Electrification and circularity
- a plasma chemistry perspective

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Motivation: Energy transition & the TeraWatt Challenge[1]

Maintaining global economic growth

& keeping atmospheric CO_2 < 450 ppm:

~30 terawatts of carbon-neutral power by 2050

[1]*M.I. Hoffert et al. Nature* ***385*** *(1998) 881*

The challenge on a personal scale

Food: 2 500 kCal daily

My solar panels: 5 000 kCal daily

Dutch daily energy consumption per capita

100 000 kCal

Difference = prosperity

Plasma and sustainable electricity

Electricity dominant form sustainable energy → Electrification

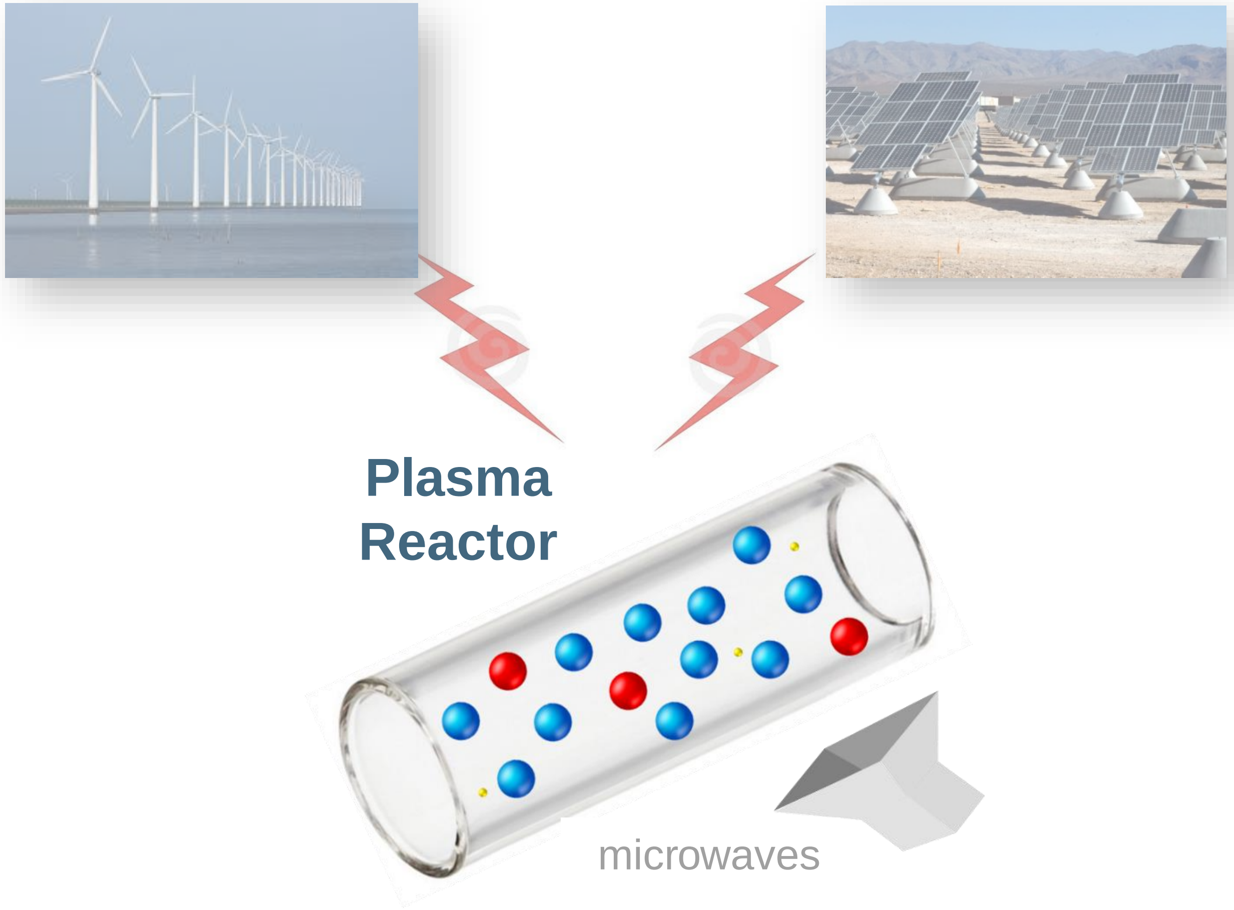
Power-to-X to address intermittency / sector integration

Traditional price hierarchy coal – oil – gas – hydrogen – electricity is broken

→ Opportunity for plasma chemistry

NEVER free electricity & efficiency = key & plasma should add uniqueness

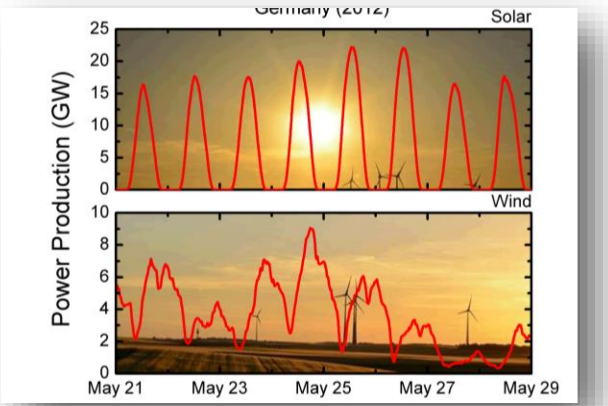
Plasma conversion as power-to-X



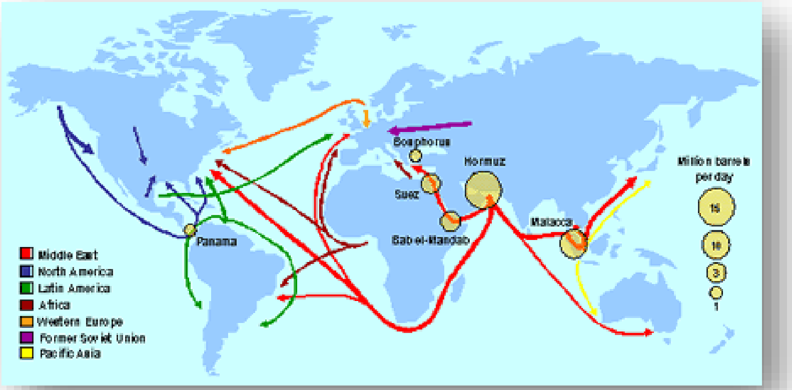
Power +… → X

Scope of Power-to-X

Energy storage



Energy transport



Sector integration

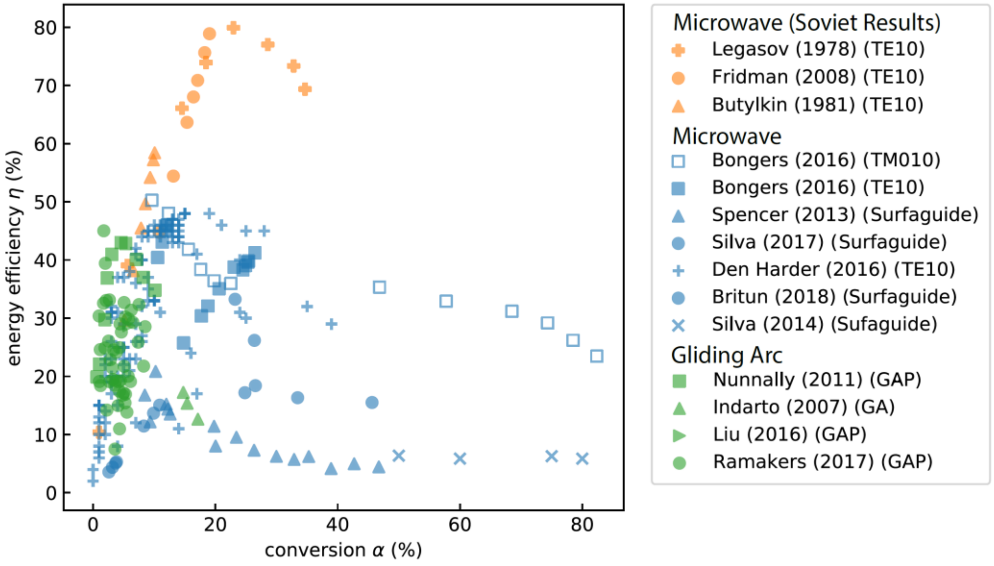
Larger deployment of sustainable electricity achieves CO_2 reductions

NOT the input CO_2 → efficiency determines climate benefit!

