DIFFER
Dutch Institute for
Fundamental Energy Research

CO_2-NEUTRAL FUELS

- CONVERSION STEP -

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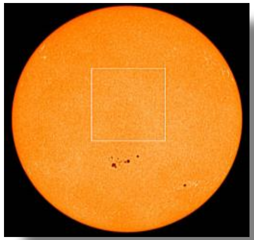
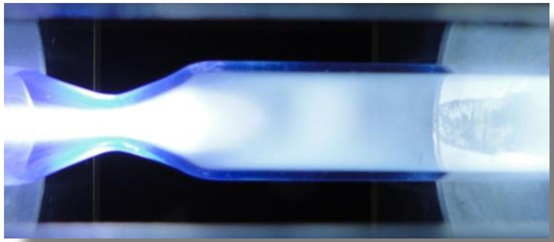


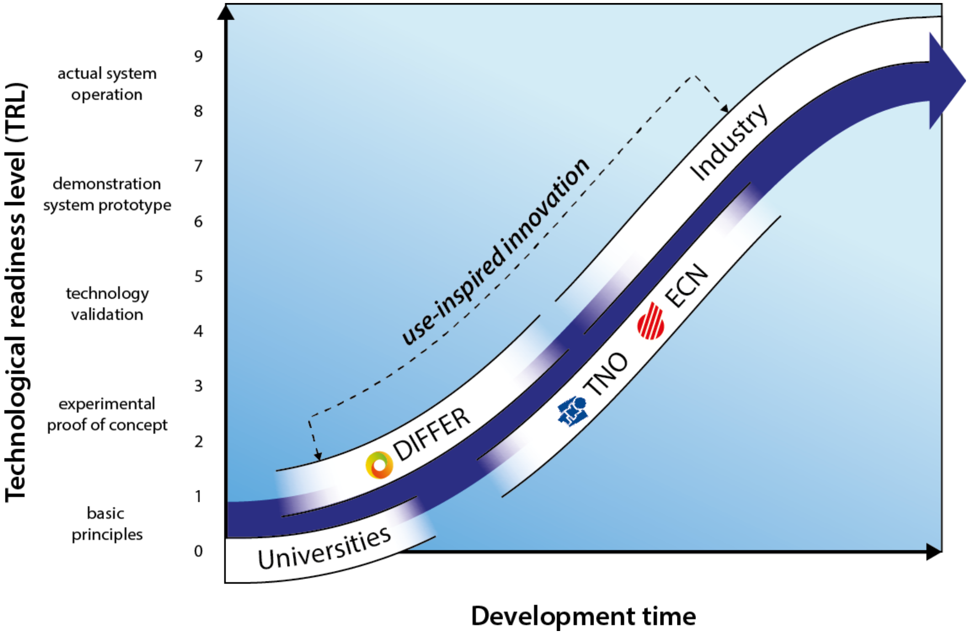

Joint EPS-SIF International School on Energy, Varenna, 17-23 July 2014

The DIFFER Institute

Science for Future Energy

Mission: Basic **scientific research** in
Fusion Energy and **Solar Fuels**,
Providing a **high-quality technical infrastructure**,
collaboration with Academia, National research facilities and Industry.
developing a **national community** (multi-disciplinary) in **energy research**.

Relocation mid 2015
University Campus Eindhoven



Outline CO_2 Neutral Fuels – lecture 2

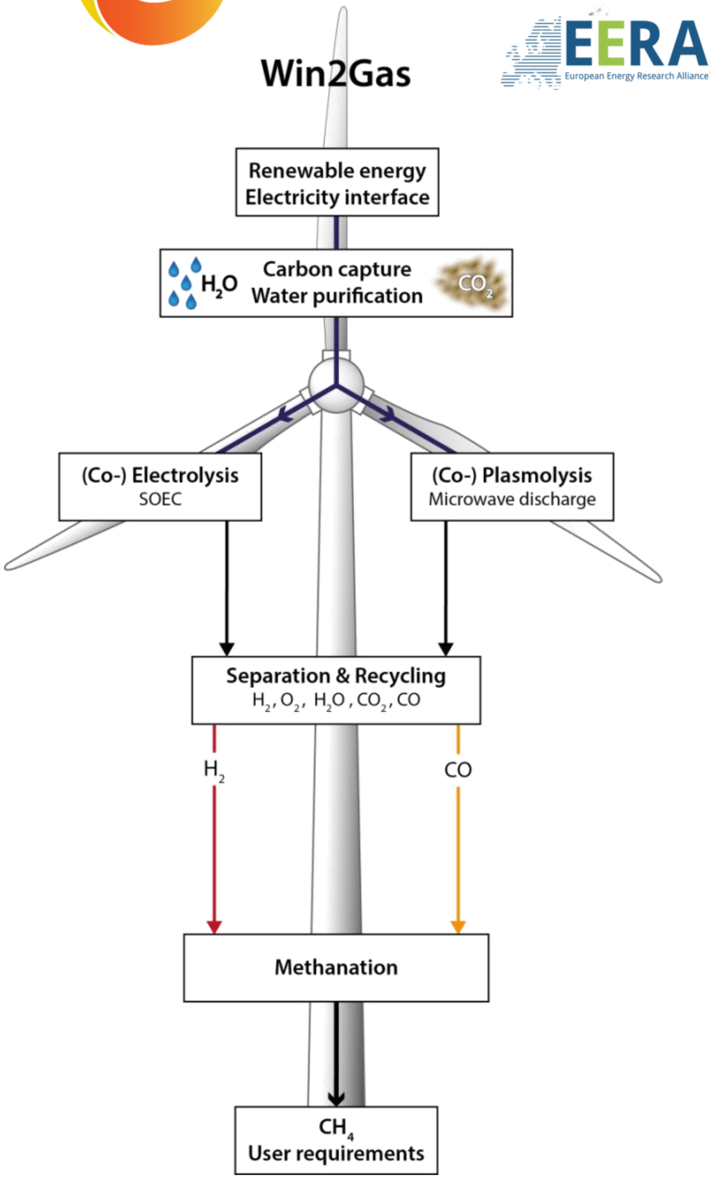
System approach

- End–to–end system: surplus wind to gas
- Carbon capture, recycling CO_2 emitted → Closing the carbon cycle
- Splitting feedstock H_2O/CO_2
- Separation of CO from CO_2 and O_2
- Syngas CO/H_2 production
- Methanation, see lecture 1

Splitting of feedstock H_2O/CO_2

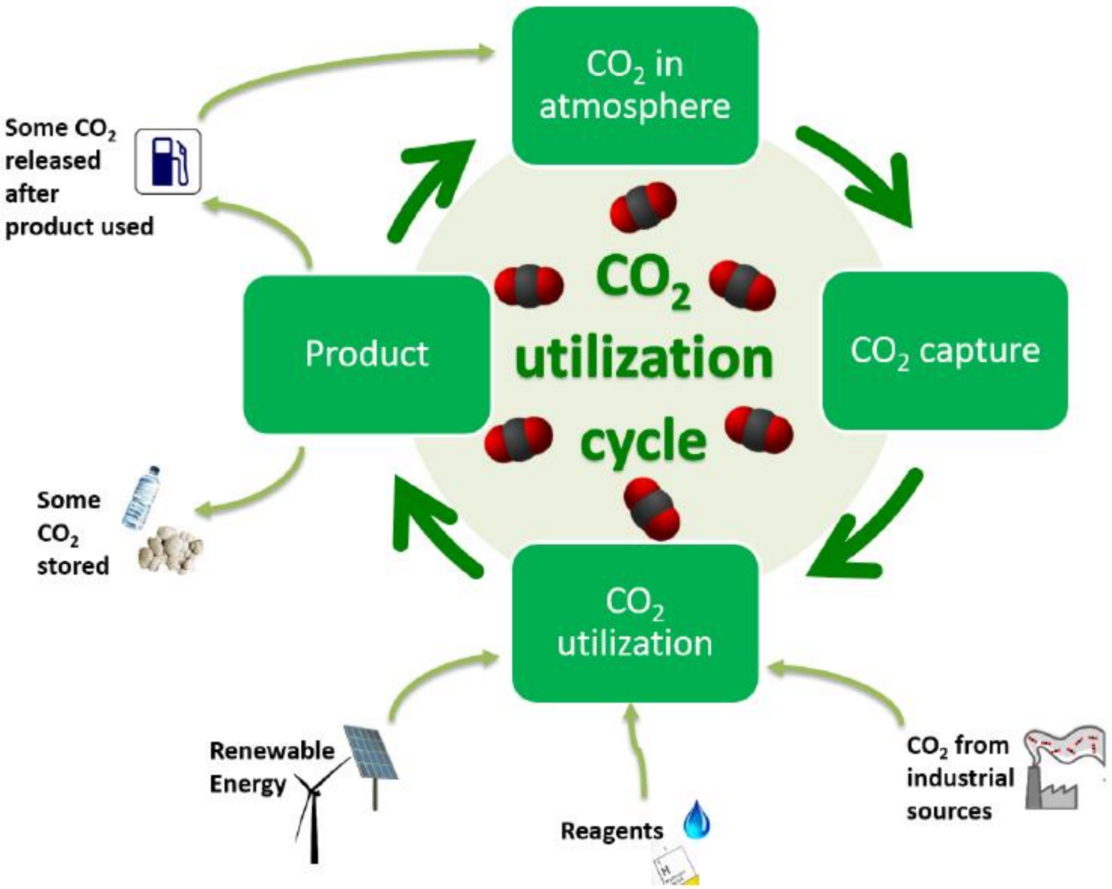
- Electrolysis, alkaline, PEM, SOEC
- Plasmolysis

