OLTP / GEC-IOPS seminar
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Modeling plasmas for CO_2 conversion:
from fundamental data to applications

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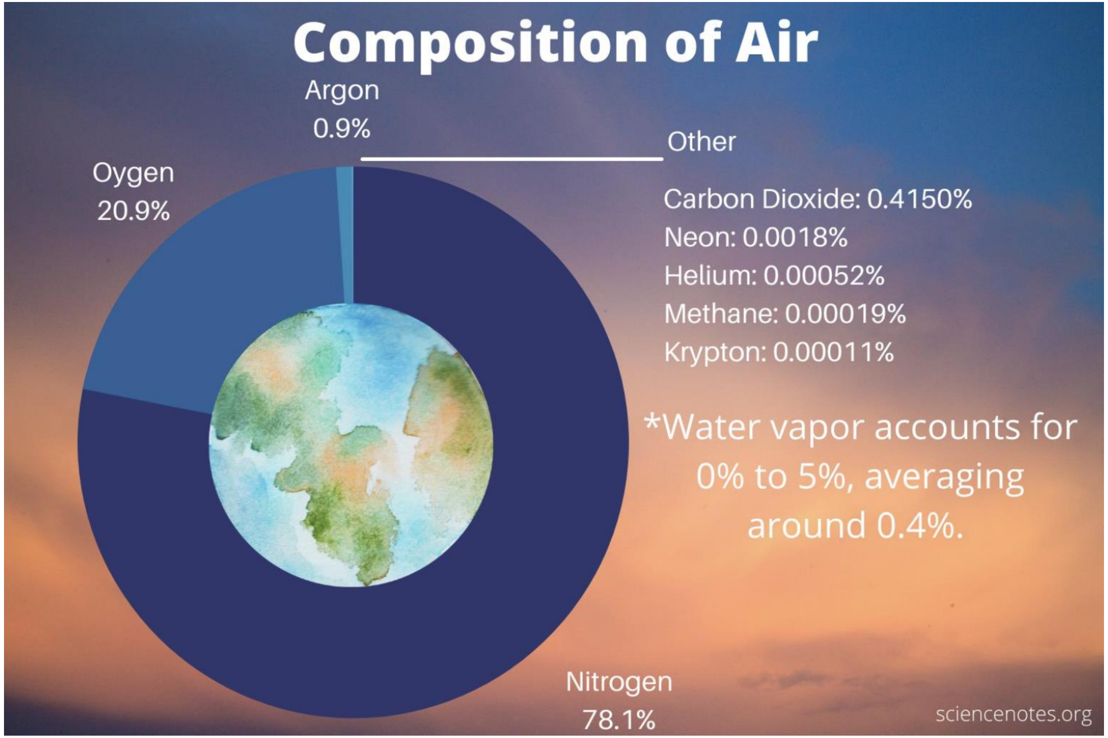
Overview

- Introduction to plasma-assisted CO_2 conversion

- Inverse problems in plasma physics:
  - Electron swarm analysis
  - Power deposition in CO_2 microwave discharges

- Summary and conclusions

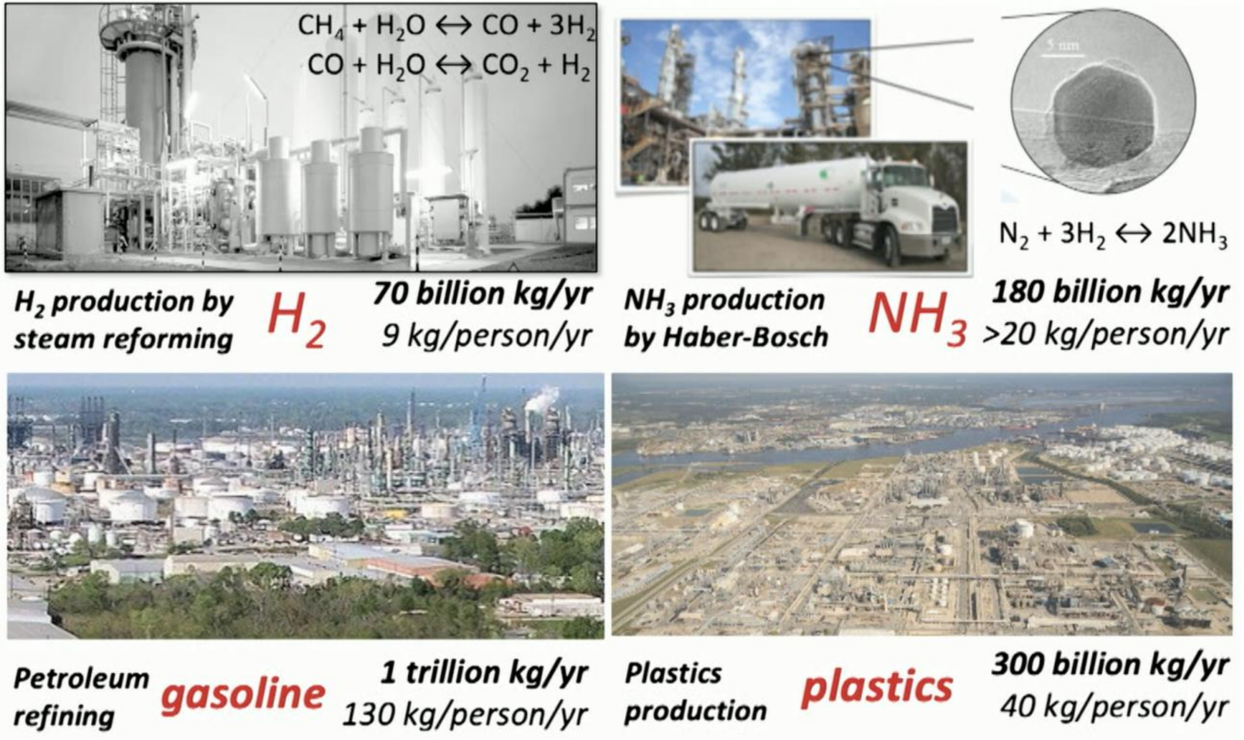
What are you breathing right now?



[https://sciencenotes.org/chemical-composition-air/]

The modern fuels and chemicals industry

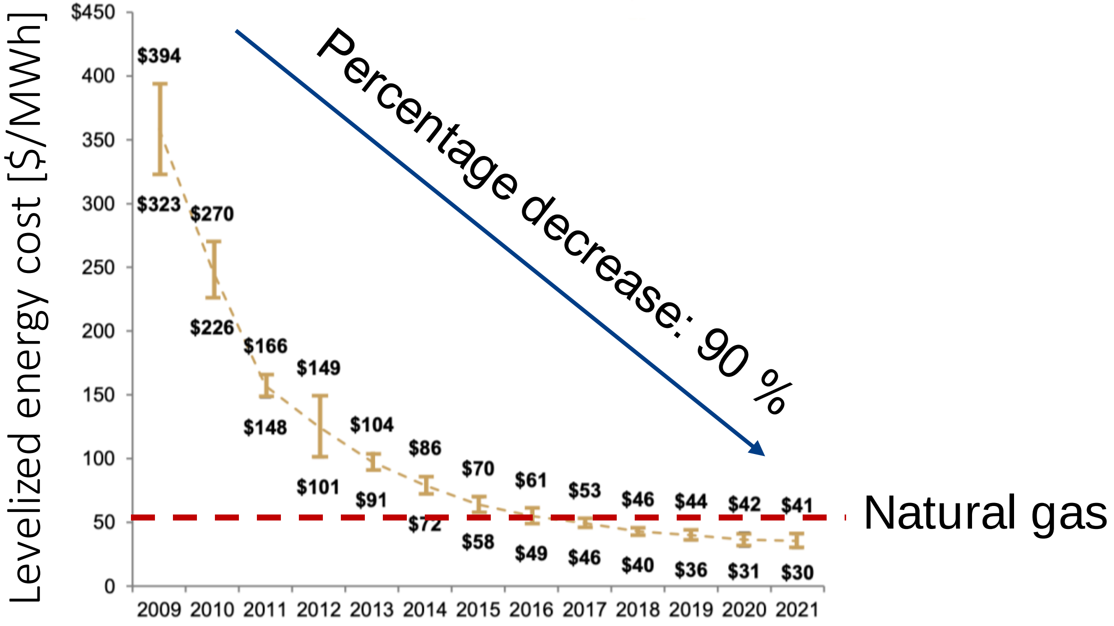
- Methanol
- Ethanol
- Hydrogen
- Hydrocarbons
- Ammonia