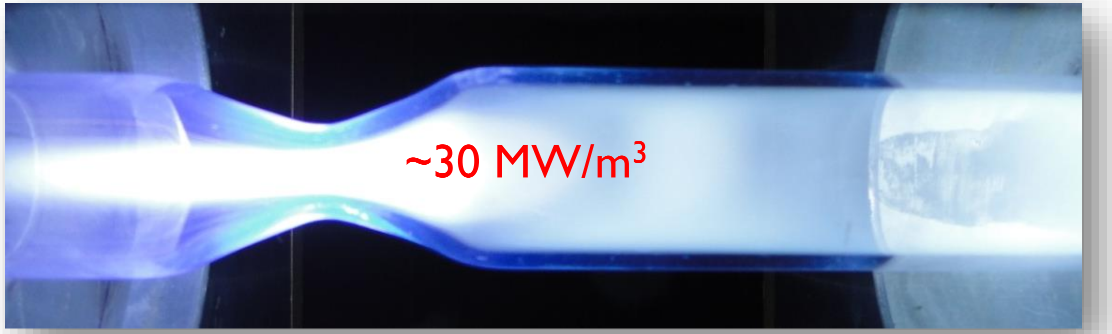
Attractiveness (uniqueness?) of the plasma approach

Promise of high energy efficiency

Wolf, 2020, thesis Univ. Techn. Eindhoven



High energy density (footprint & kinetics)



Low investment & “inertia” (intermittency)
no scarce materials (scalable)

Prevailing model in CO_2: vibrational ladder climbing

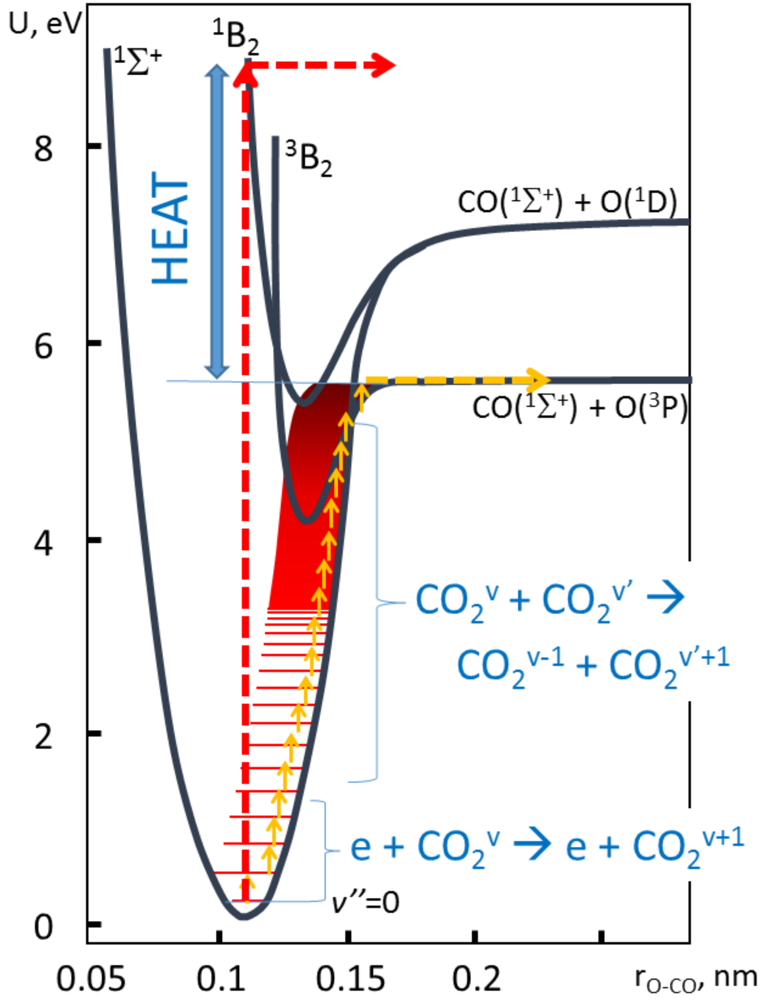
- Vibrational ladder climbing up to dissociation limit provides most efficient reaction channel

- A robust channel if $T_{vib} >> T_{gas}$

- v-T relaxation and back reactions degrade energy efficiency

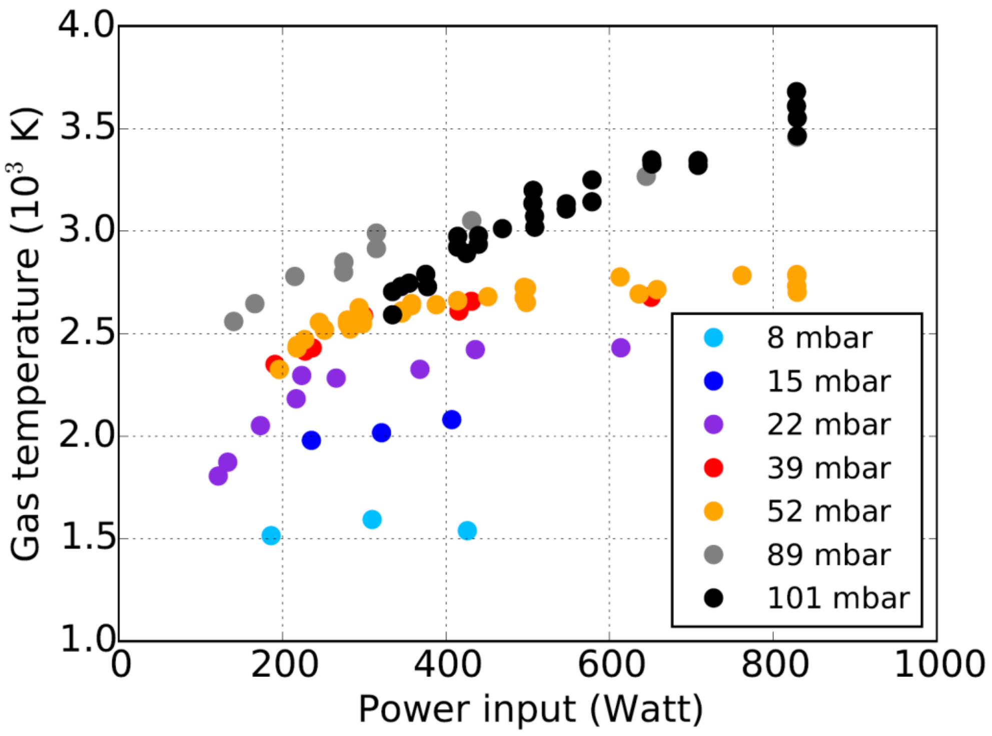
  therefore, strong non-equilibrium is essential! (i.e. $T_{vib} >> T_{gas}$)

- Scheme particularly promising for CO_2 (asymmetric stretch) and N_2 → large quantum difficult to convert into heat