Process flow wind to gas energy storage



- End-to-end system
  - Input: wind electricity (surplus)
  - Output: feed CH_4 into gas grid (P2G)
- Research challenges individual elements
  - Carbon capture
    - Novel materials for direct air capture
  - Energy efficiency splitting of H_2O and CO_2
    - (Co-)Electrolysis: SOEC
    - Plasmolysis: microwave
  - Separation
  - Methanation
- System integration Wind Energy to Gas
  - Requirements:
    - Energy efficiency (cost)
    - Fast dynamic response (intermittency)
    - High energy density (scalability to MW)
    - Use of abundant materials (sustainability)

CO_2 neutral fuel: Closing the carbon cycle



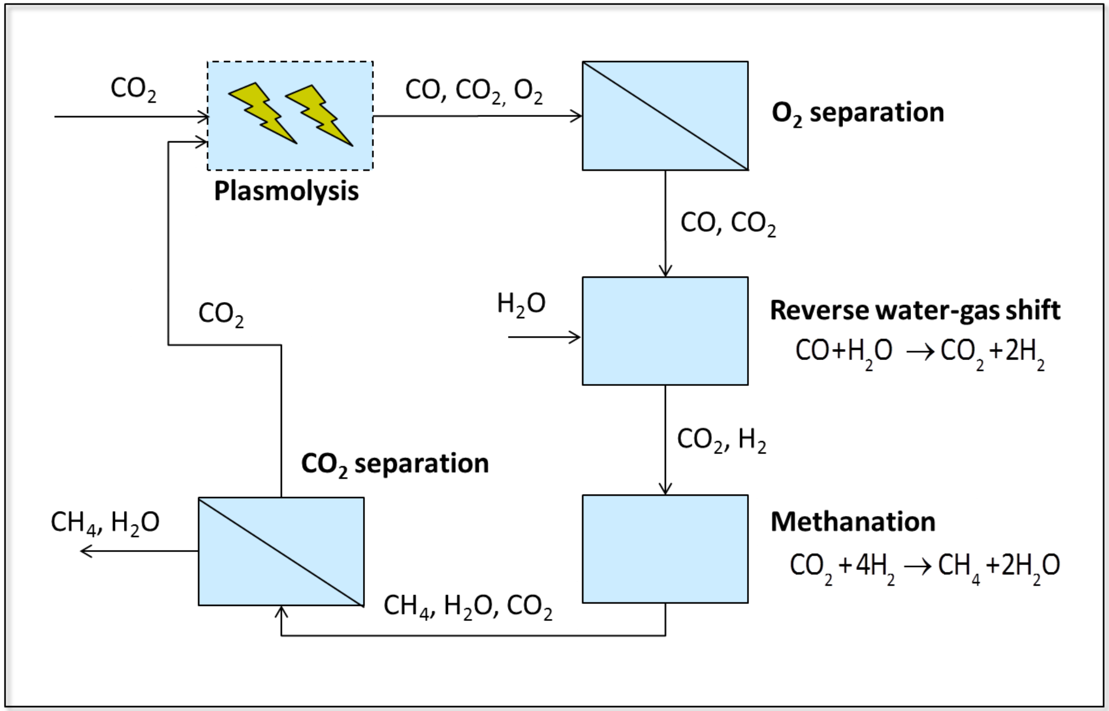
Absorption or adsorption on sorbent.
Materials: amine sorbents MEA, or novel ionic liquid-gas absorption

Cost of carbon capture:
- Point source ~0.04€/kg
- Direct air ~0.40 €/kg

H_2 production cost: 6 €/kg

Source: Peter Styring Univ Sheffield

Separation of exit gas streams



Challenge: separation of gases CO_2, CO and O_2 of similar kinetic diameter.

Various membrane options for gas separation to be explored:

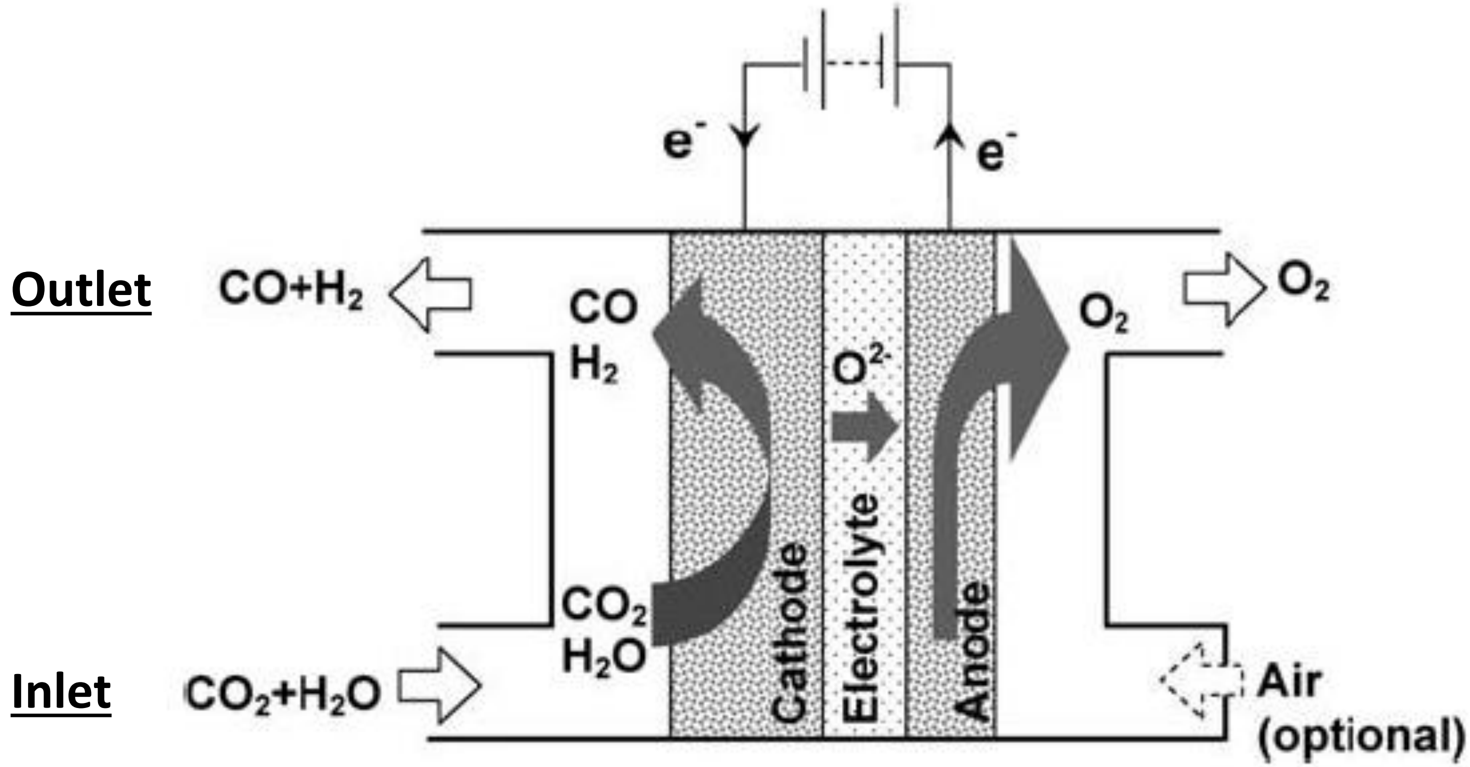
- Polymeric membranes, ceramic micro porous membranes, mixed oxygen ionic-electronic conducting membranes, carbonate based membranes, electro-chemical oxygen pumps (Univ Twente/Strathclyde)

Electrolysis of H_2O and CO_2

- **Alkaline** electrolyte (100 yrs mature technology)
  - Power density low (< 0.5W/cm^2)
  - Low hydrogen output pressure (< 30bar)
  - Safety (caustic electrolyte)
- **PEM** (polymer electrolyte membrane), pre-commercial
  - Power density ~1W/cm^2
  - Rapid dynamic response
  - Degradation membrane
  - Catalyst material Pt (Scarce)
  - 1 to 1000W units
- **SOEC** (solid-oxide electrolyser cell)
  - High power density, energy efficiency, output pressure
  - High Temperature operation (800˚C and pressure 50-100 bar)
  - Degradation under high current density
  - Co-electrolysis H_2O and CO_2 possible