[T. Jaramillo, ESW New Energy Carriers and Fuels, oral presentation, Stanford (2023)]

Cheap electrons are coming…

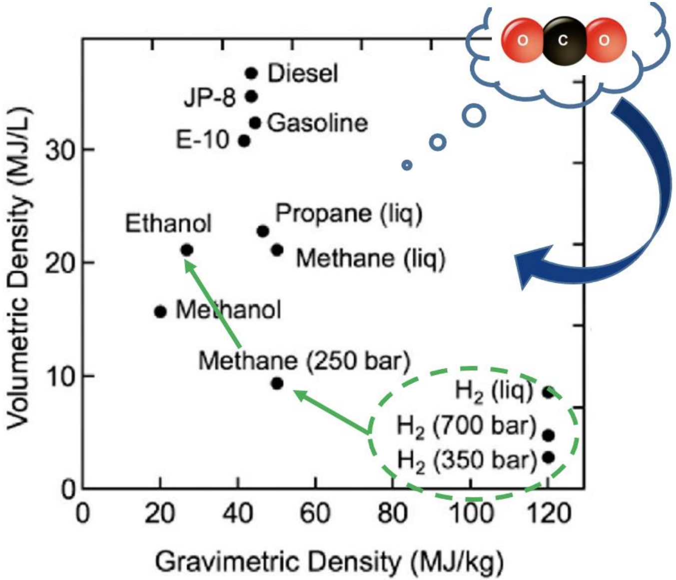
Drop in price of renewables electricity



[Lazard's Levelized Cost of Energy Analysis, U.S. Energy Information Administration (2021)]

Need new technologies to recycle CO_2

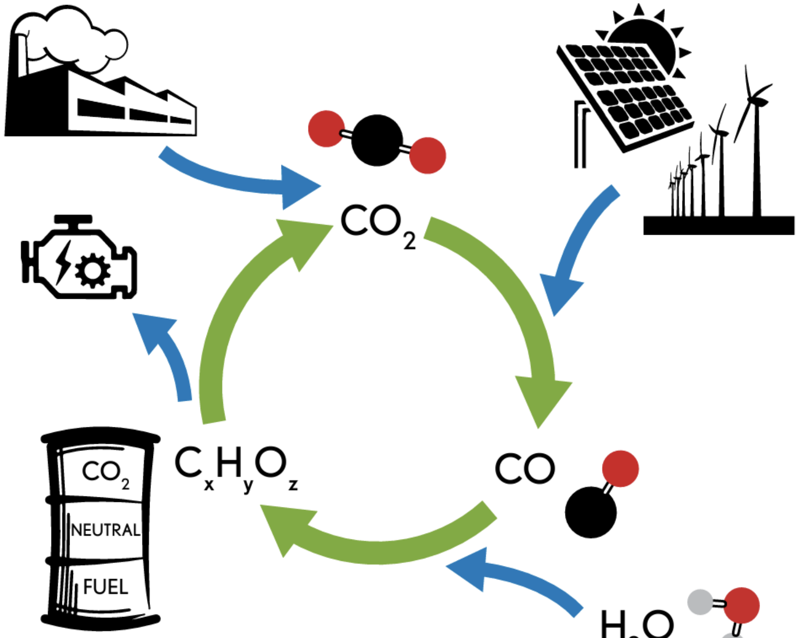
Can we leverage renewable electricity and H_2 to regenerate liquid fuels from CO_2?



[E. Dundar-Tekkaya, Y. Yurum, *Int. J. Hydrogen Energy* **41**, 9789-9795 (2016)]
[O. Guaitella, OLTP Seminar, 2021]

