure 5	tridentate, 1.21, 1.2.1
1568	1286	1018	~2850[b]	CO_2 on activated CeO_2	Figure 5	tridentate, 1.3.1
1592	1290	1003		CO on hydroxylated CeO_2	Figure 9	tridentate, 1.3.1, in vicinity of Ce^{3+} or/ar
1596	1303	990		CO on activated CeO_2	Figure 7	tridentate, 1.3.1
1618	1281[a]	*a*		CO on activated CeO_2	Figure 7	tridentate, 1.3.1
1722	1147	*a*		CO on activated CeO_2	Figure 7	bidentate, 1.30
1732	1136	*a*		CO_2 on activated CeO_2	Figure 5	bidentate, 1.30
ν(OH)	ν(CO)	ν(CO)	δ(COH)	ν(CO)			Hydrogen Carbonates
3616	1602	1397	1218	1030[a]	CO_2 on activated CeO_2	Figure 5	
2672			965		CO_2 on deuteroxylated CeO_2	Figure S3	
ν(CH)	ν(CO)	δ(OCH)	ν(CO)	comb			Formates
2850	1547	1372	1360	2935, 2725[b]	CO on hydroxylated CeO_2	Figure 8	
	1561					Figure 8	
2845	1547	1373	1358		CO on hydroxylated CeO_2, stable after treatment in O_2	Figure 9	
2151	1539	1018	1332		CO on deuteroxylated CeO_2, stable after treatment in O_2	Figure 9	

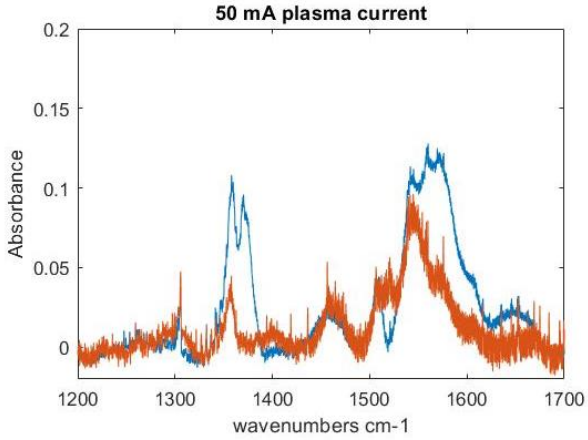
[a] The precise position of the band cannot be identified due to overlapping bands in this region. [b] Wide combination band with variable peak maximum depending on the conditions.

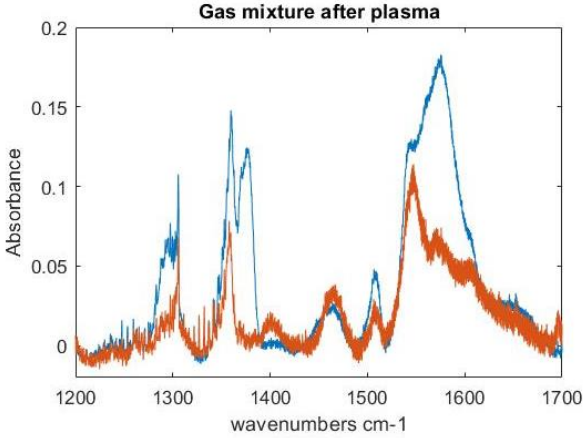
Comparison of different gas mixture can be helpful

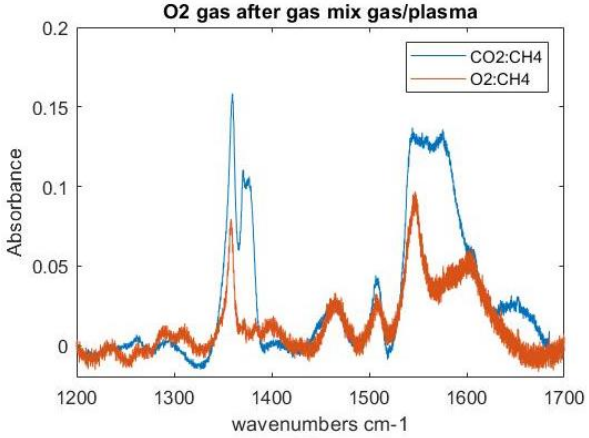
Comparison of CO_2/CH_4 and O_2/CH_4 experiment











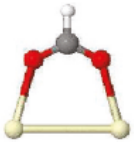
Formation of formates at peaks 1360 ad 1370 confirmed by the bands at 2850 and 2936 cm-1 during plasma and after