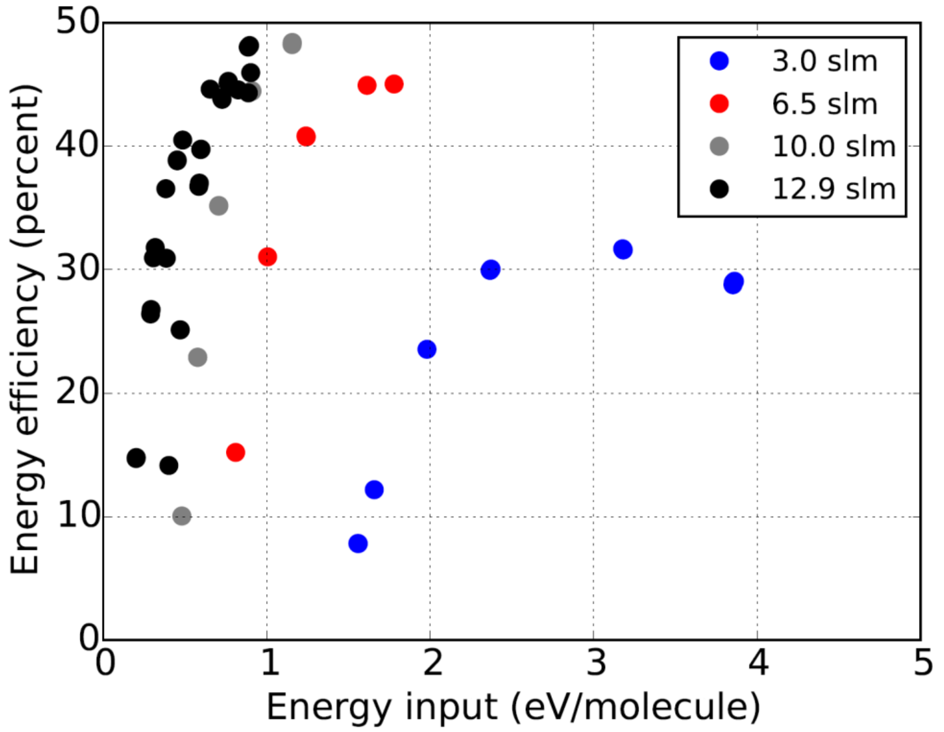


High central gas temperatures point to thermal chemistry!

Gas temperature (@13 slm)



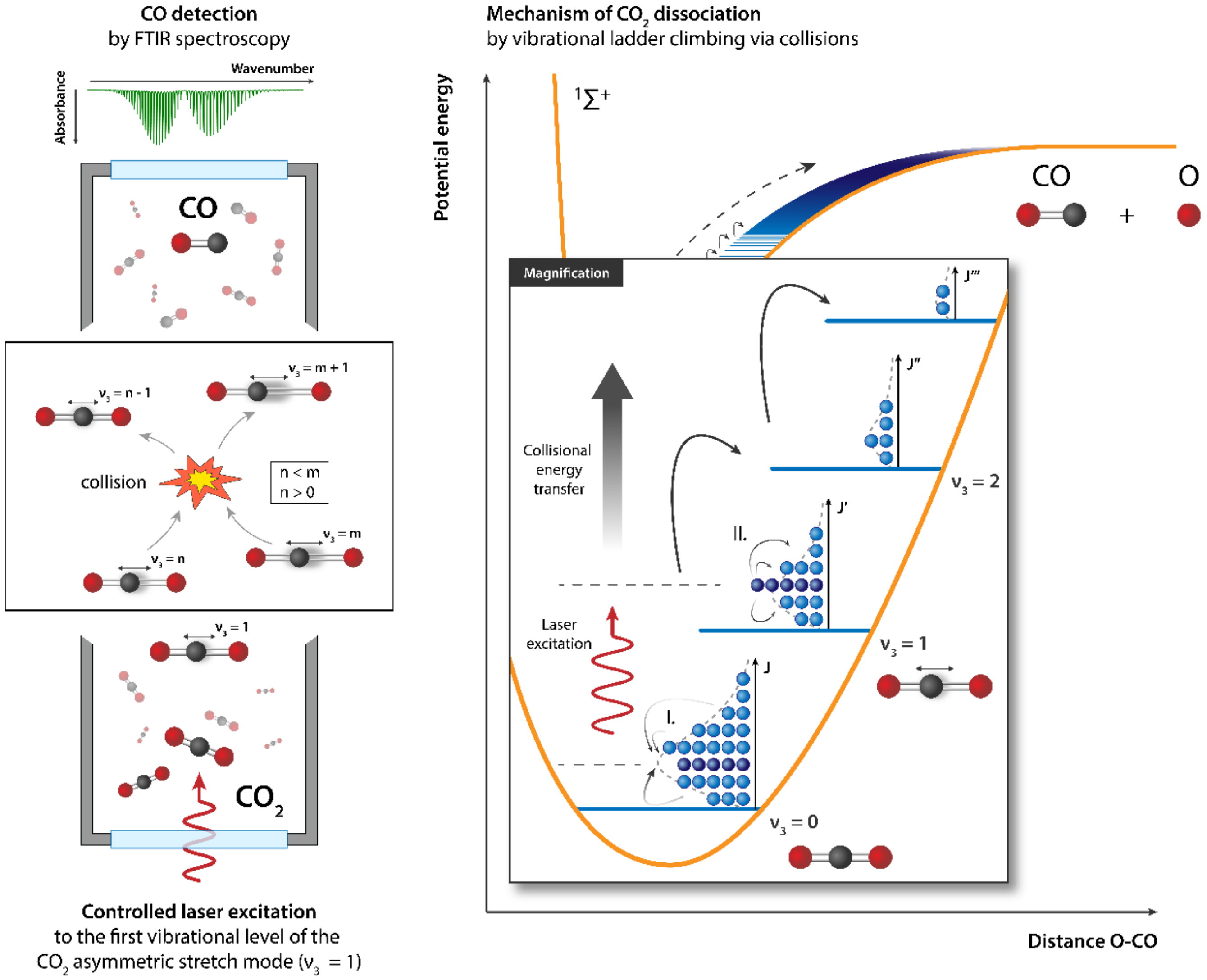
Energy efficiency – scan of flow @ 100 mbar



Van Rooij et al., Faraday Discussions, 2015, DOI: 10.1039/C5FD00045;
Harder et al., Plasma Process Polym, 2017, DOI 10.1002/ppap.201600120;
vd Bekerom et al., Plasma Sources Sci. Technol. 28 055015

What about ladder climbing? – a laser experiment

Question: does the ladder reach to dissociation?



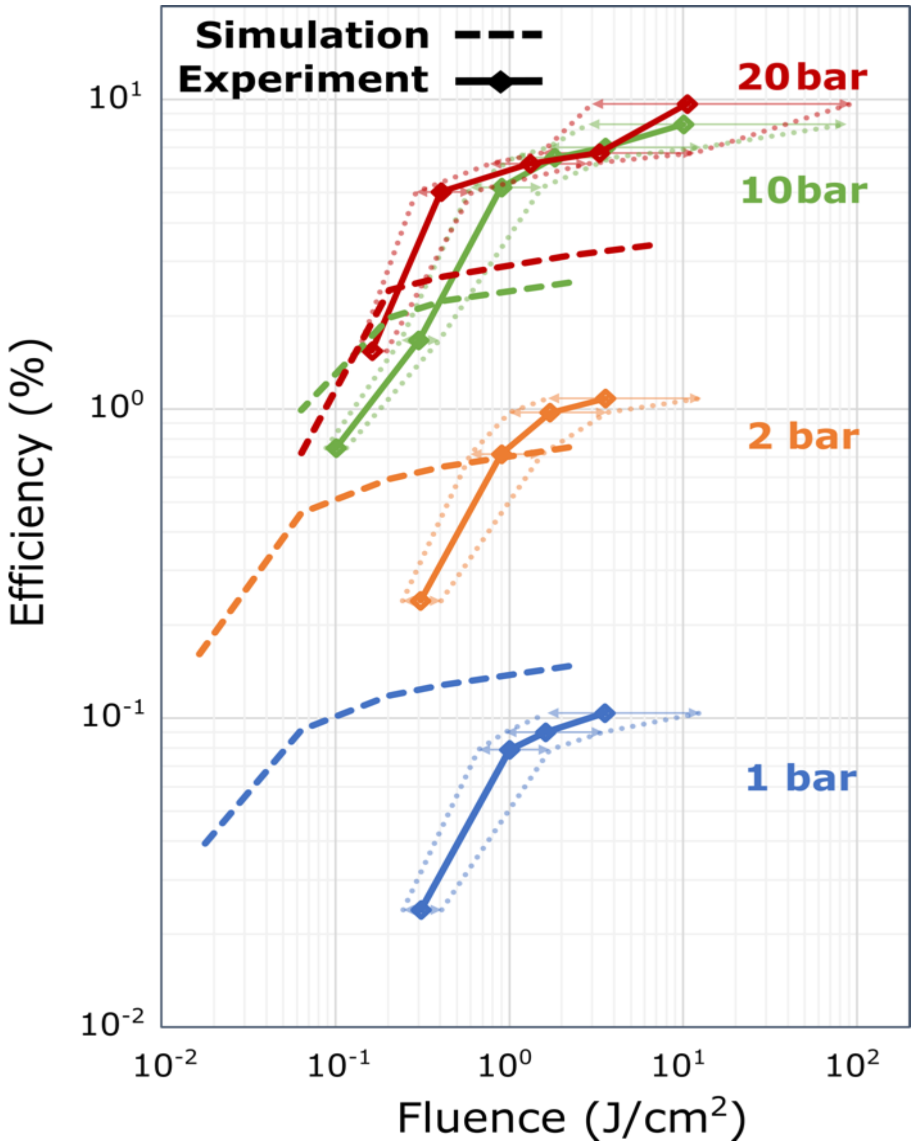
CO production demonstrates ladder dissociation

Thermal chemistry ruled out on basis of modelled temperatures

Saturation values well captured – ladder climbing dynamics!