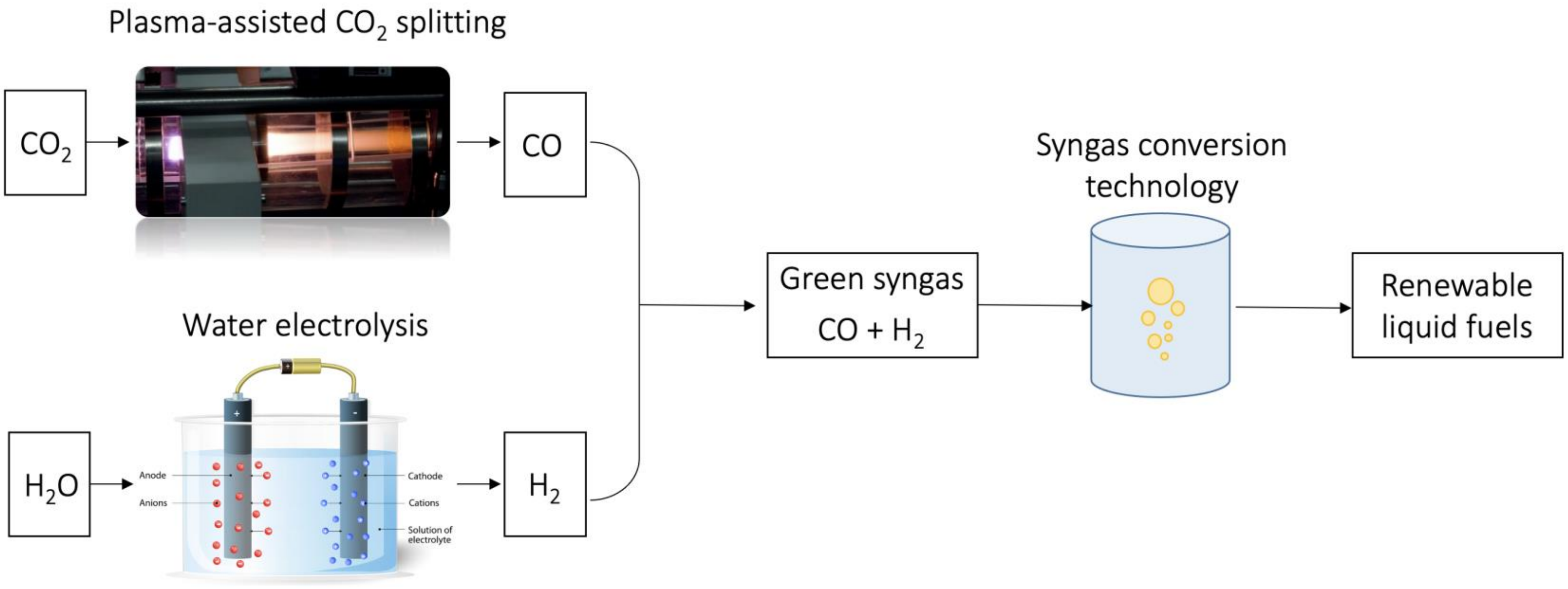
Scientific feasibility

Renewable electricity is used to dissociate CO_2



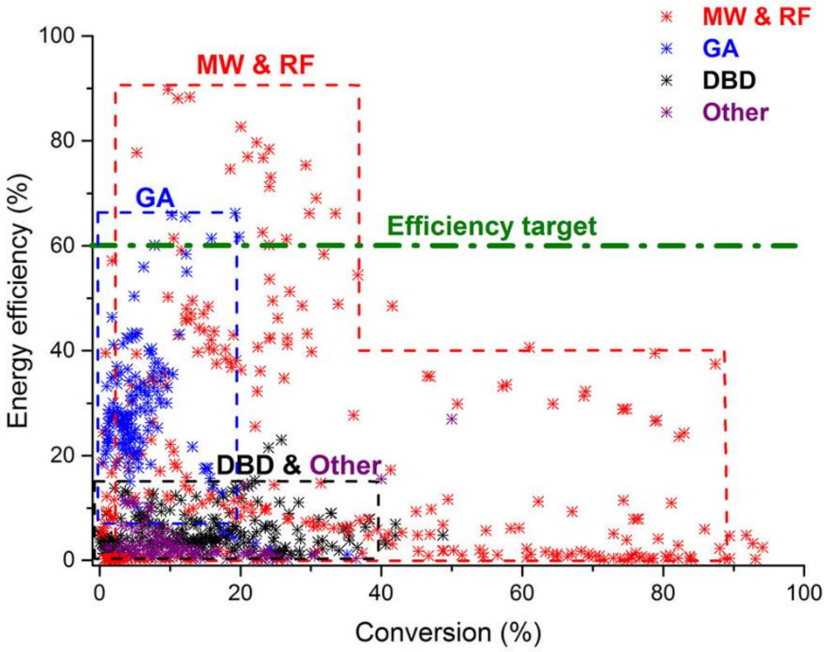
Technological feasibility

Distributed, sustainable, chemical production



Economical feasibility

Microwave discharges seem to offer high(est) energy efficiency. However…

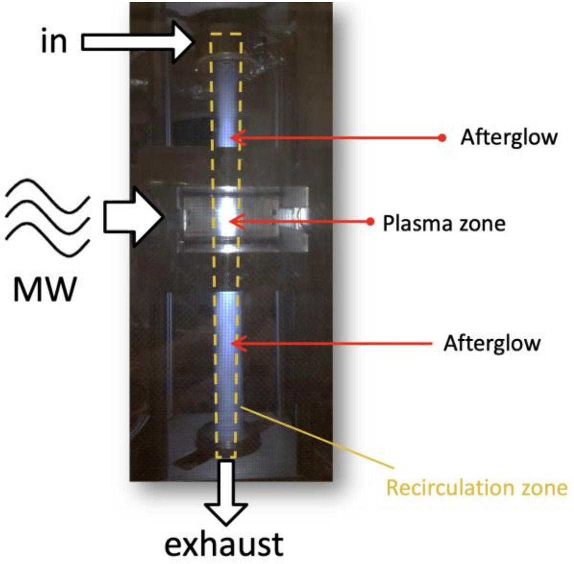


[A. Bogaerts and G. Centi, *Front. Energy Res*. **8**, 111 (2020)]

From applied research… to basic research

We cannot design what we don't understand!

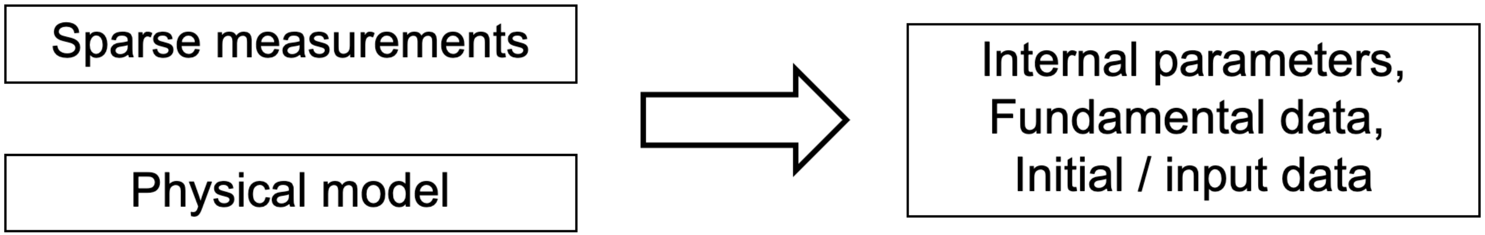
Microwave setup @ 2.45 GHz
(up to 1000 W input MW power)



- Lack of fundamental data
- Complex chemistry
- Complex gas flow dynamics

The challenge of inverse problems

- Lack of fundamental data
- **Goal**: to unfold fundamental data from measurements and models



ill-posed problem

The challenge of inverse problems

- Lack of fundamental data
- **Goal**: to unfold fundamental data from measurements and models

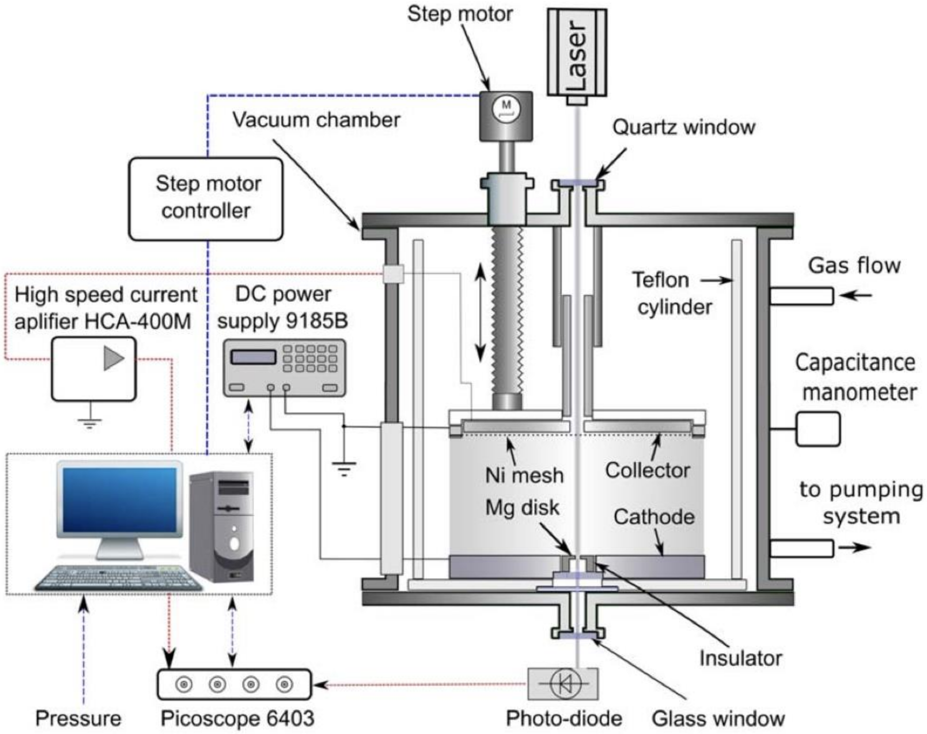
Electron-impact cross sections

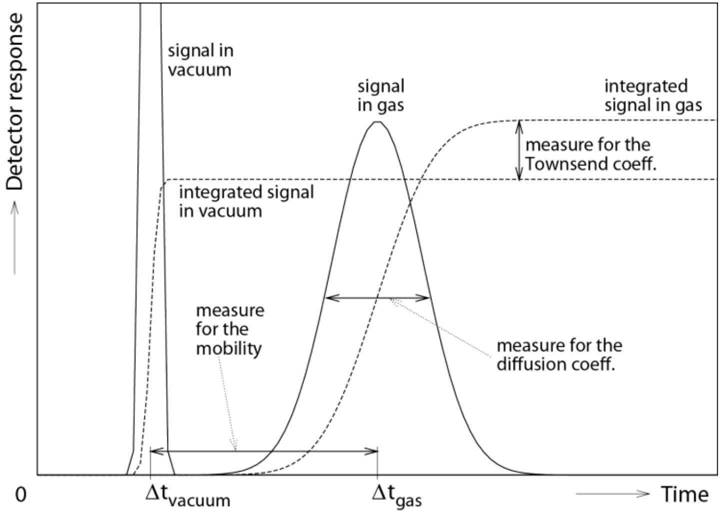
L. Vialetto *et al*., PSST **30**, 075001 (2021)