Time evolution of identified bands

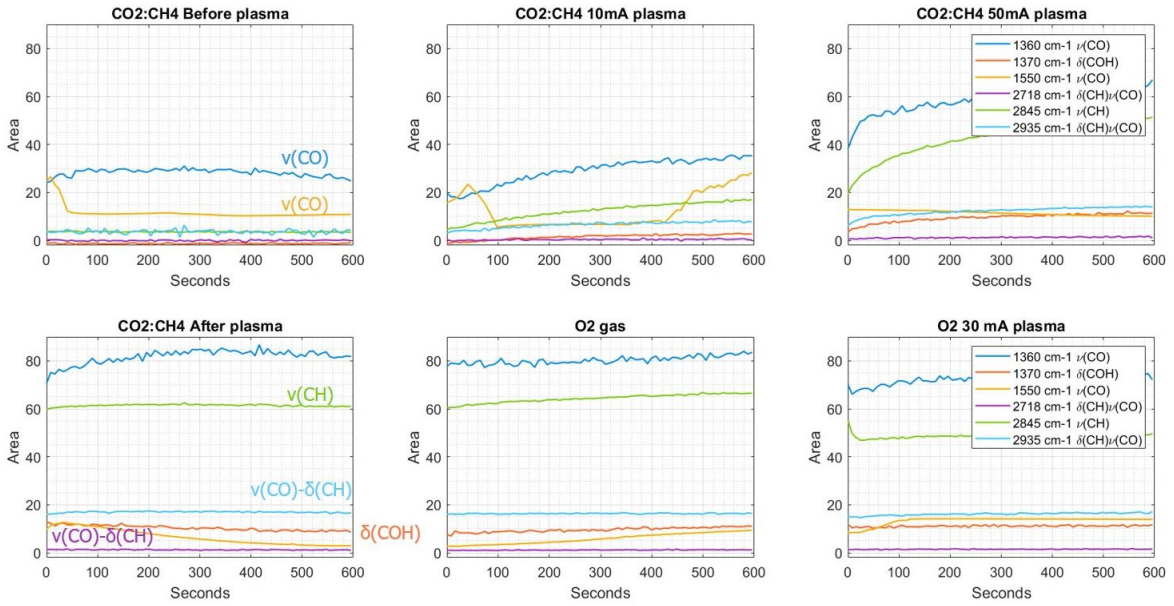
70% CO_2 / 30% CH_4

1 Torr

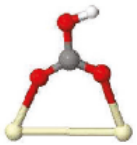
Formates



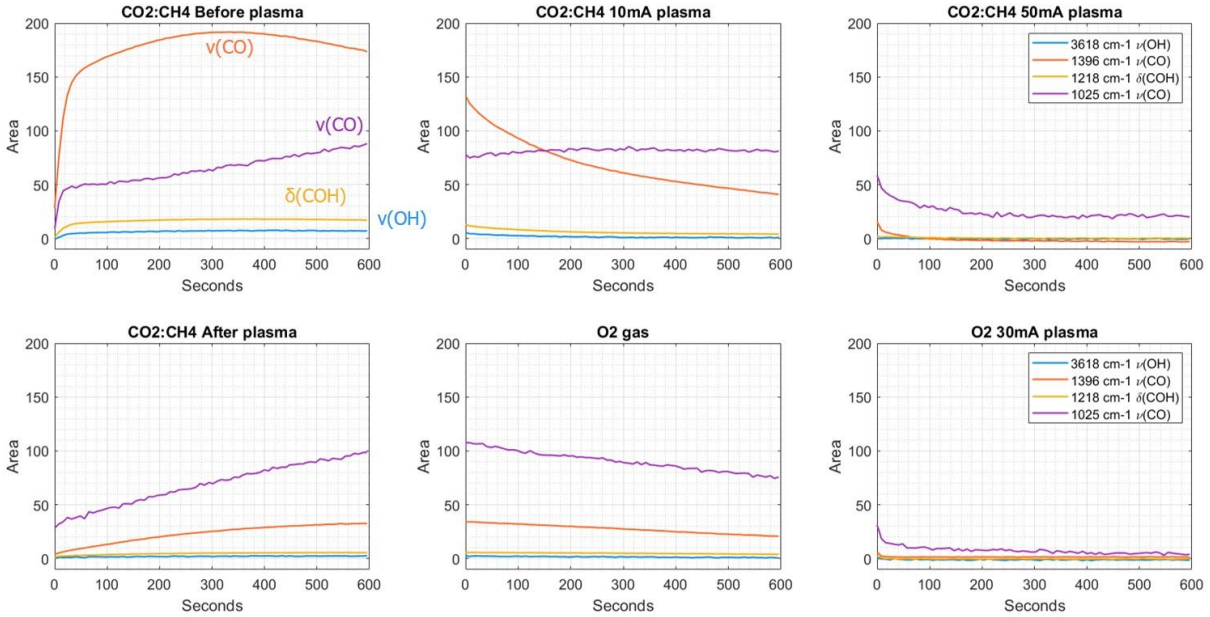
- Formates get adsorbed during plasma
- Increase with current
- Strongly adsorbed (not removed by O_2 plasma)



Hydrogen carbonates



- Hydrogen Carbonates appears during gas flow
- CO2/CH4 plasma converts them
- Weakly adsorbed



Conclusions

- Combining time resolved measurement in flowing condition and duty cycle ratio variation in static condition is a powerfull tool for plasma kientics studies

- In pure CO2:
    - Vibrational kinetics of first 72 levels validated
    - Quenching by O atoms quantified
    - Cross section for e- impact dissociation of CO2 constrained between [40; 105] Td
    - Evidence of the key role of CO(a3Pi)
    - Role of O(1D) to be clarified
- In CO2/CH4:
    - Vibrational kinetics investigated: strong quenching of byproducts of CH4, mostly on CO2
    - Complex chemistry being traced with isotopic labelling
    - Plasma phase and adsorbed phase on catalyst measured in the same plasma for a better understanding of plasma/Catalysis interaction

Thank you for your attention !