Treanor – Gordietz distribution essential = anharmonicity essential

Disagreement threshold behavior?



Preferential vibrational excitation assessed in pulsed operation

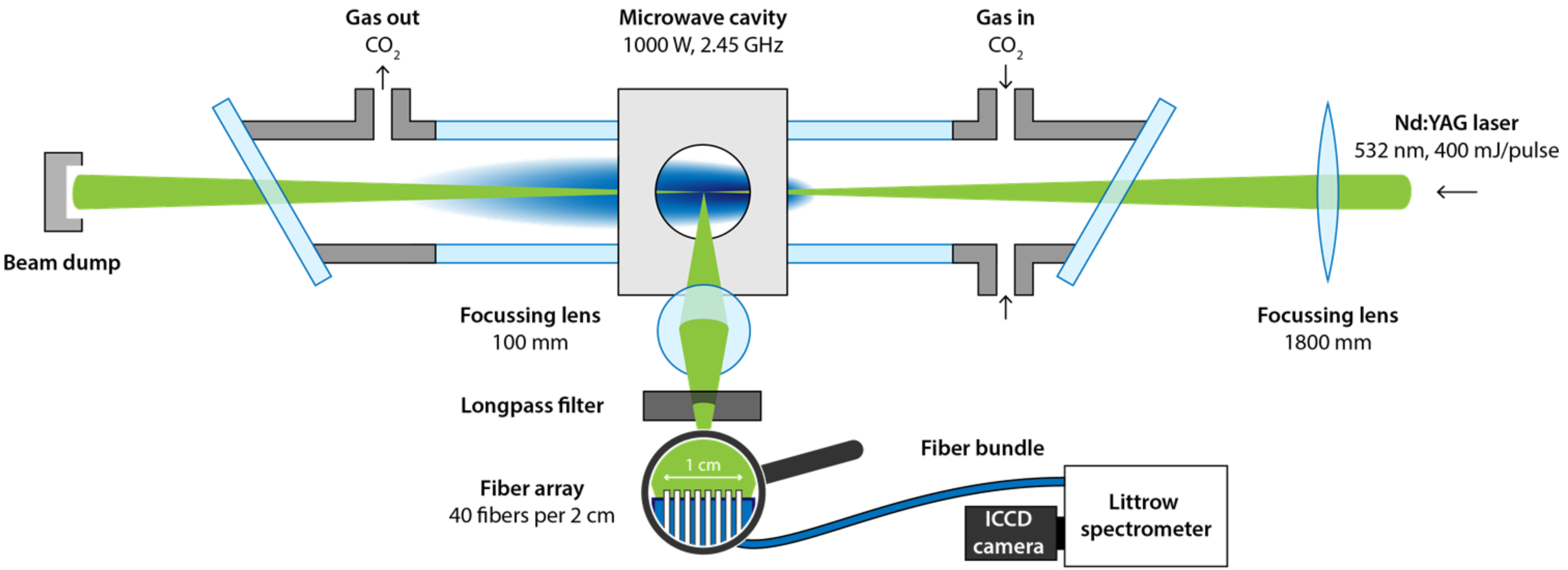
ON

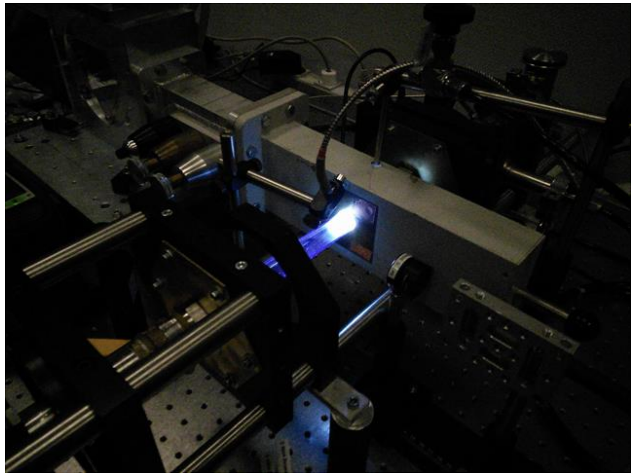
OFF

T_{ON}=100 μs - T_{OFF}=33ms

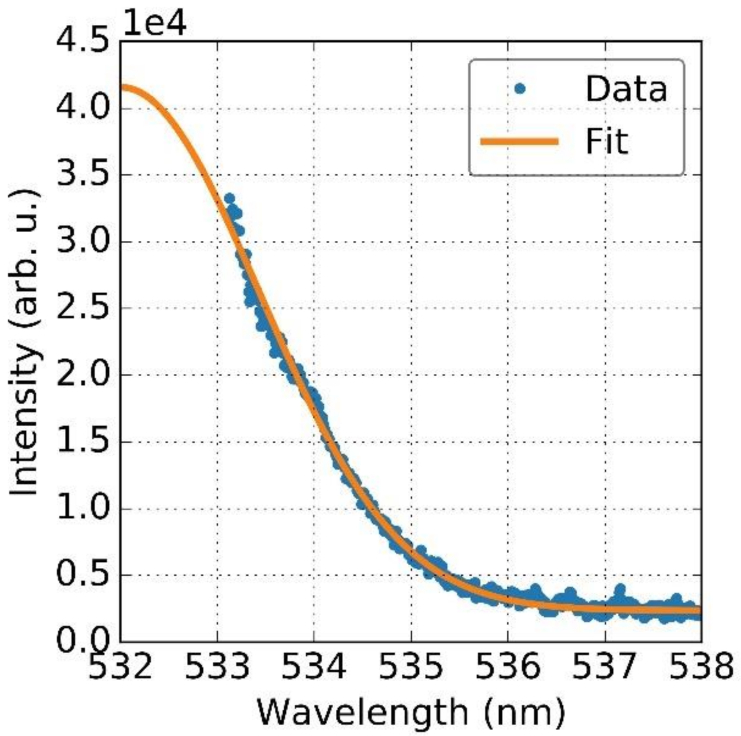
600W, 25 mbar, 4 slm

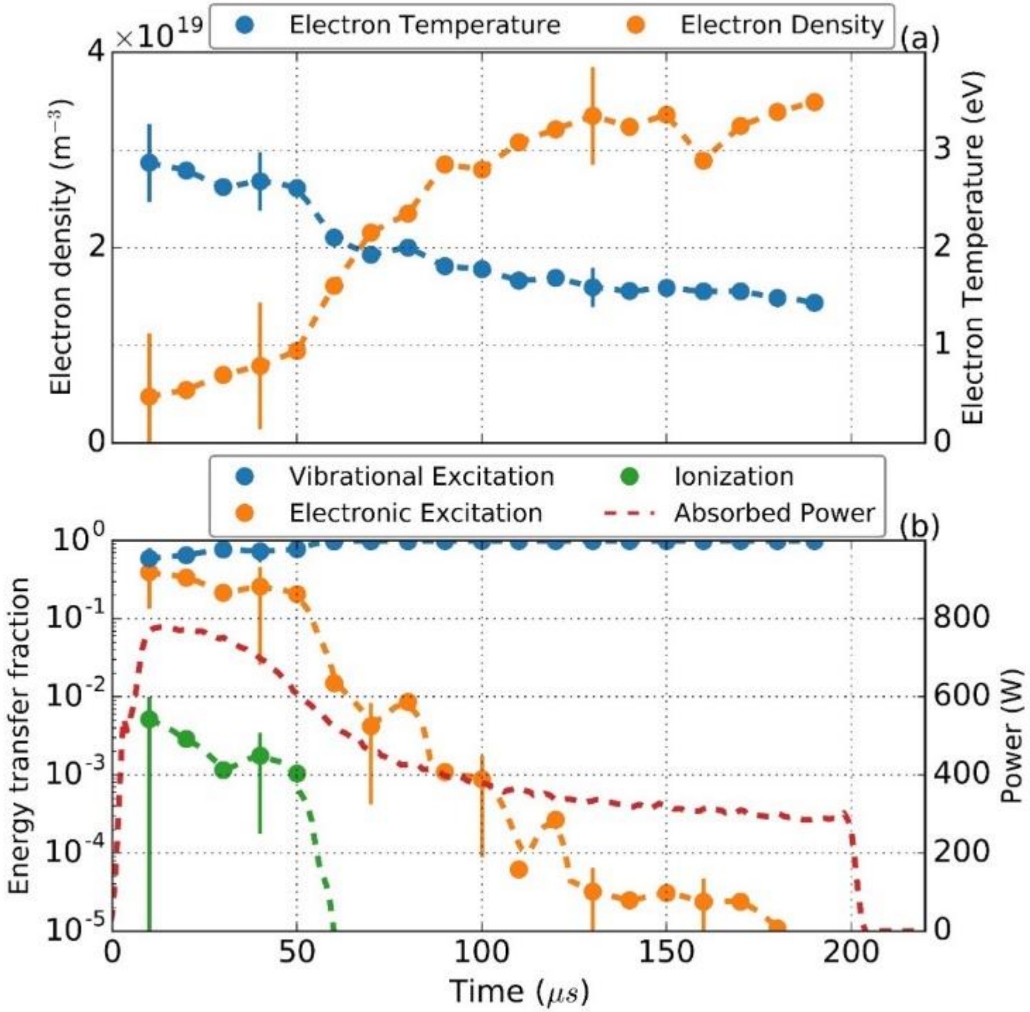
Thomson, rotational, vibrational Raman scattering