Power density in microwave discharges

L. Vialetto *et al*., PSST **31**, 055005 (2022)

A look at a swarm experiment

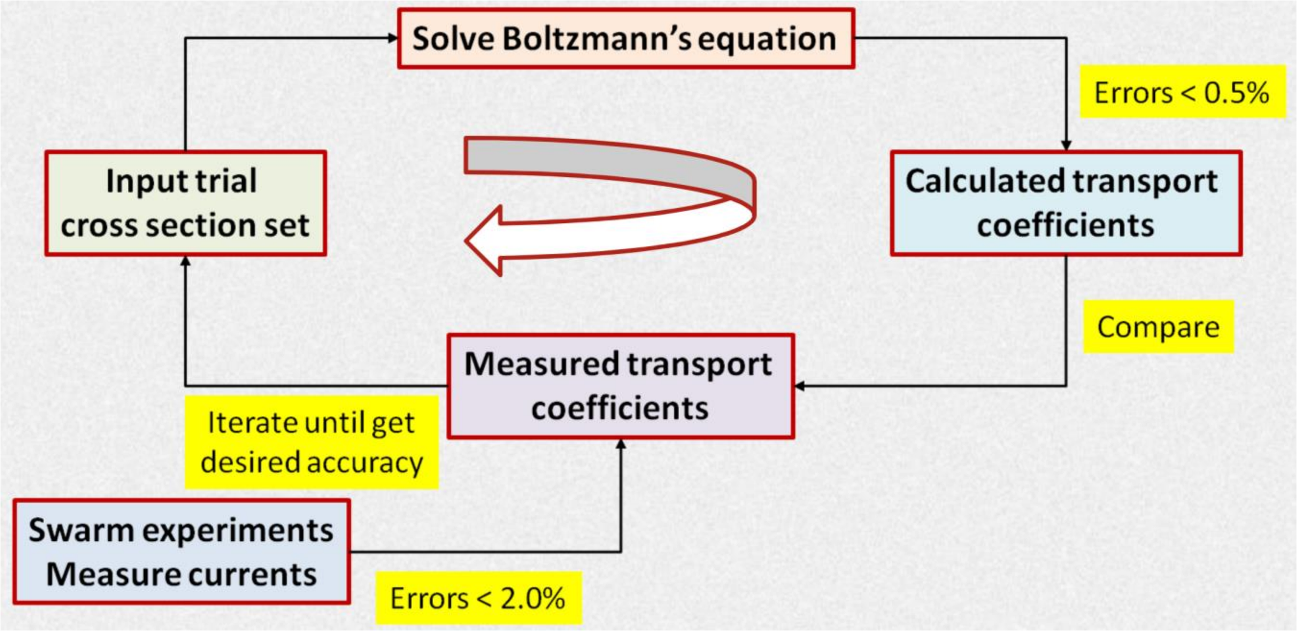




[Donko *et al*., *Plasma Sources Sci. Technol.* **28**, 095007 (2019)]

Swarm analysis

An iterative procedure is employed to derived electron-impact cross sections:



[S. Dujko, Plasma Seminar, Eindhoven (the Netherlands), 2021]

(Popular) methods for solutions of the electron Boltzmann equation

Direct numerical solutions

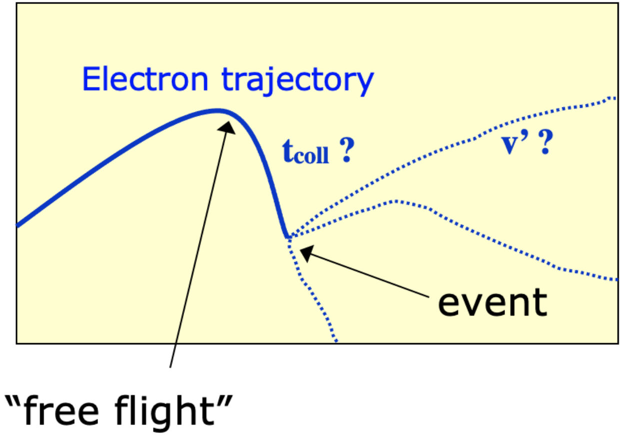
- Two-term approximation

[G.J.M. Hagelaar and L.C. Pitchford, *PSST* **14**, 722-733 (2005)]

- Multi-term approximation

[J. Stephens, *J. Phys. D: Appl. Phys.* **51**, 125203 (2018)]

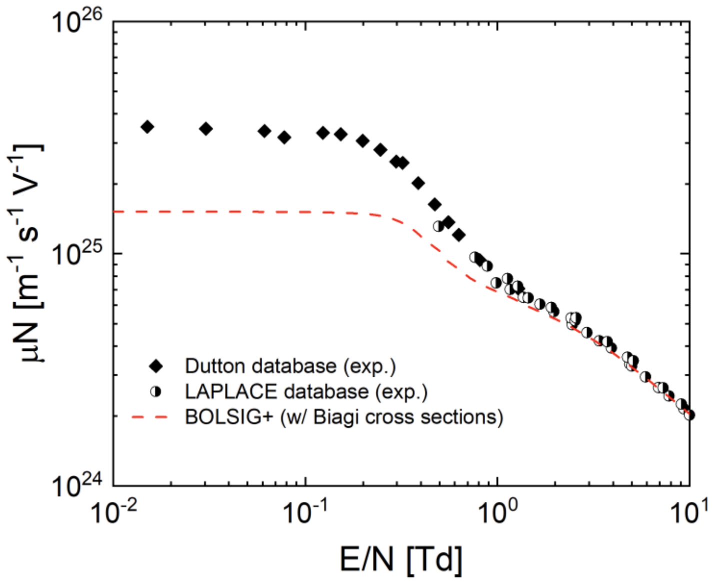
Monte Carlo simulations



[S. Longo, *PSST* **15**, S181-S188 (2006)]

The problem of electron transport in CO

- Large discrepancy between numerical results and experiments
- *Are cross sections for electrons in CO accurate?*