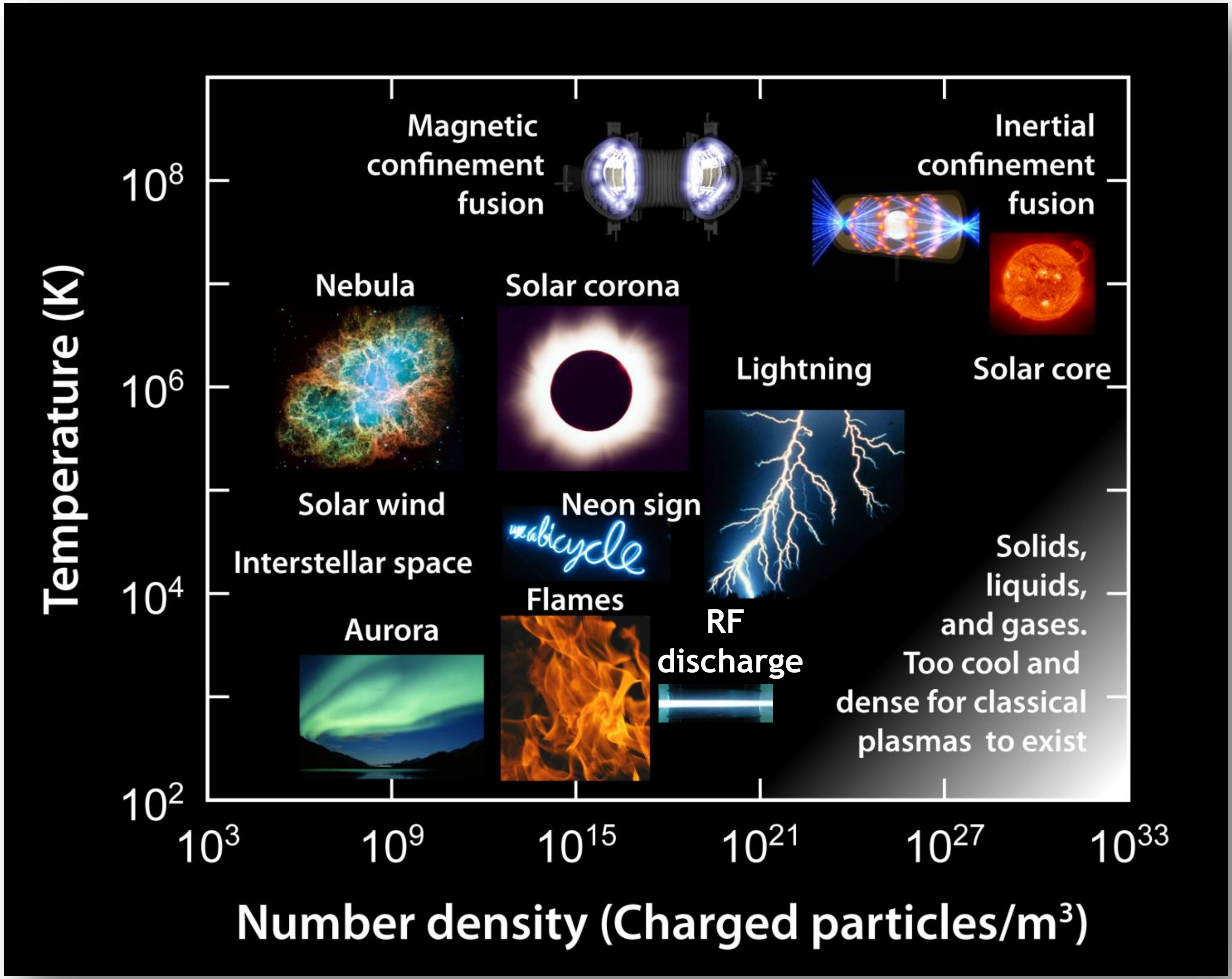
Principle of Solid Oxide Electrolysis Cell

External dc voltage pumps O^{2-} ions from porous **cathode** (Ni/YSZ) through dense solid **electrolyte** (YSZ = Yttrium Stabilised Zirconium) to porous **anode** ($La_{1-x}Sr_xMnO_3$/YSZ)



Source: Qingxi Fu, et.al., Energy & Env Science 2010, 3, 1382

What is a plasma?



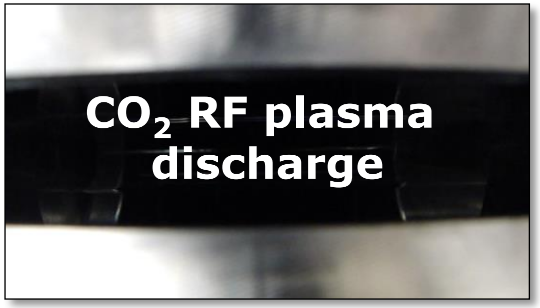
Why plasma for CO_2 conversion?

Plasmolysis

- High energy efficiency (~60% demonstrated)
- High power density (45W/cm^2 needed for upscaling to MW level)
- Fast dynamic response (intermittent power supply)
- No scarce materials employed (Pt catalyst in PEM)

Characteristics for a plasma used for CO_2 conversion:

- Low temperature (T_e~1eV, T_i~0.1eV), weakly ionised (10^{-5}-10^{-6}) gas
- Purpose: ease conditions for splitting CO_2 by creating conditions far away from thermo-dynamic equilibrium
  → energy channelled in breaking chemical bond.



Plasmolysis out of equilibrium chemistry

Energy efficient CO_2 splitting:

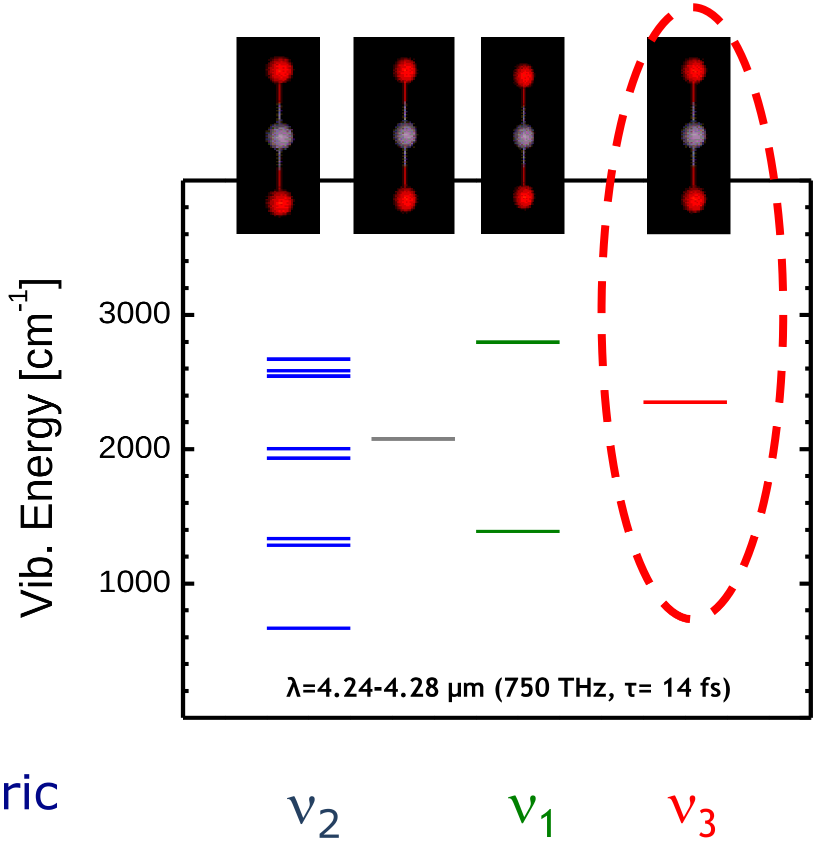
CO_2 → CO + O (ΔH=5.5 eV)

followed by re-use energetic oxygen radical

CO_2 + O → CO+ O_2 (ΔH=0.3 eV)

Net reaction:

CO_2 → CO + ½ O_2 (ΔH=2.9 eV)



Efficiency to be increased by

Concentration of electron energy in vibrational excitation of CO_2 in asymmetric stretch mode (ν_3).

Electron energy tuned to max cross-section for ν_3 vibration mode

Key parameter: reduced electric field E/n [V cm^2]