CH_4 - Electron temperature confirms preferential vibrational excitation



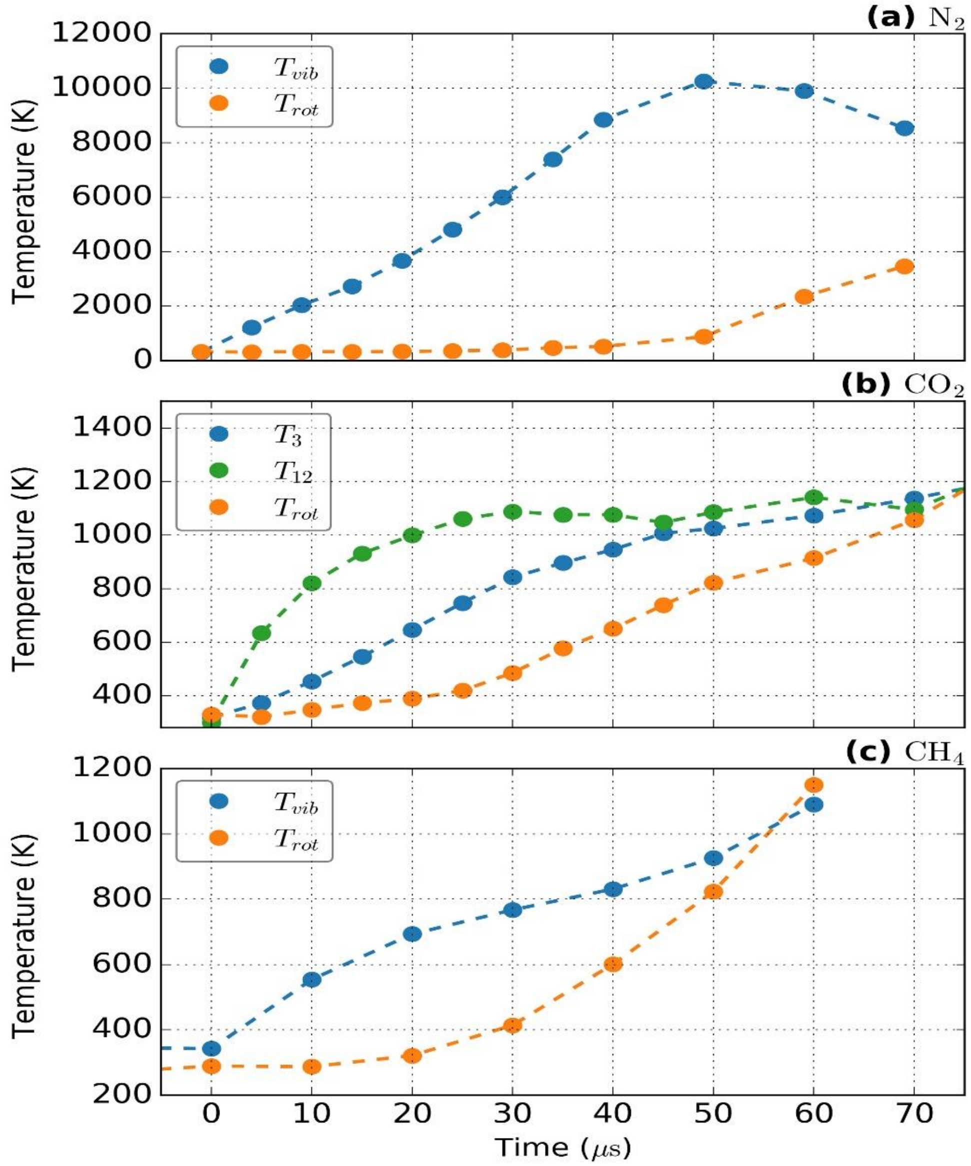


A W van de Steeg et al 2020 Plasma Sources Sci. Technol. 29 115001

Non-equilibrium dynamics captured in μs pulsing

T_{ON}=100 μs - T_{OFF}=33ms
600W, 25 mbar, 4 slm

No significant dissociation!
~3% energy efficiency



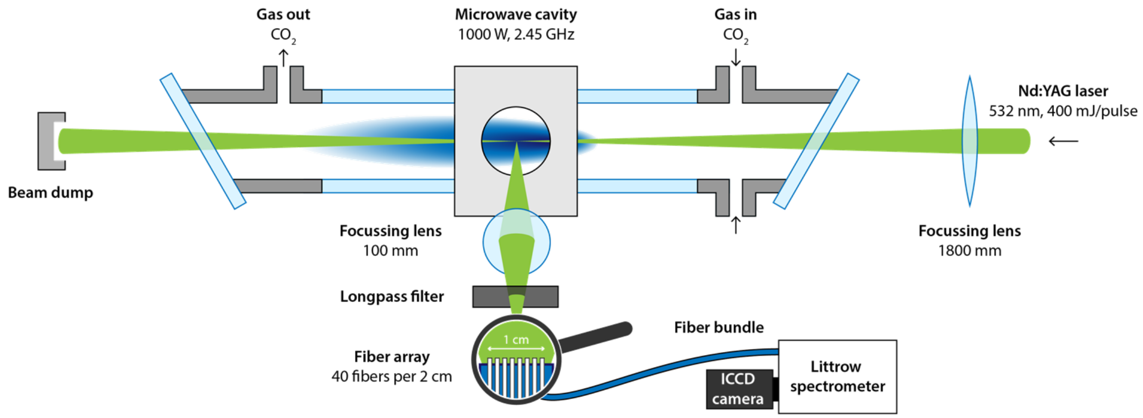
N-quenching

50% vT-quenching, 50% ??