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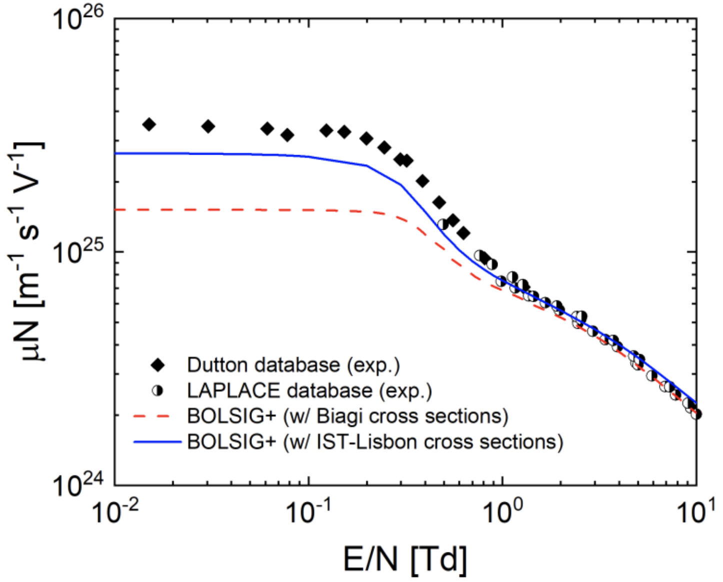
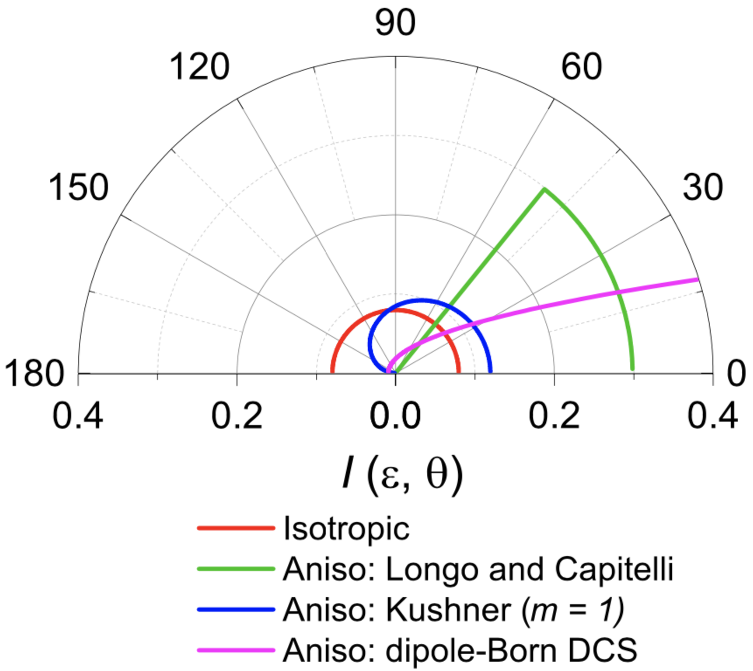


[P. Ogloblina *et al*., *PSST* **29**, 015002 (2020)]

Anisotropic treatment of rotational collisions

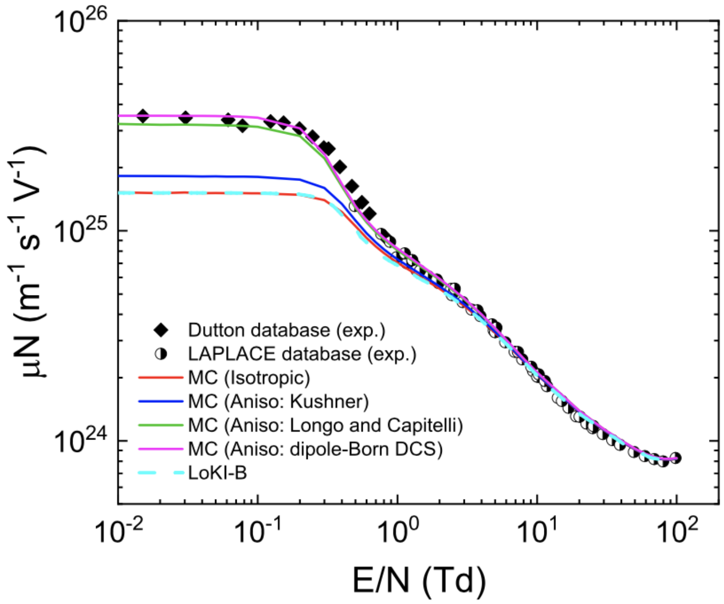
- At low energy, rotational (dipole) collisions are not isotropic
- Different assumptions for the angular scattering distributions are used



Angular scattering distribution

Influence of anisotropic scattering on electron drift

Large discrepancies between the models and experiments are found when changing the angular scattering model



[L. Vialetto *et al.*, *PSST* **30**, 075001 (2021)]

Implementation in a two-term Boltzmann solver

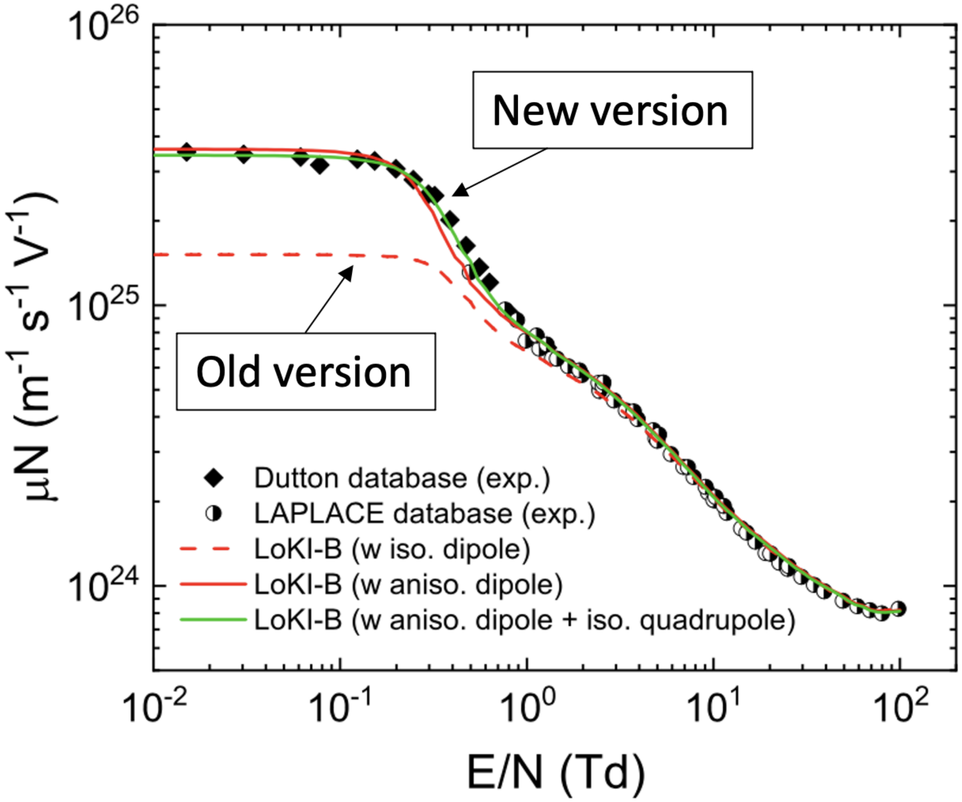
- Anisotropic scattering can be included in two-term Boltzmann solver by modification of the "effective" cross section:

$$\Omega_c(\epsilon) = \Bigg\{ \underbrace{\overbrace{\sum_i \delta_i \sigma^{mt}_{i,ela}(\epsilon)}^{\text{elastic}} + \overbrace{\sum_{i,j>i} \left[\delta_i \sigma^0_{i,j}(\epsilon) + \delta_j \frac{g_i}{g_j} \frac{\epsilon + V_{i,j}}{\epsilon} \sigma^0_{i,j}(\epsilon + V_{i,j}) \right]}^{\text{inelastic}}}_{\text{Isotropic term}} \Bigg\} + \underbrace{\{[1]\}}_{\text{Anisotropic}}$$

- The anisotropic scattering term have been implemented also in the open-source code LoKI-B [1,2]

[1] L. Vialetto *et al.*, *PSST* **30**, 075001 (2021)
[2] A. Tejero-del-Caz et al., *PSST* **28**, 043001 (2019)

Results using a two-term Boltzmann solver (LoKI-B)



Take home messages (1)

- Remember to check validity of cross sections set with (measured) electron transport parameters!