Rusanov et al. Usp. Fiz. Nauk. 134 185 (1981

Cross section CO_2 assym vibrational excitation

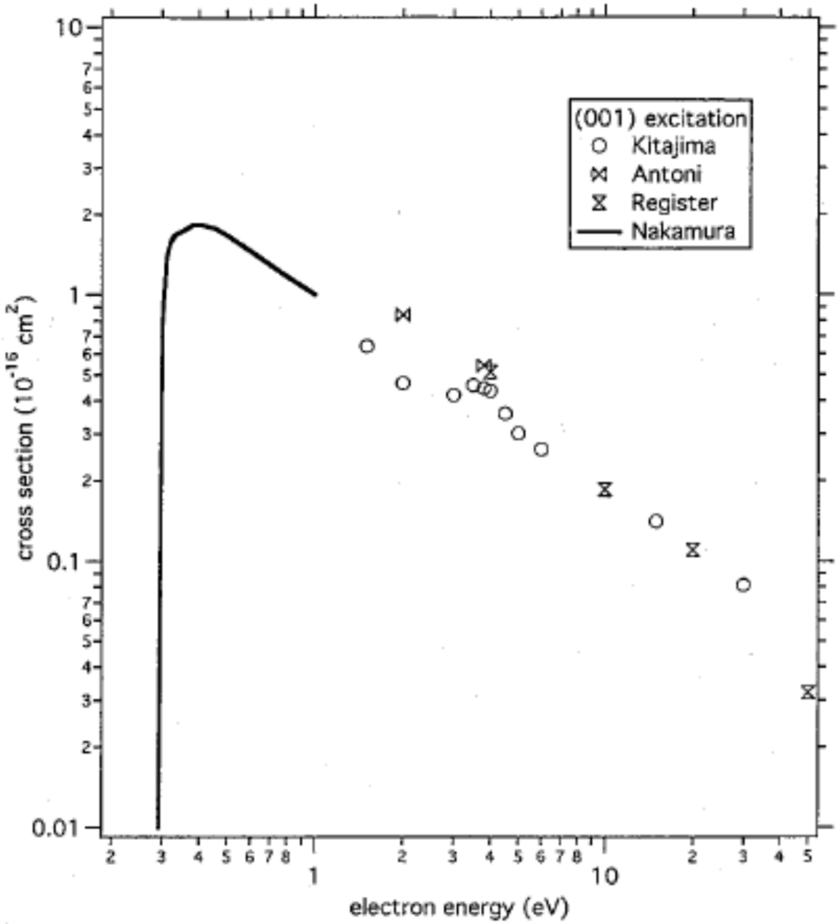


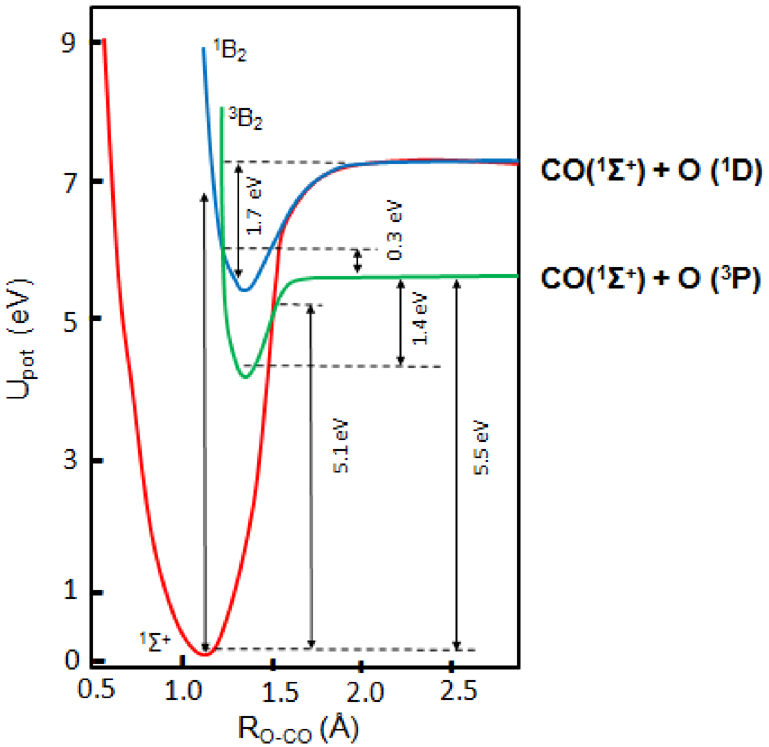
FIG. 7. Cross sections for the electron-impact excitation of the vibrational state (001) of CO_2. Comparison of the beam experiments by Kitajima *et al.*,[32] Antoni *et al.*,[33] and Register *et al.*,[26] and the swarm result of Nakamura[31] is shown.

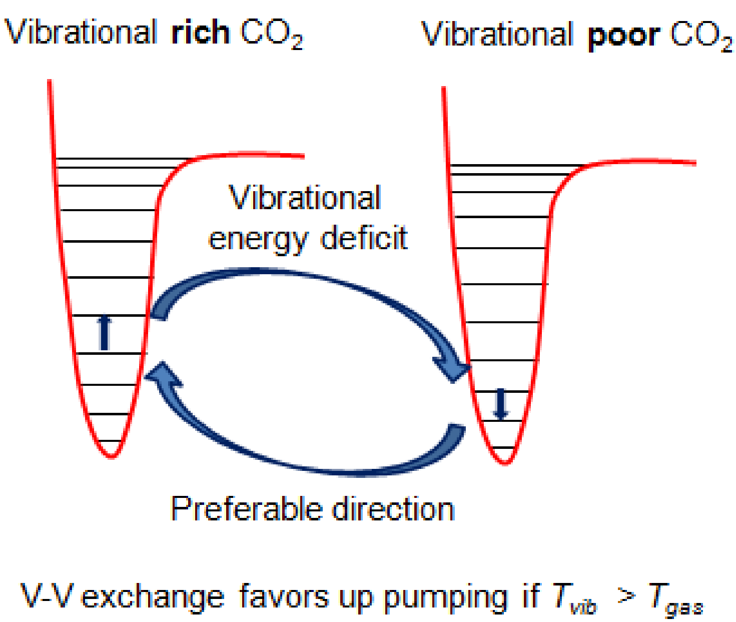
- Vibration excitation of asymmetric stretch mode reaches maximum at electron energy 0.4 eV
- 1/v dependence renders collision frequency independent of energy

Itikawa, J. Phys. Chem. Ref. Data 31 749 (2002)

Vibrational excitation of CO_2

vibrational energy levels as function of inter-nuclear distance





Vibrational excitation of CO_2 by electron impact
Highly vibrational excited CO_2 molecules exceed dissociation threshold
Activation energy reduced by vibration energy $k = A \exp{(\alpha E_v - E_a)/kT}$

Electron energy transfer in CO_2 plasma

electrons

⇩

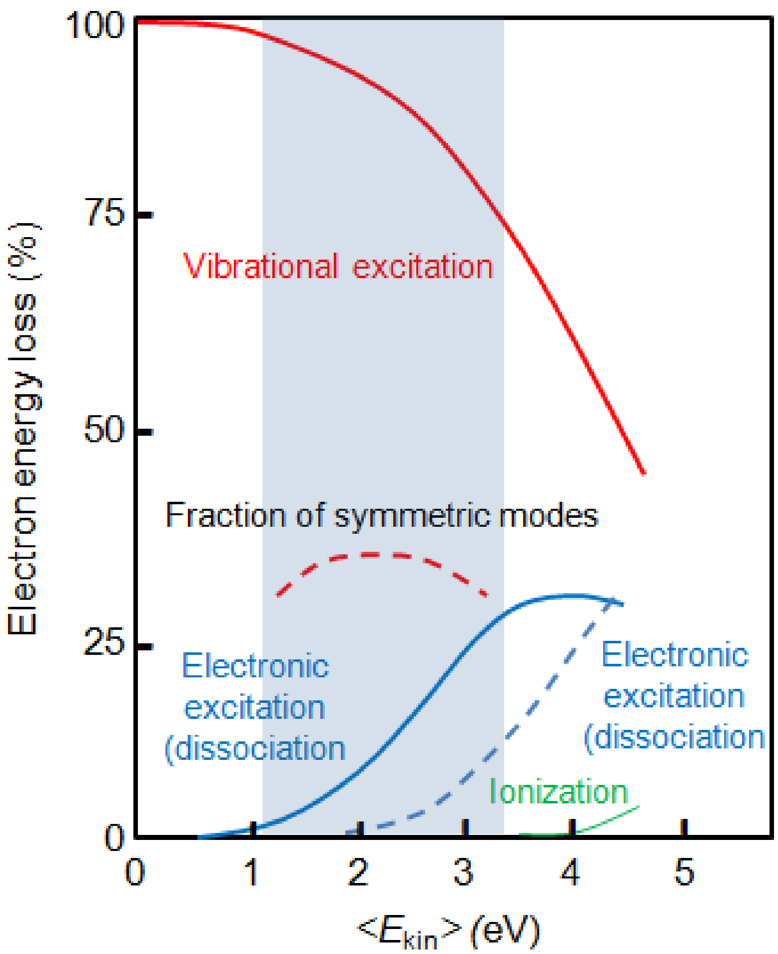
electric field

⇩

collisions

⇩

vibrational excitation



Rusanov et al. Usp. Fiz. Nauk. **134** 185 (1981)

Vibration Excitation CO_2 vs. Reduced E-Field

Few electrons

⇩

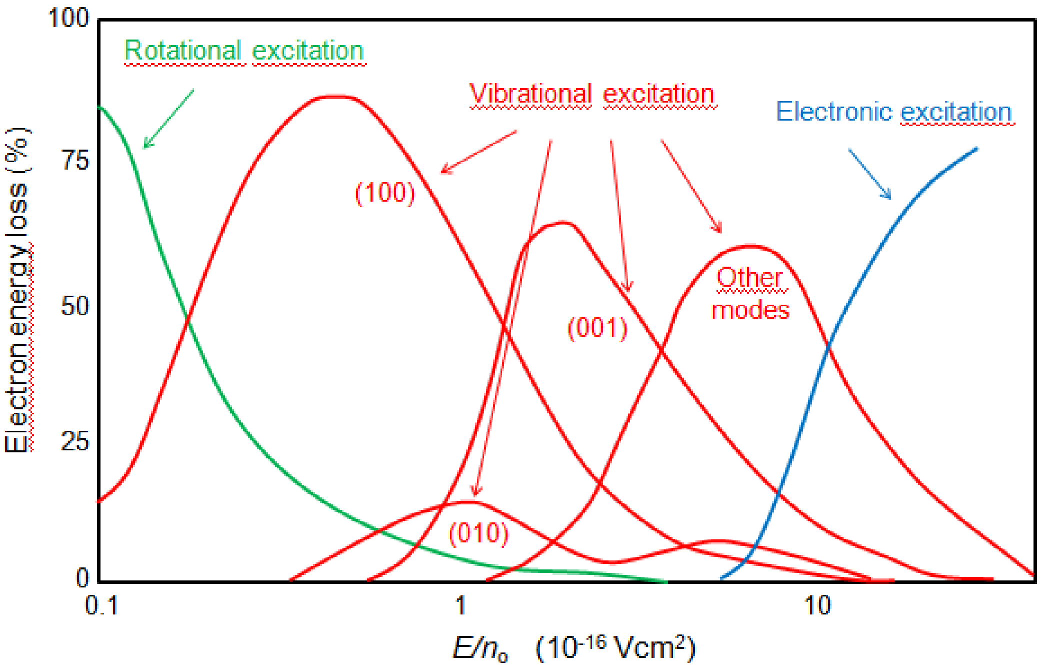
Low reduced electric field

⇩

Electron-neutral collisions

⇩

vibrational excitation



ν_3 (001) = CO_2 asymmetric stretch mode
Max excitation at $E/n = 2\times10^{-16}$ Vcm^2

Rusanov et al. Usp. Fiz. Nauk. **134** 185 (1981)