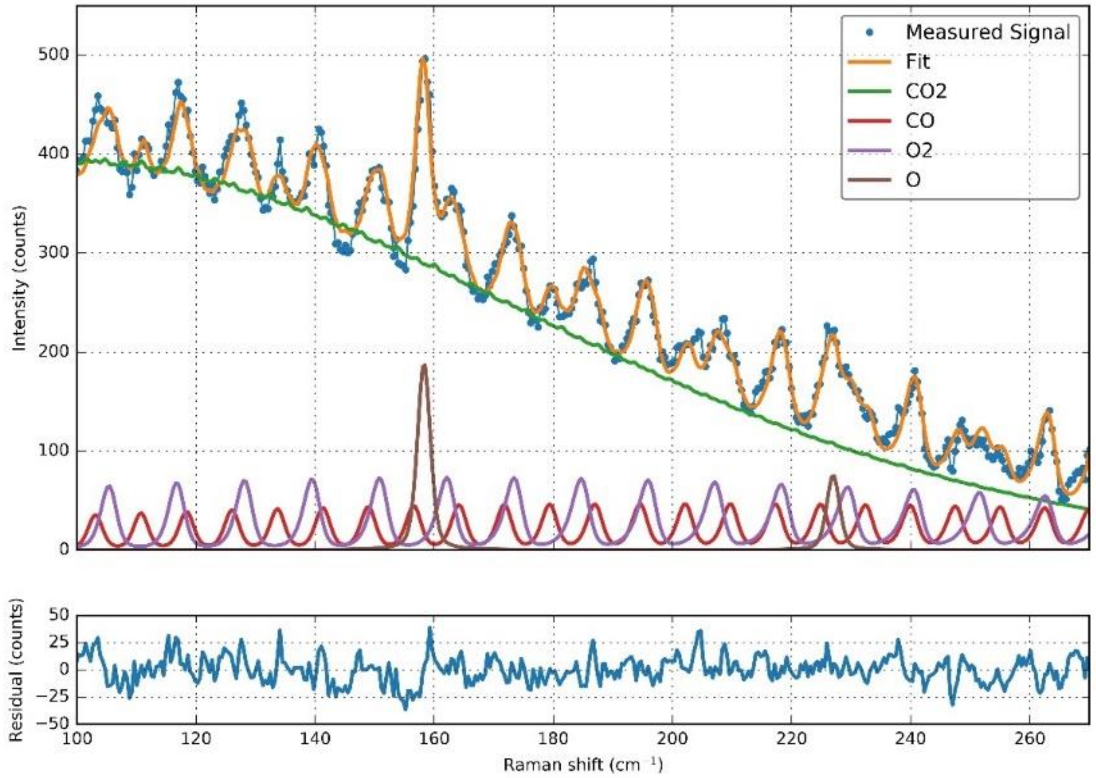
vT-quenching

A W van de Steeg et al 2020 Plasma Sources Sci. Technol. 29 115001

Species mapping in cw microwave CO_2 plasma

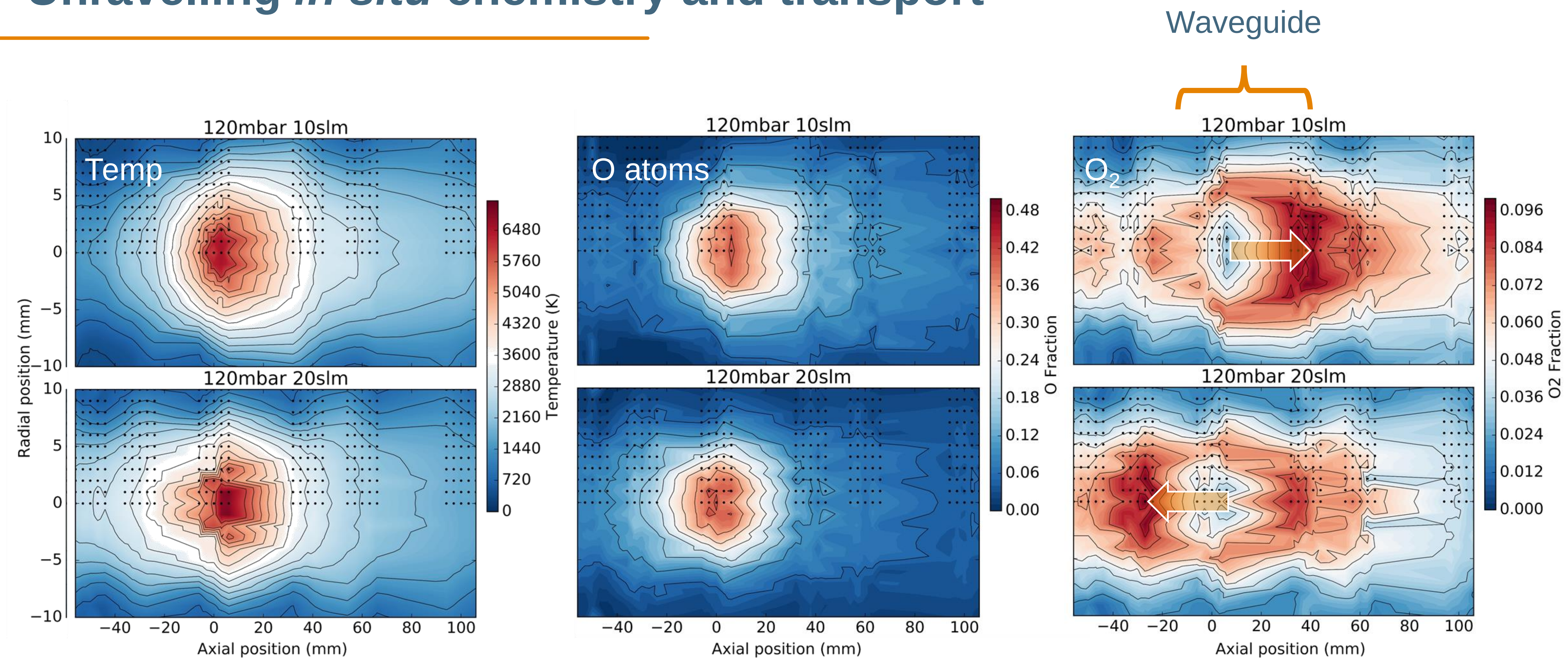


Rotational Raman spectrum



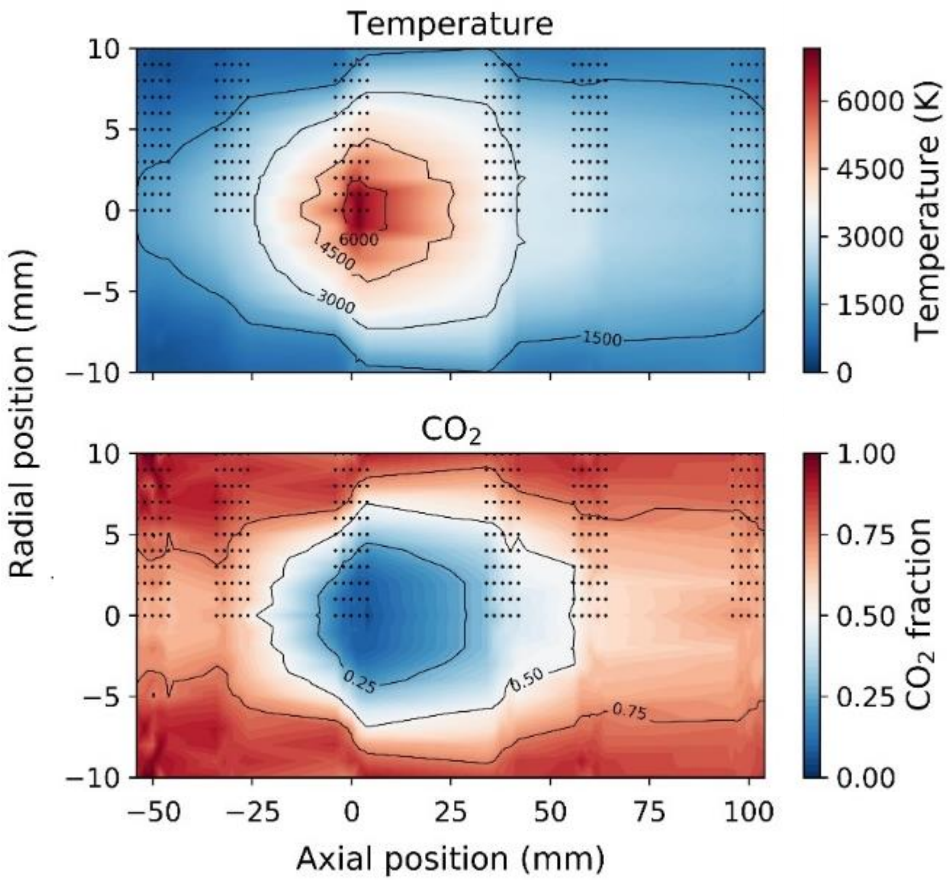
A W van de Steeg et al 2021 Optics Letters, accepted