- Besides CO, anisotropic scattering of electrons plays an important role also for NO [1], H_2O [2,3], NH_3 [4]

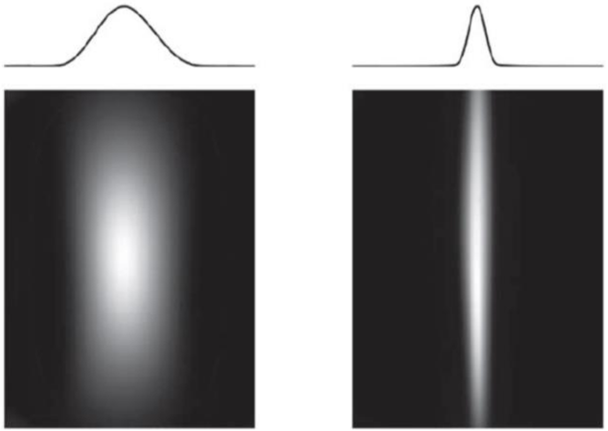
- Anisotropic scattering in multi-term Boltzmann solver has now been implemented [5]

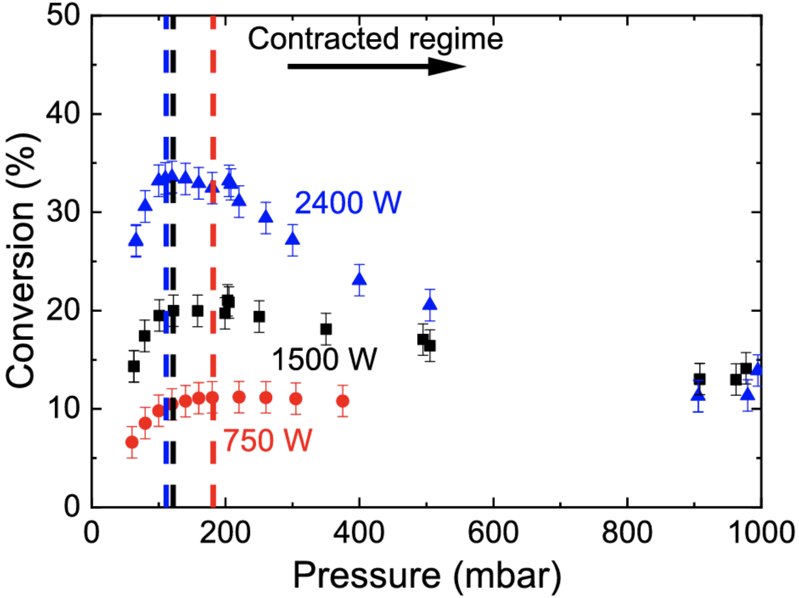
[1] V. Laporta, L. Vialetto, V. Guerra, *PSST* **31**, 054001 (2022)
[2] M. Budde, T.C. Dias, L. Vialetto, *et al*., *J. Phys. D: Appl. Phys*. **55**, 445205 (2022)
[3] M. Budde, T.C. Dias, L. Vialetto, *et al*., *J. Phys. D: Appl. Phys*. **56**, 255201 (2023)
[4] R. Snoeckx, J. Tennyson, M. Suk Cha, *PSST* **32**, 115020 (2023)
[5] M. Flynn, L. Vialetto, A. Fierro, A. Neuber, J. Stephens, *submitted*

CO_2 microwave plasma contraction

Understanding plasma contraction is important for maximization of CO_2 conversion

Diffuse regime (100 mbar) ***Contracted regime*** (250 mbar)





[F.A. D'Isa *et al.*, *PSST* **29**, 105009 (2020)]

Modeling CO_2 microwave plasmas

A multi-physics model is required for accurate modeling

Major challenge: *how to model diffuse and contracted plasma?*

Electromagnetism
- MW cavity
- Power deposition

Radiation
- Spontaneous emission
- Stimulated emission

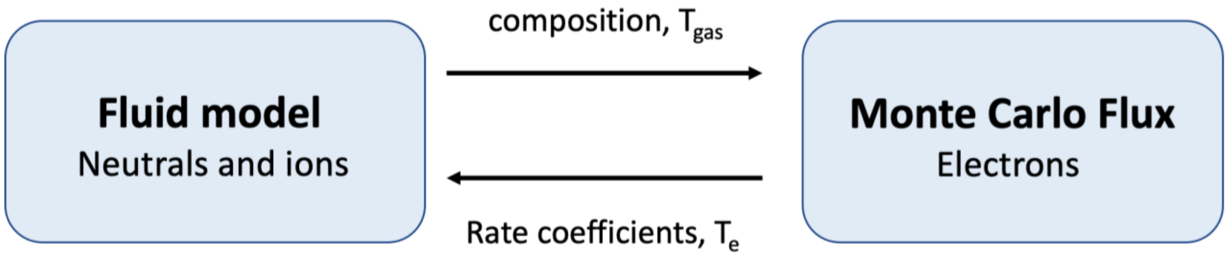
Transport
- Mass
- Momentum
- Energy

Chemistry
- Thermal chemistry
- Vibrational kinetics
- Electron kinetics

Two-temperature plasma model

A 1-D radial fluid model has been developed for diffuse and contracted plasmas

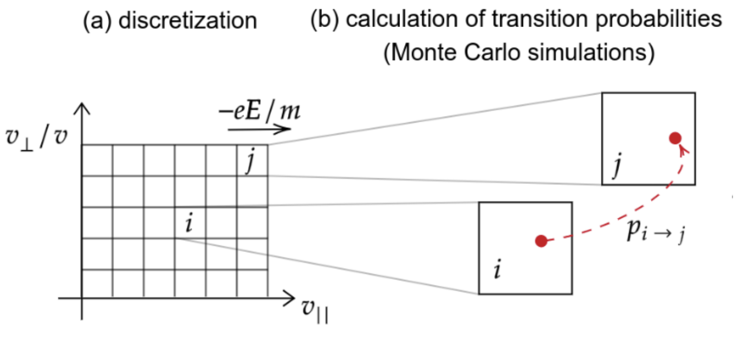
INPUT: deposited power density, electron-impact cross sections, heavy species rate coefficients



OUTPUT: species molar fractions, T_e, T_{gas}

[L. Vialetto *et al*., *PSST* **31**, 055005 (2022)]