Non-equilibrium: Treanor distribution

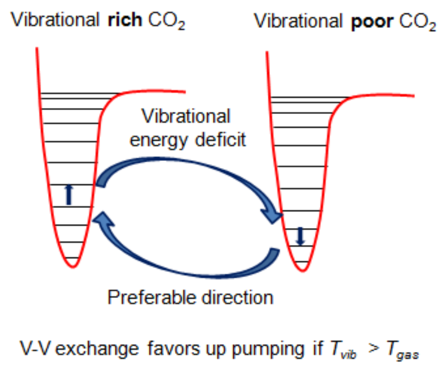
electrons

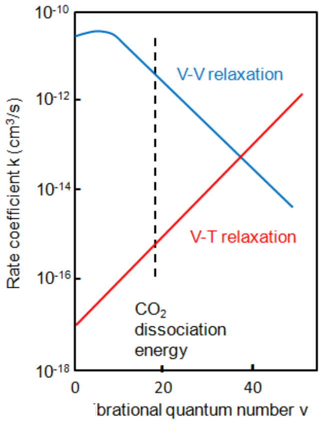
electric field

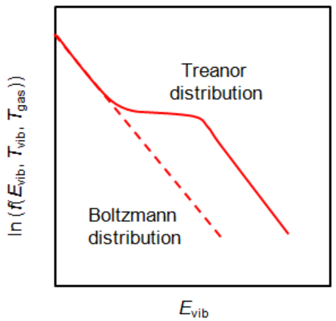
collisions

vibrational excitation

$$T_{\text{electron}} > T_{\text{vib}} > T_{\text{gas}}$$



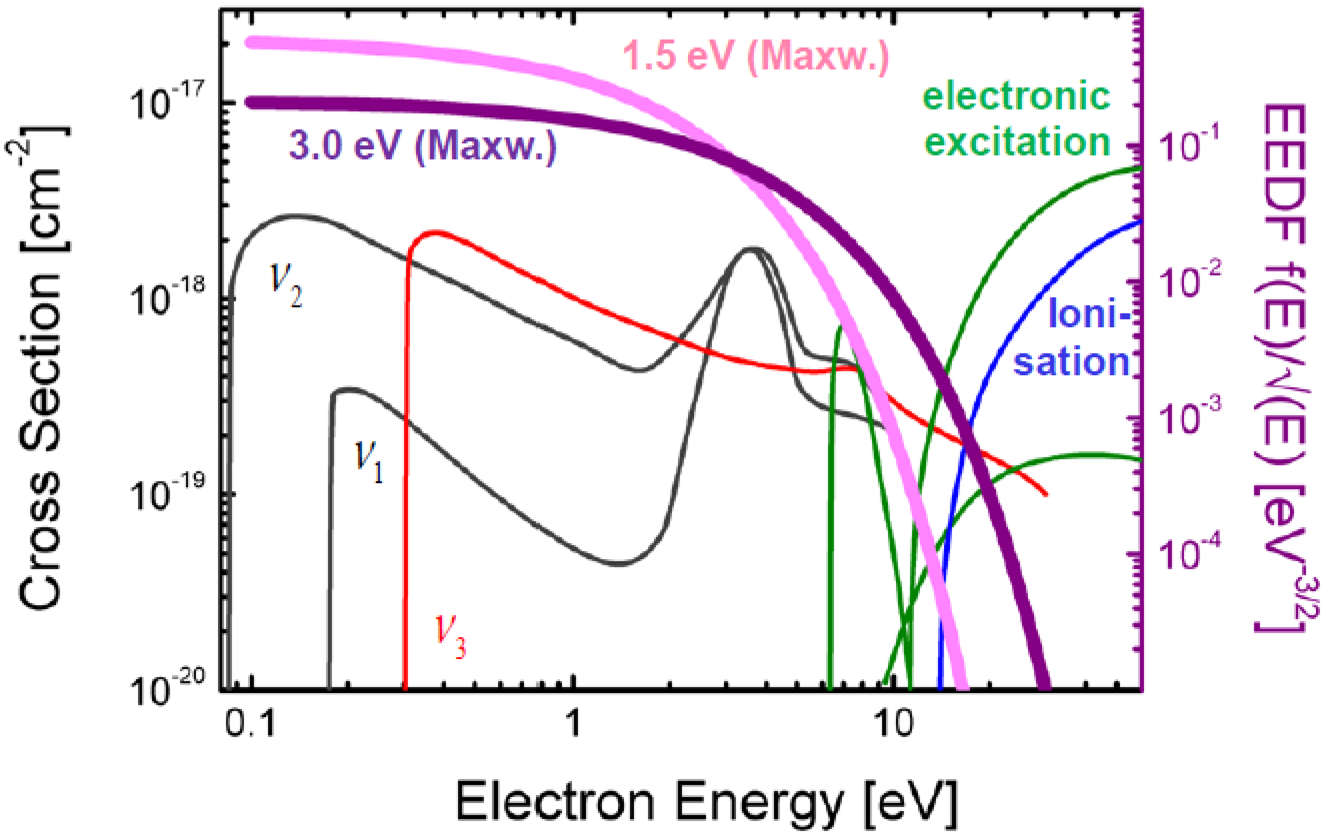




Treanor distribution: overpopulation of higher vibrational states leads to lower activation energies, faster kinetics

Rusanov et al. Usp. Fiz. Nauk. **134** 185 (1981)

X-section electron-CO_2 molecule interaction vs. electron energy distribution at T_e=1.5 and 3 eV



- Conflicting requirements on plasma temperature T_e < 1eV for vibrational excitation and T_e>1eV for ionisation

Efficiency, Particle and energy balance

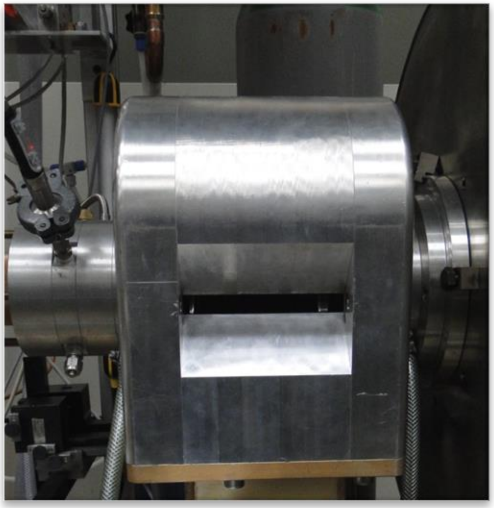
- **Energy efficiency:** $\eta = H/E_{co}$

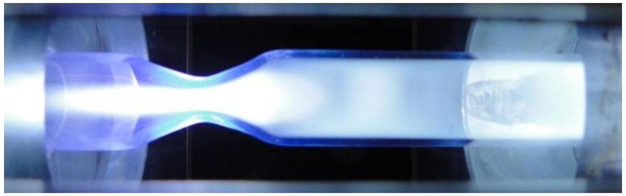
  E_{co} = energy to produce one CO molecule, H = minimum enthalpy = 2.9eV
- **Conversion ratio:** $\alpha = CO_{out}/CO_{2\ in}$
- **Energy E_v per incoming CO_2:** $E_v = W/CF$; W=RF power, F=gas flow
- $E_v = \alpha E_{co}$ → $\mathbf{E_v = \alpha/\eta\ H}$ where α is measured quantity
- **Particle balance:** $2v_B = n_0\, r <\sigma v>_{ionization}$

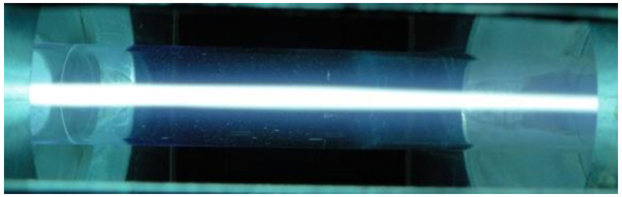
  → electron temperature through $v_B = \sqrt{(kT_e/m_i)}$
  - Contraction of plasma r at increased gas density n_0
  - $E/n \sim kT_e$
- **Energy balance:** $P_{RF} = n_e n_0\, \Sigma_i <\sigma v>_i\, \Delta\varepsilon_i\, V$