Unravelling *in situ* chemistry and transport

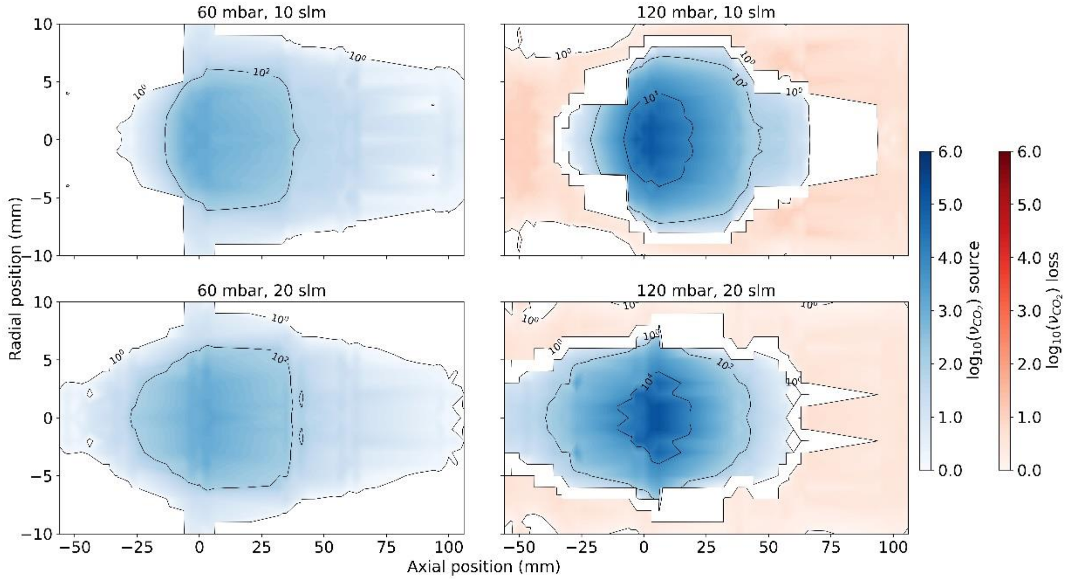


Reversal central transport

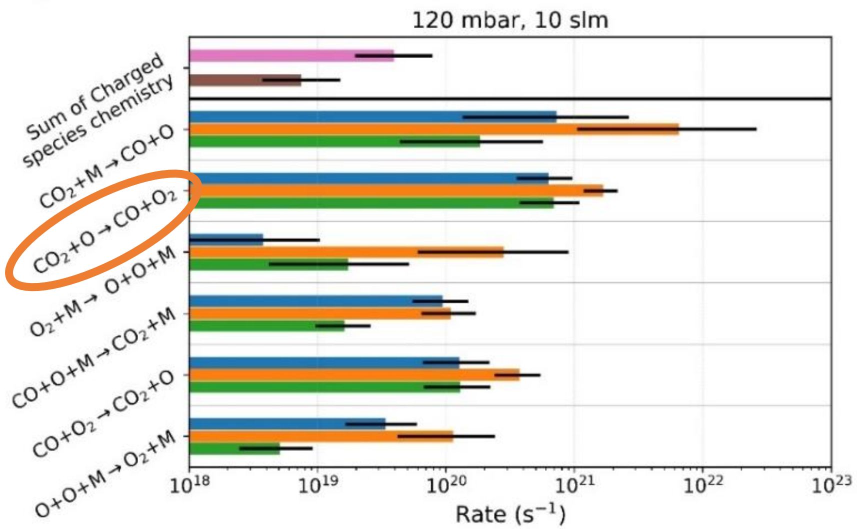
Revealing strong chemical non-equilibrium