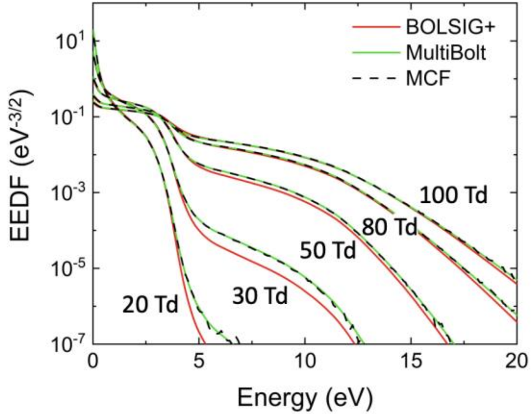
The Monte Carlo Flux method



(c) solution of Master Equation

$$f_i(t + \Delta t) = \sum_j p_{i \to j}(\Delta t)\, f_j(t)$$

Electrons in CO_2 gas

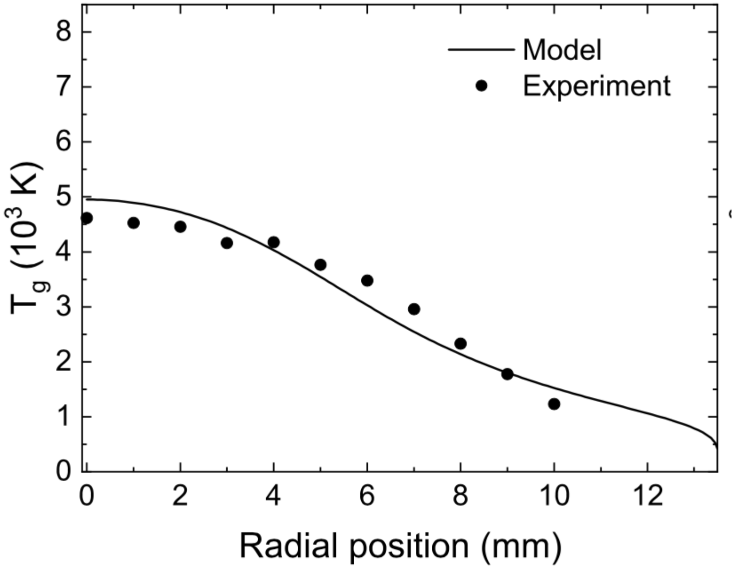


Excellent agreement with multi-term solutions

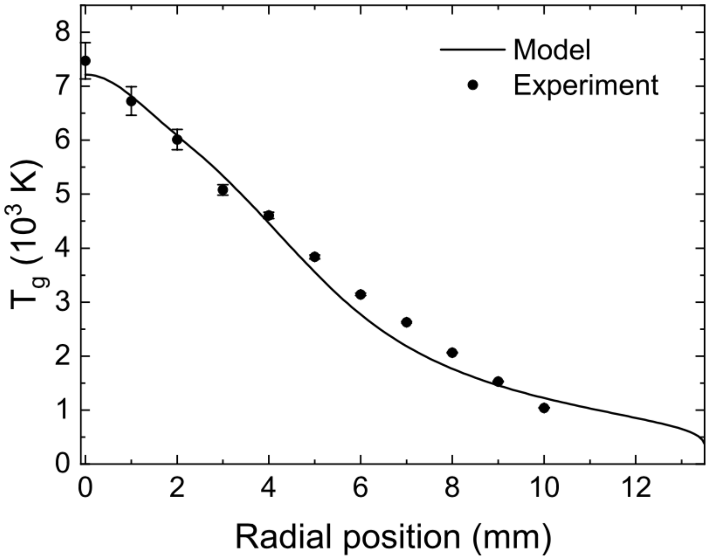
[G. Schaefer and P. Hui, *J. Comput. Phys.* **89**, 1-30 (1990)]
[L. Vialetto, S. Longo, P. Diomede, *PSST* **28**, 115015 (2019)]
[L. Vialetto, P. Viegas, S. Longo, P. Diomede, *PSST* **29**, 115006 (2020)]
[L. Vialetto, H. Sugawara, S. Longo, *in preparation*]

Gas temperature in diffuse and contracted regimes

Diffuse (100 mbar)



Contracted (250 mbar)

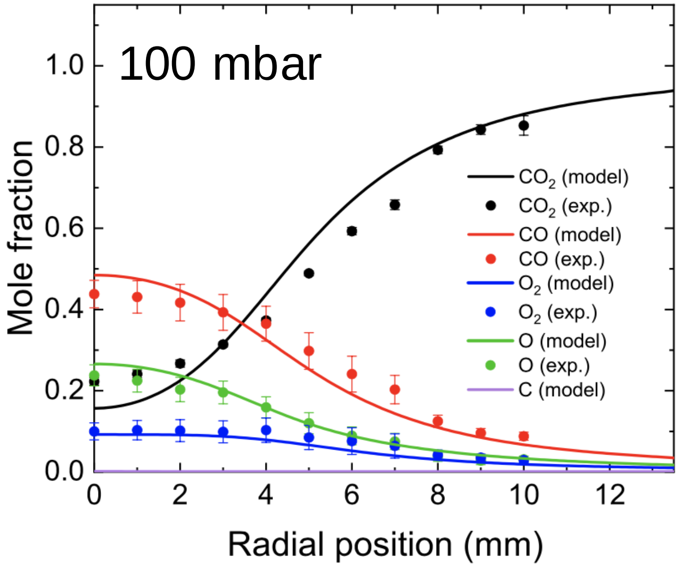


[L. Vialetto *et al.*, *PSST* **31**, 055005 (2022)]

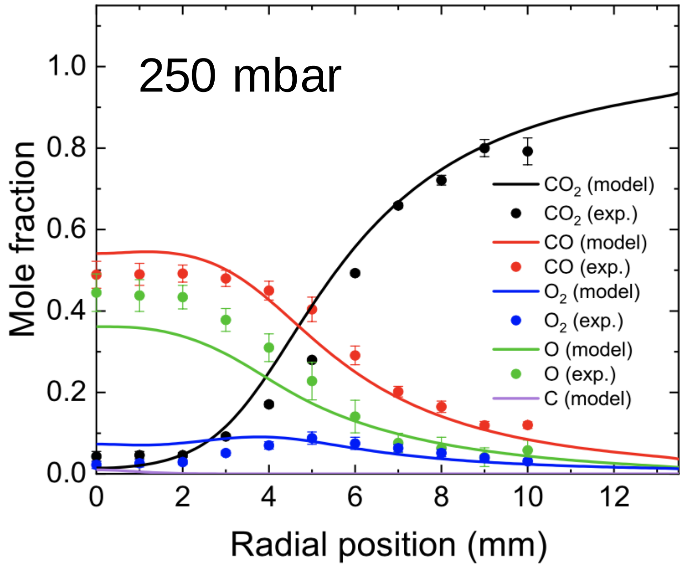
Neutral species radial profile

CO_2 dissociation driven by high gas temperature in the core

Diffuse



Contracted

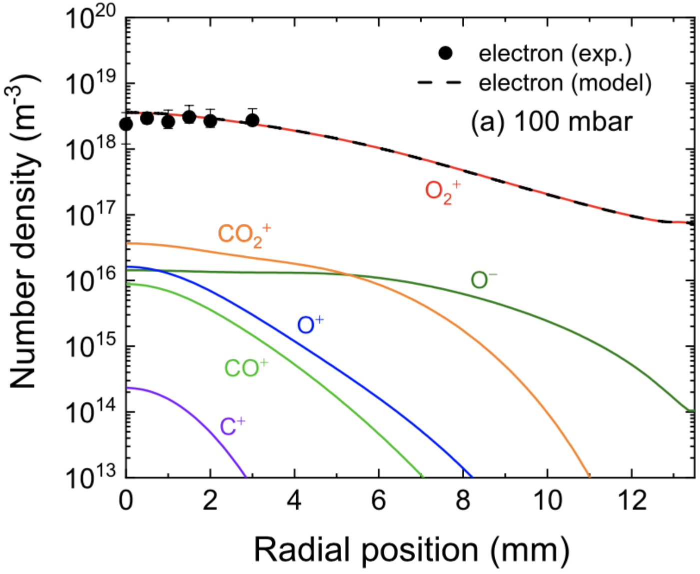


[L. Vialetto *et al*., *PSST* **31**, 055005 (2022)]