  → electron density and ionisation degree

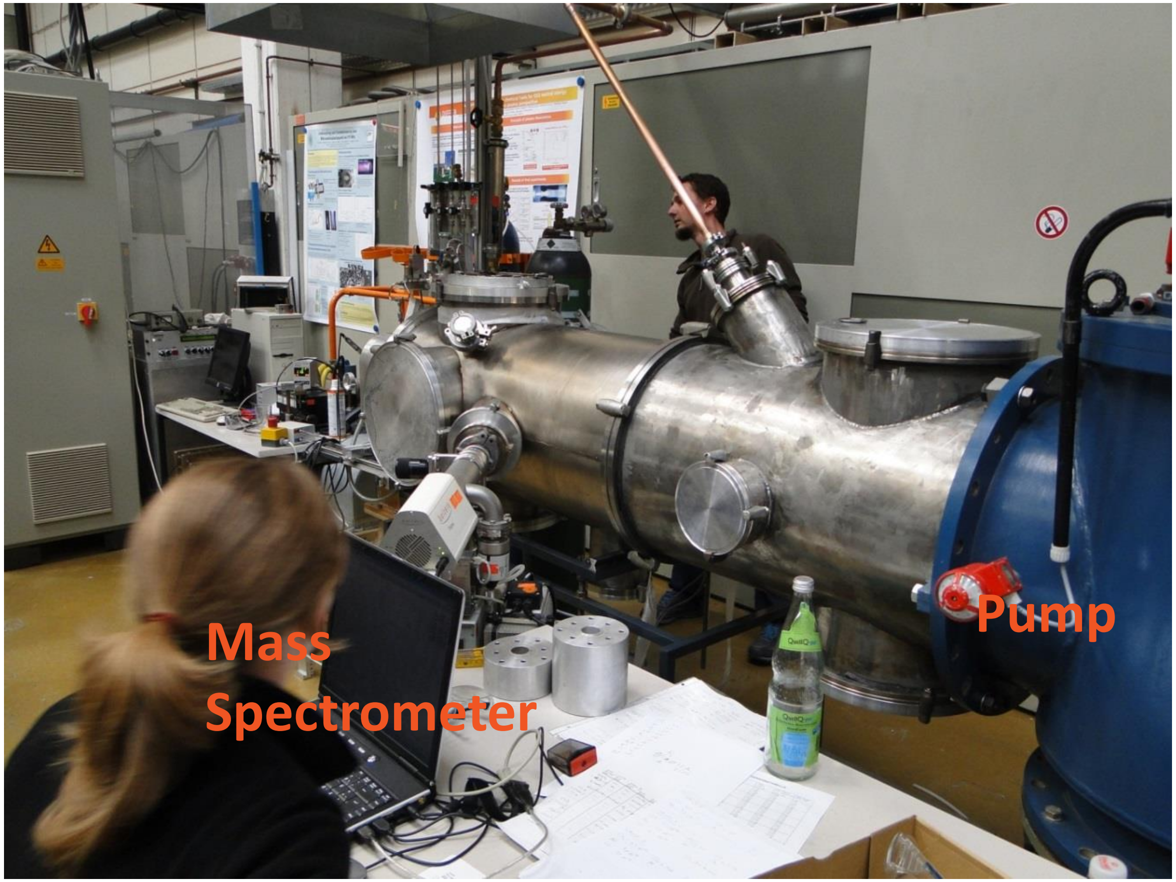
Experiments at IPF Stuttgart





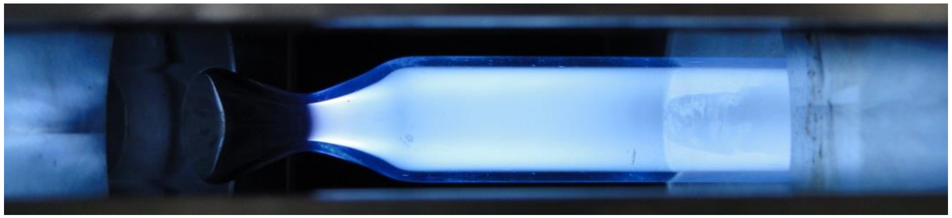


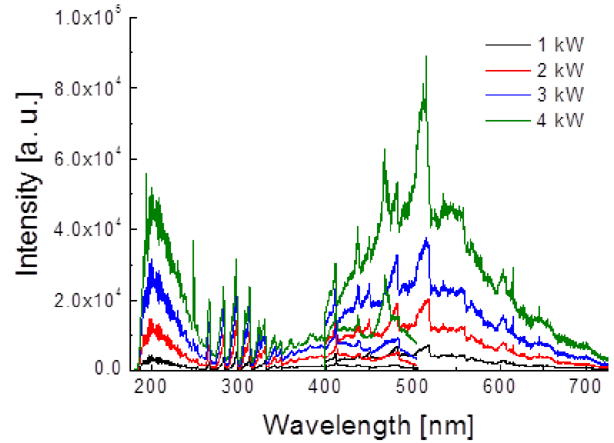
Microwave input 30 kW @ 915 MHz

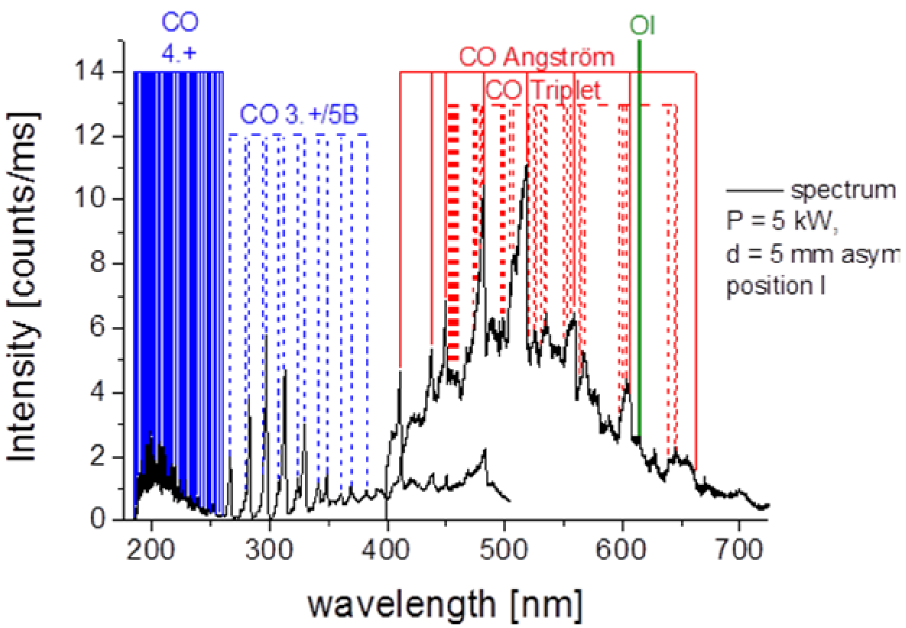


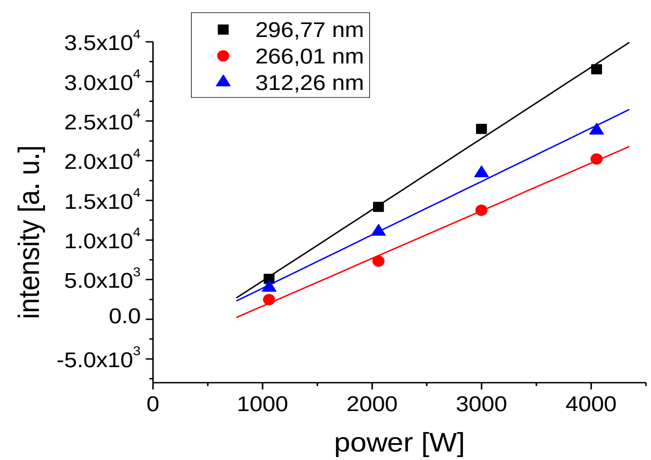
- **High and low reduced electric field CO_2 plasma**

Type I discharge: Optical Emission Spectroscopy









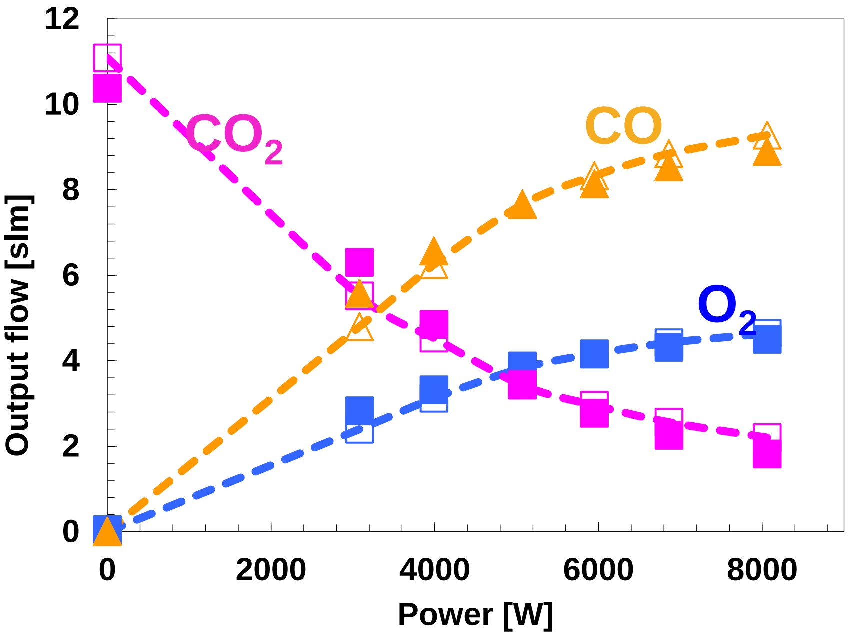
- CO 3rd positives, 4th positives, Angstrom and triplet bands identified.
- CO line intensity increases linear with power in supersonic regime