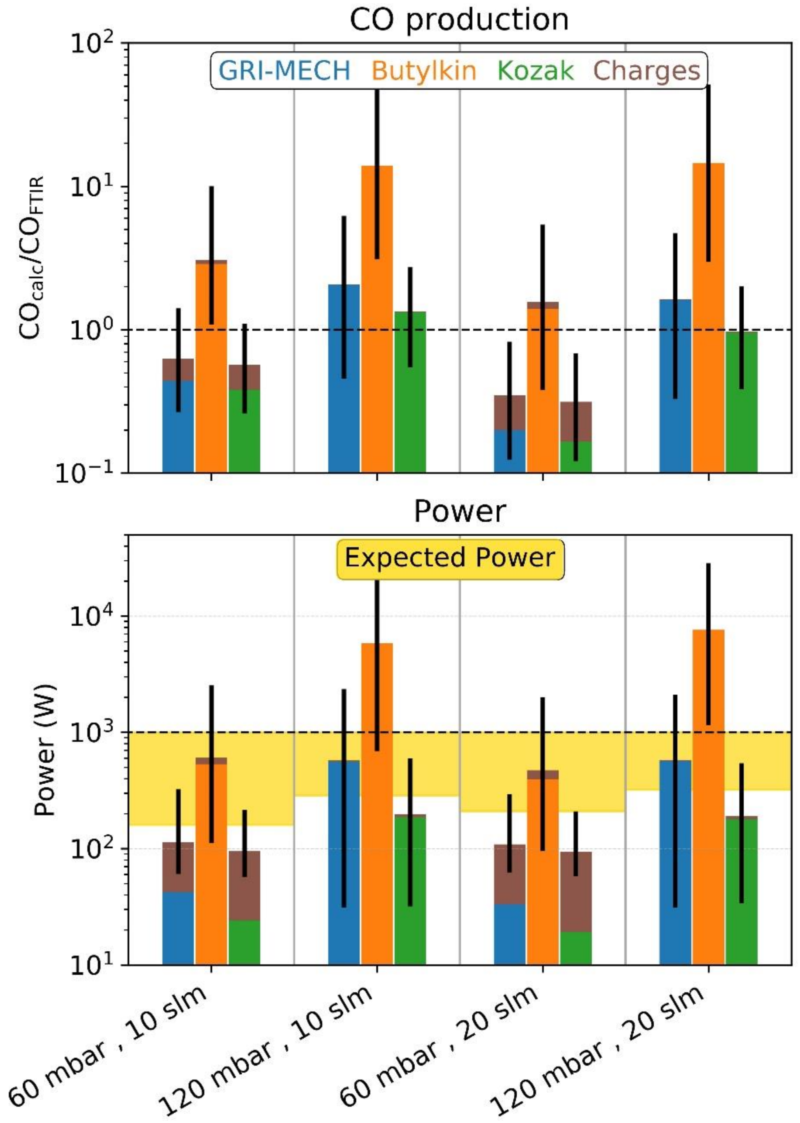


- 6000 K in equilibrium means only CO + O
- 25% CO_2 observed → fast transport



Benchmarking available chemistry sets

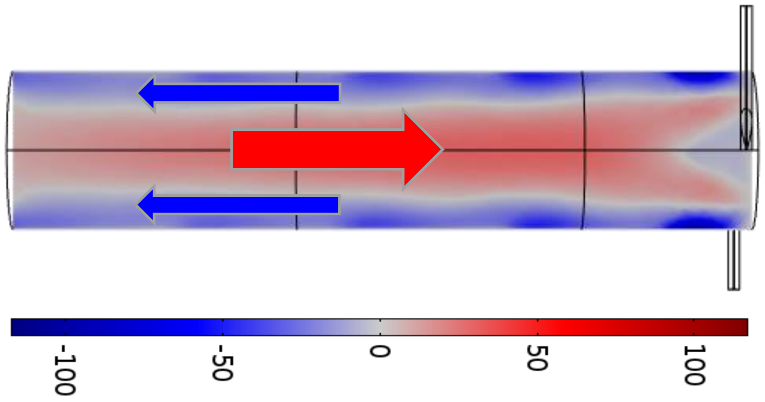




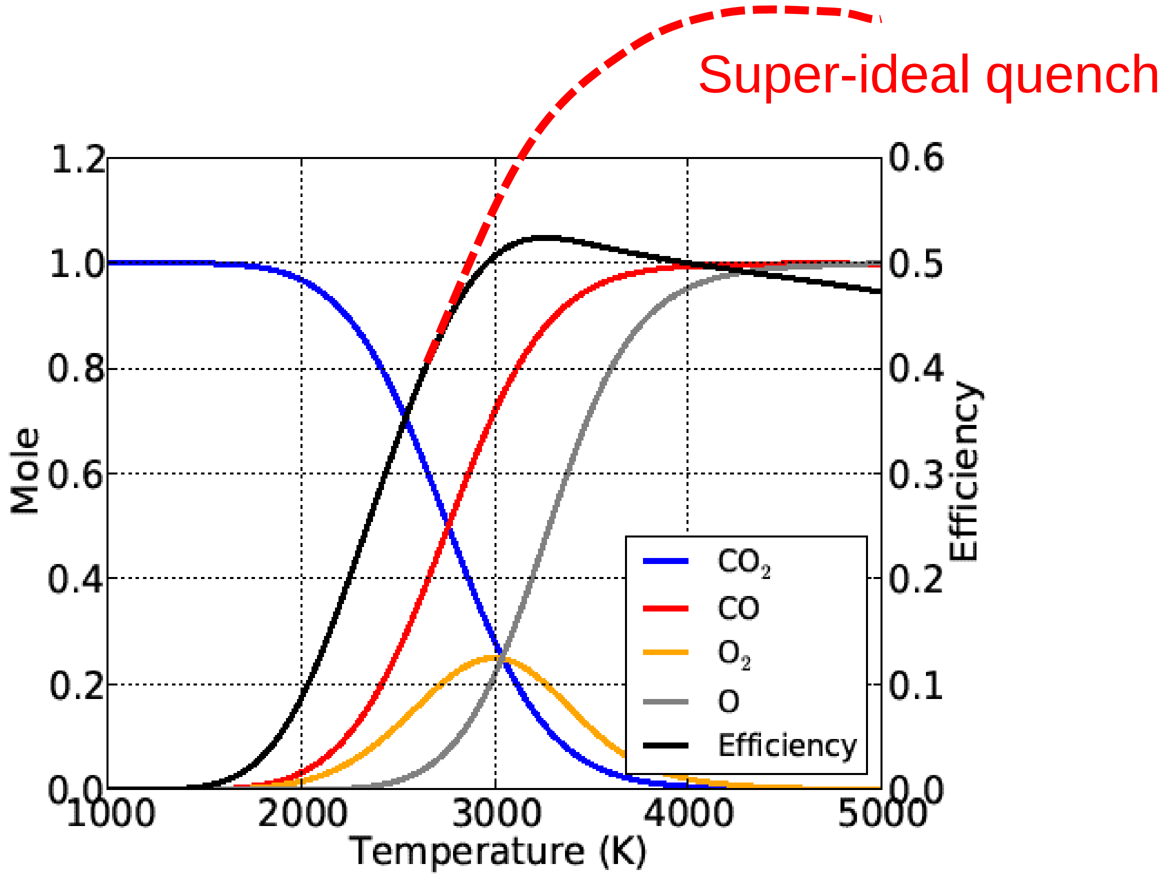
- O radical utilization
- Neither scheme can describe kinetics properly
- Terra incognito of high temperature regime → excited species – plasma chemistry

Room for non-equilibrium in a thermal regime via O-atoms

Vortex flow → mixing responsible for fast cooling = freezing products



Axial velocity (m/s)



- Super-ideal quenching goes beyond thermal equilibrium: $CO_2^{r,v} + O \rightarrow CO + O_2$
- Vibrational excitation (with ladder climbing?) in edge regions where T_{gas} is low

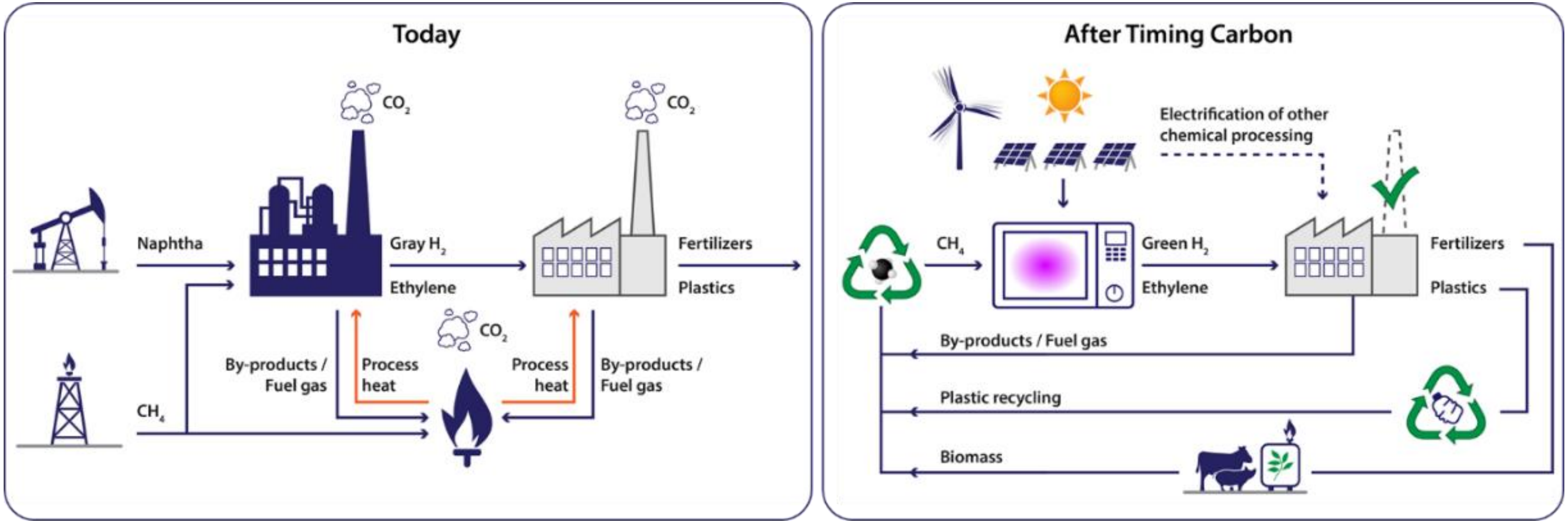
Plasma landing at the CHEMELOT industrial site

On site Maastricht University plasmalab

Plasmalab part of "Brightsite" = consortium with industry

Connected to "Circular Engineering" Bachelor

CH_4 as green platform chemical – Hüls is benchmark



In effect, CH_4 turns from fossil into green platform chemical

Higher carbon atom and energy efficiency than via e.g. H_2 from electrolysis

Conclusions

The future is electric!

Intermittent energy storage and conversion are essential

Plasma chemistry opportunities for uniqueness

→ interface with sustainable electricity: scalable, cheap, low inertia

→ preferential vibrational excitation offers efficiency opportunities

→ high temperature chemistry capabilities, potentially beyond equilibrium performance (efficiency and/or selectivity): CO_2, N_2 and CH_4

Acknowledgements

- DIFFER - Non-equilibrium fuel conversion - Alex van der Steeg, Qin Ong, Ana Sovelas Da Silva, Ashley Hughes, Niek den Harder, Dirk van den Bekerom, Tom Butterworth
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