Charged species radial profile

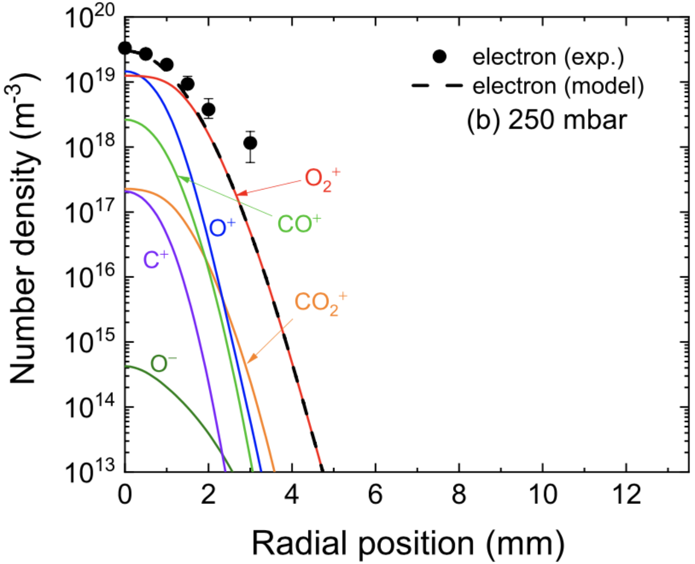
Diffuse

Broad n_e profile, O_2^+ dominant ion



Contracted

Narrow n_e profile, O_2^+ dissociated in core

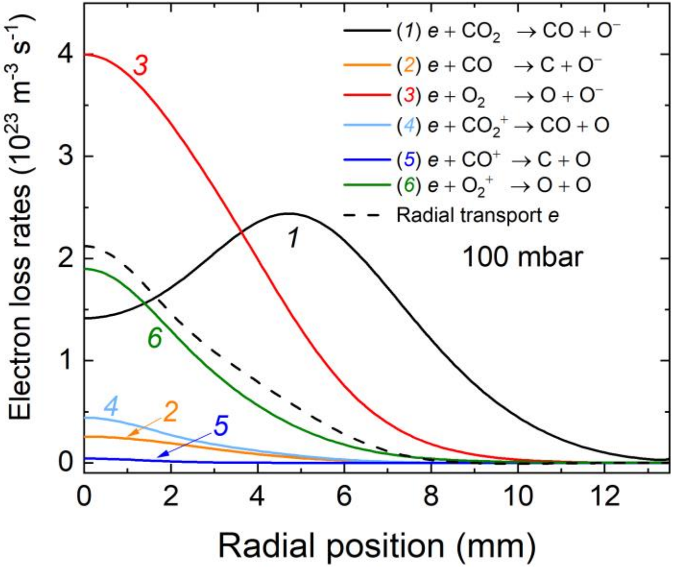


[L. Vialetto *et al.*, *PSST* **31**, 055005 (2022)]

Net electron loss rates

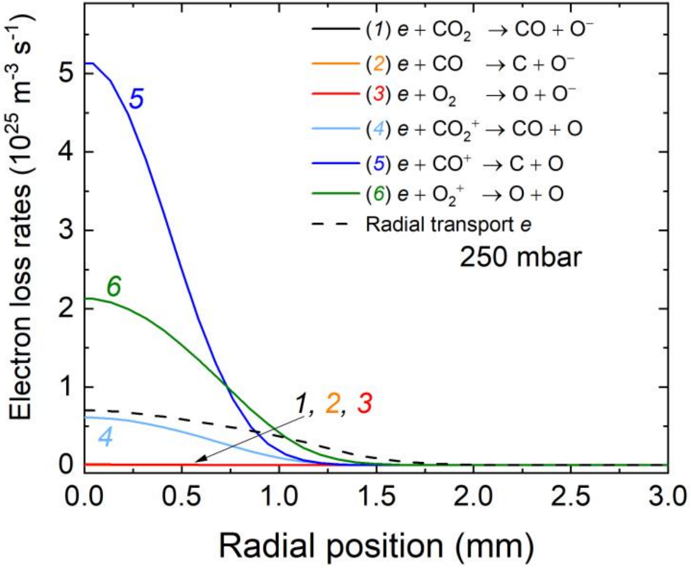
Diffuse

Dissociative attachment of electrons



Contracted

Electron-ion recombination



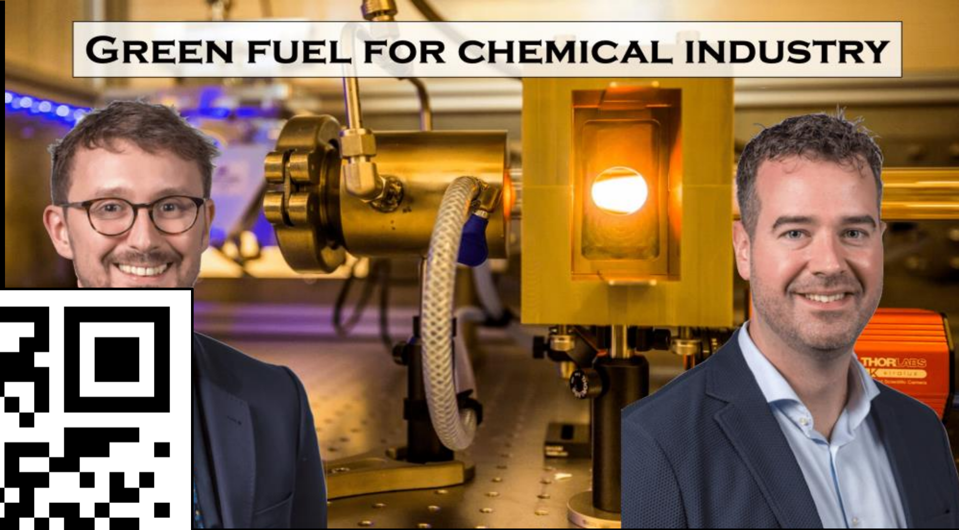
[L. Vialetto *et al.*, *PSST* **31**, 055005 (2022)]

Take home messages (2)

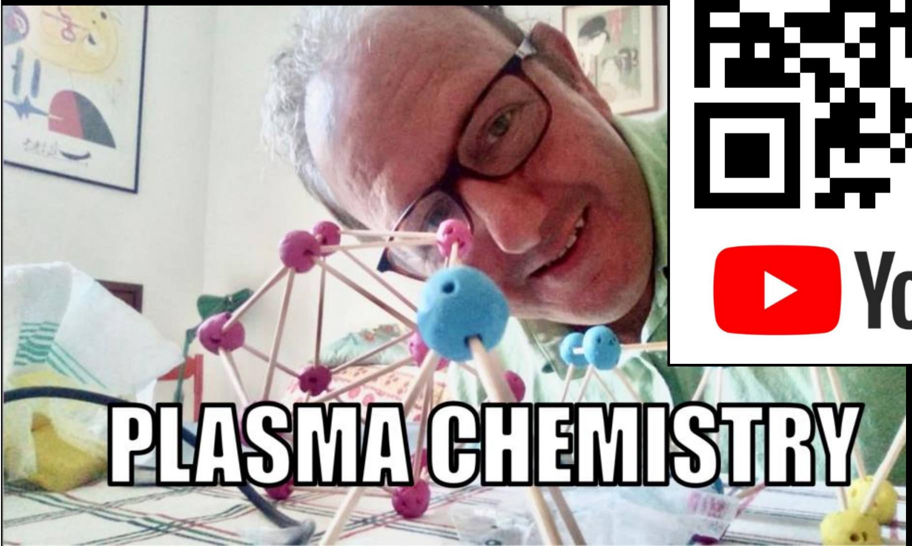
As pressure increases:

- T_{gas} increases in the core from 3000 K to 6000 K
- Change in neutral species composition:
  - Favors associative ionization over electron impact ionization
- Change in charged species composition:
  - From molecular (O_2^+) to atomic ions (O^+)
  - Reduced electron transport with increasing pressure


Can AI Do All
Of This Faster?


GREEN FUEL FOR CHEMICAL INDUSTRY

YouTube


PLASMA CHEMISTRY


Cat PROJECT
ng for plasma models

Conclusions

- Inverse problems are often encountered in plasma physics and chemistry

- Currently, the solution of those problems is based on physical intuition

- New (unbiased) approaches are required for estimation of fundamental data or internal plasma parameters !

Thank you for your attention!