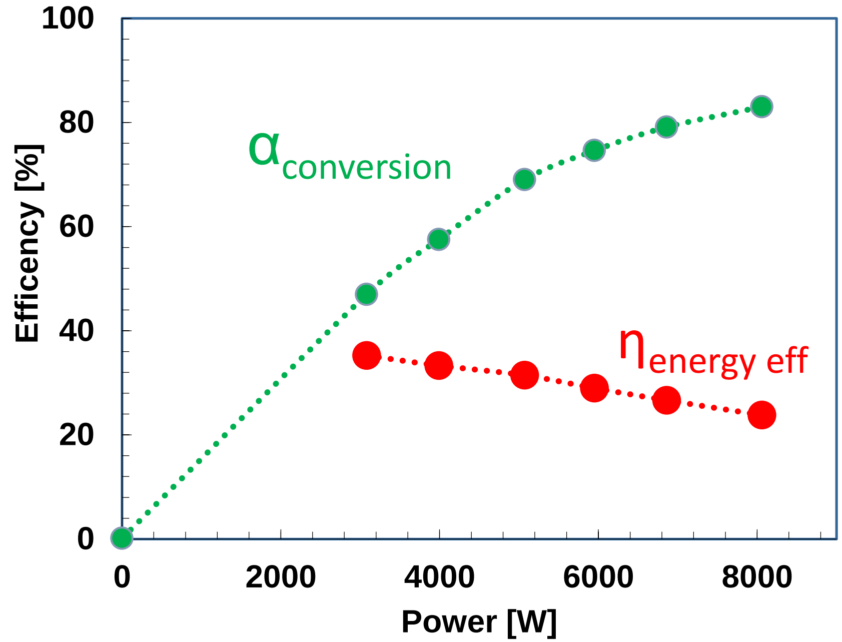
Type II discharge, mass spectroscopy

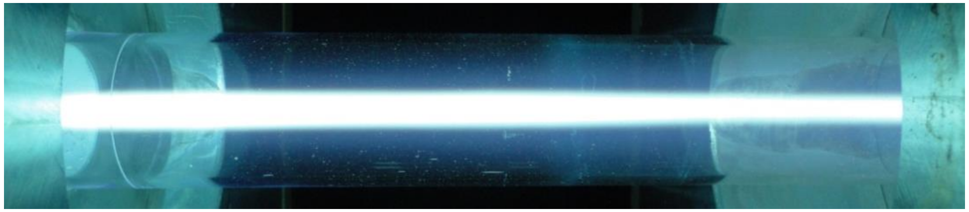
CO produced at expense of CO_2

CO_2 flow 11.1 slm

$CO_2 \rightarrow CO + ½O_2$ stoichiometry

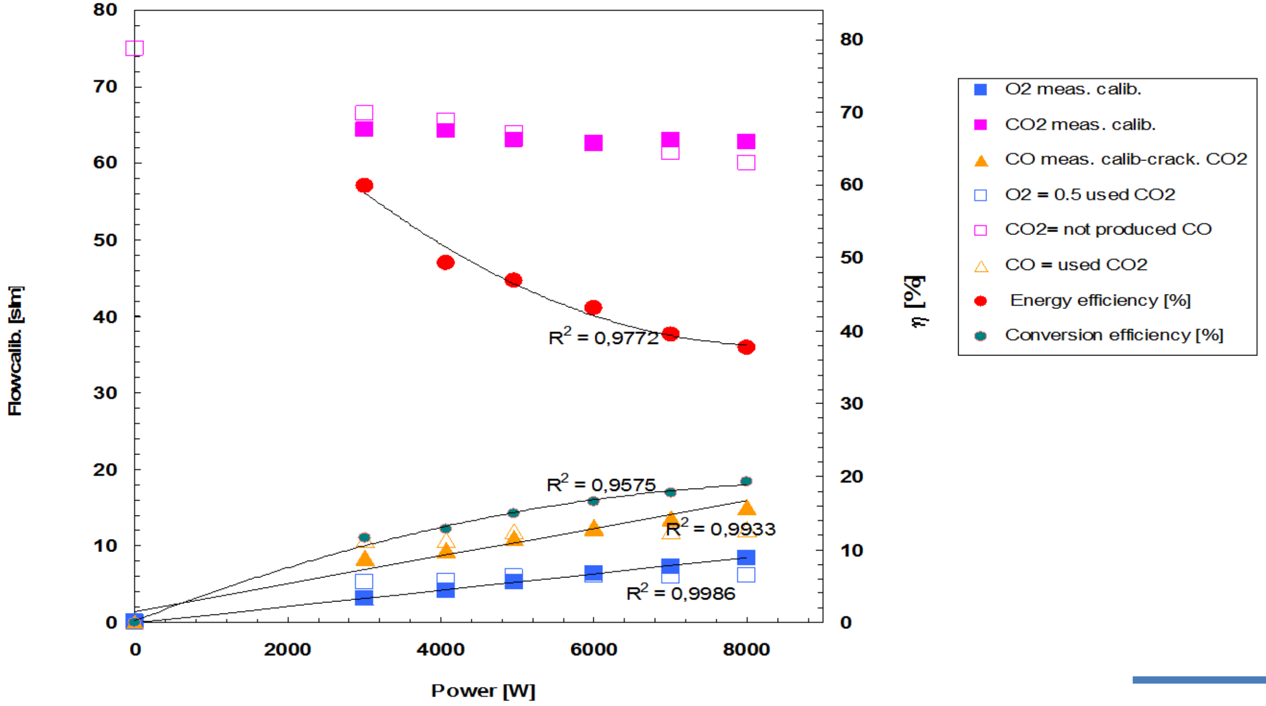




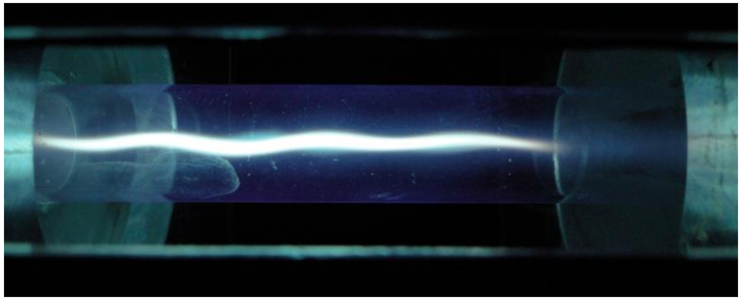


$$\eta = \Delta H / E_{CO}$$

Lower reduced E field to enhance efficiency



Gas flow



- High gas flow 75 slm CO_2
- Gas pressure reaction chamber 190-250 mbar
- **Energy spent per CO_2 molecule 0.56 - 1.49 eV**

Intermezzo: Vortex High flow CO_2

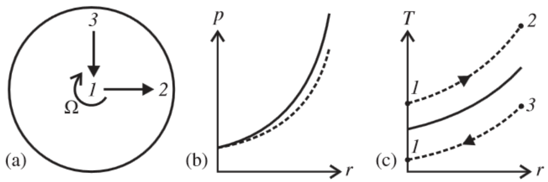
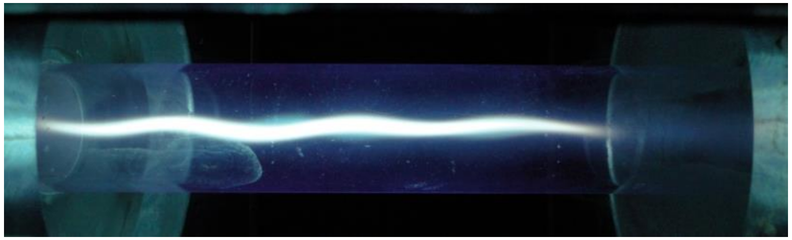


FIG. 2. Rotating cylinder with radial flow. (a) Rotating cylinder filled with gas. (b) Pressure as a function of the radial coordinate. (c) Temperature as a function of the radial coordinate. The solid lines in the middle and right figure show adiabatic conditions.



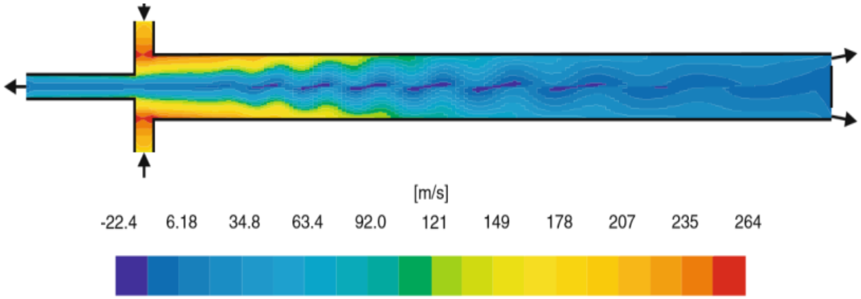
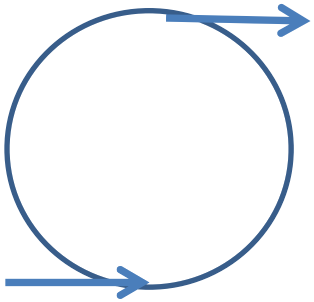


Fig. 22 Contour plot of the absolute swirl velocity obtained from numerical simulation

Tangential Pressure measurement: 190 mbar



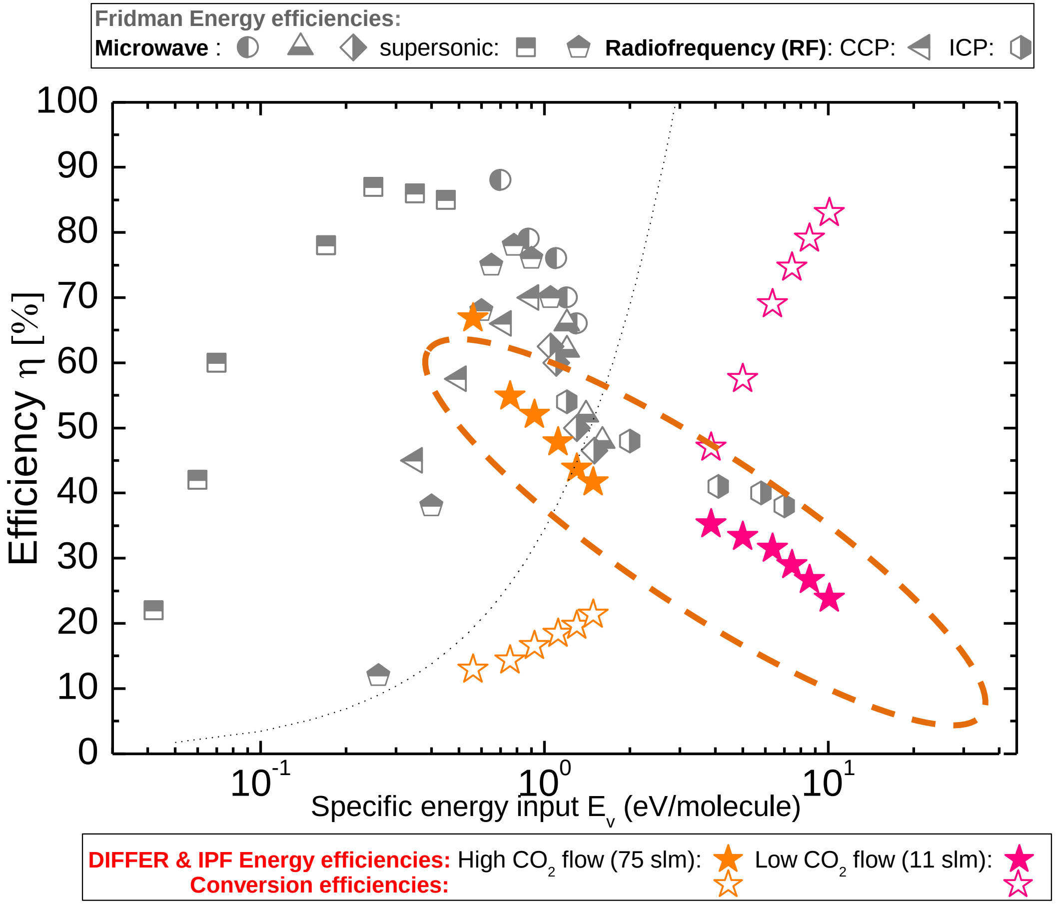
Tangential Gas feed in 75 slm

R. Liew, J. C. H. Zeegers, J. G. M. Kuerten,W. R. Michałek, 3D Velocimetry and droplet sizing in the Ranque–Hilsch vortex tube Experiments in Fluids December 2012, 54:141

Pressure in plasma centre reduced by 10-30%

Constant CO_2 flow of 75 slm (15.6 kW@100% E. efficiency)

Overview results DIFFER/IPF



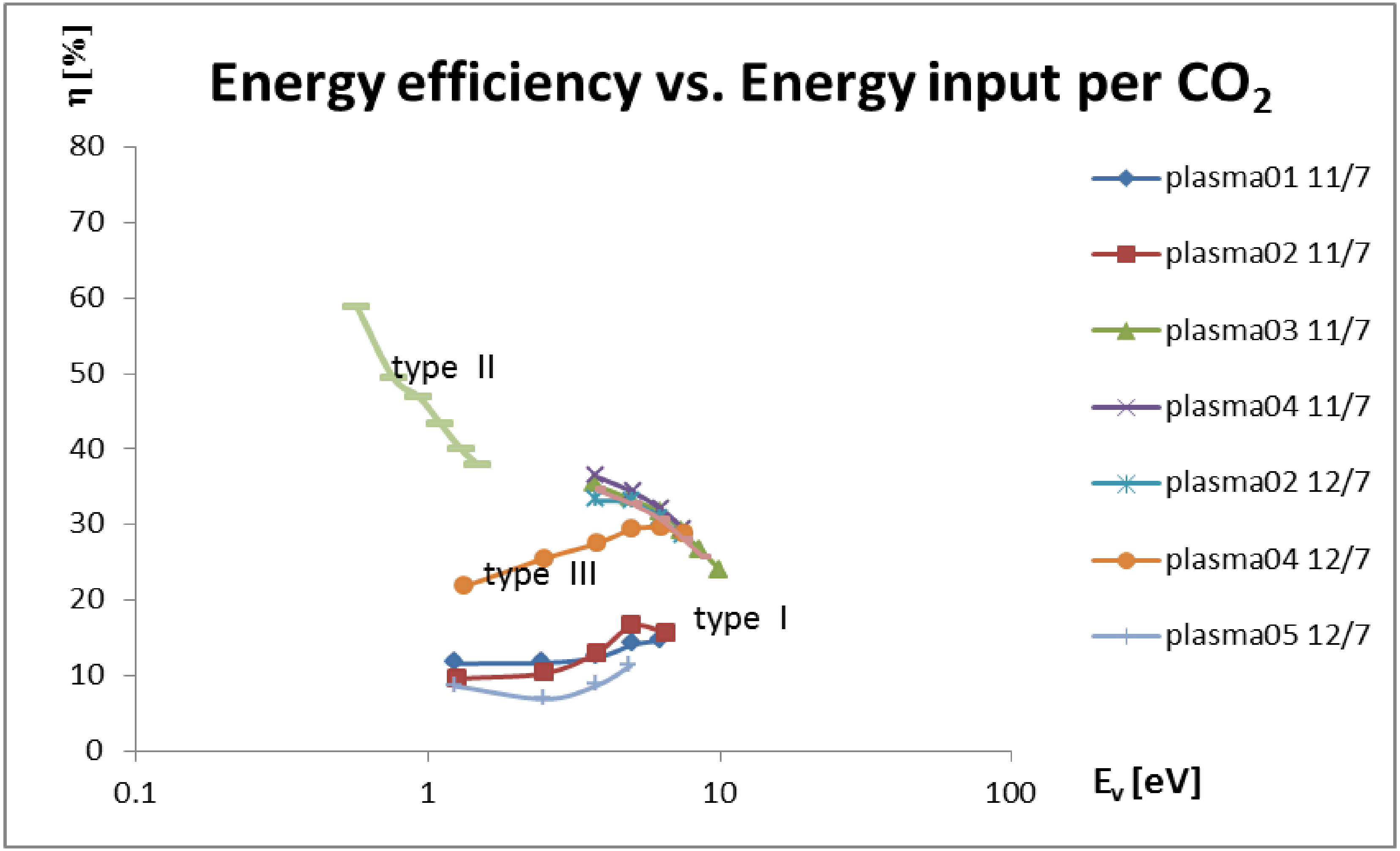
$CO_2 \rightarrow CO + ½O_2$ $\Delta H = 2.9$ eV

Adapted From A. Fridman, "Plasma Chemistry" (2009)

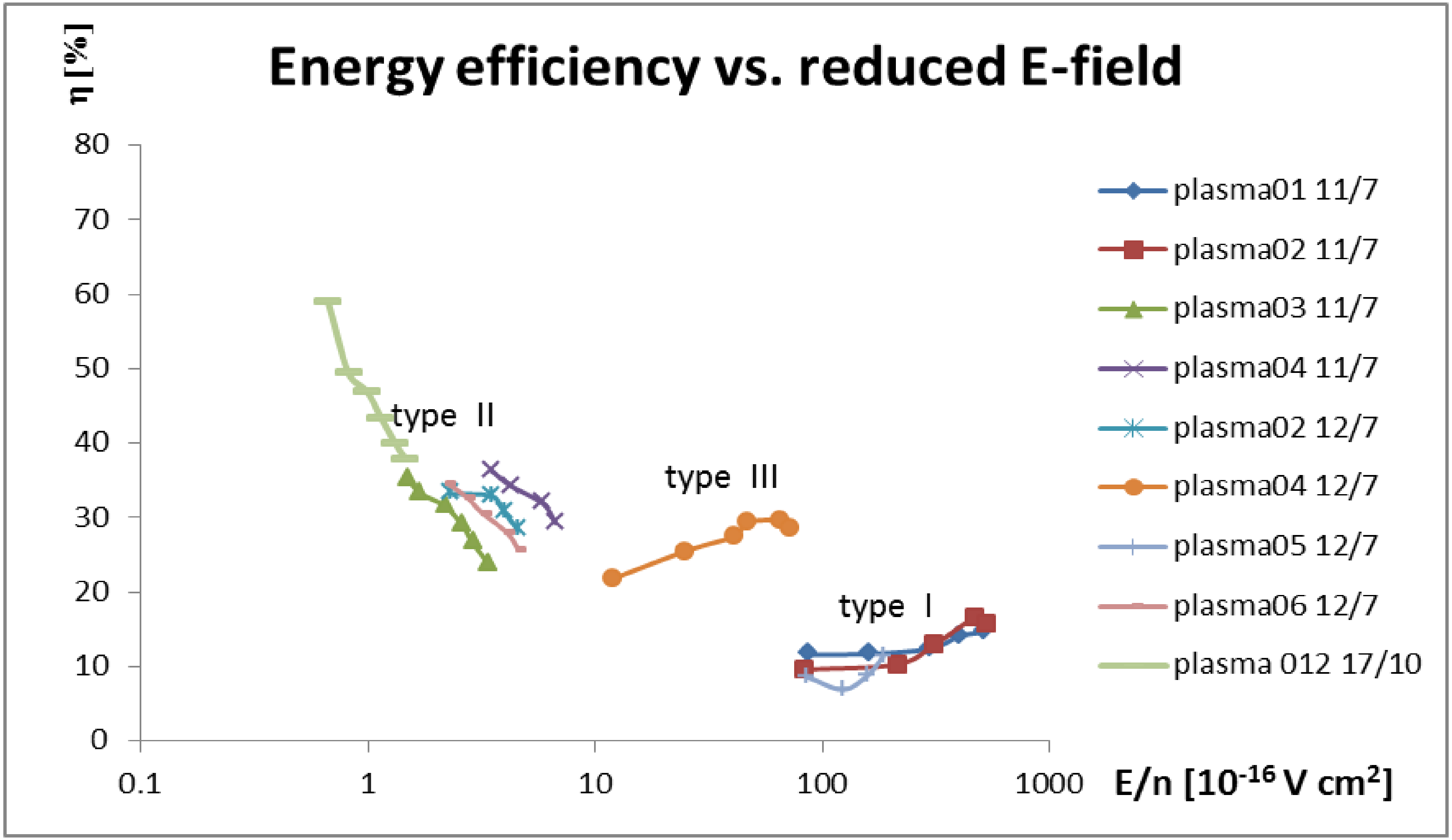
Energy efficiency goes up by lowering specific energy E_v per incoming CO_2 molecule below minimum enthalpy required for CO_2 splitting:

Conversion ratio goes down→ energy concentrated in one out of many molecules

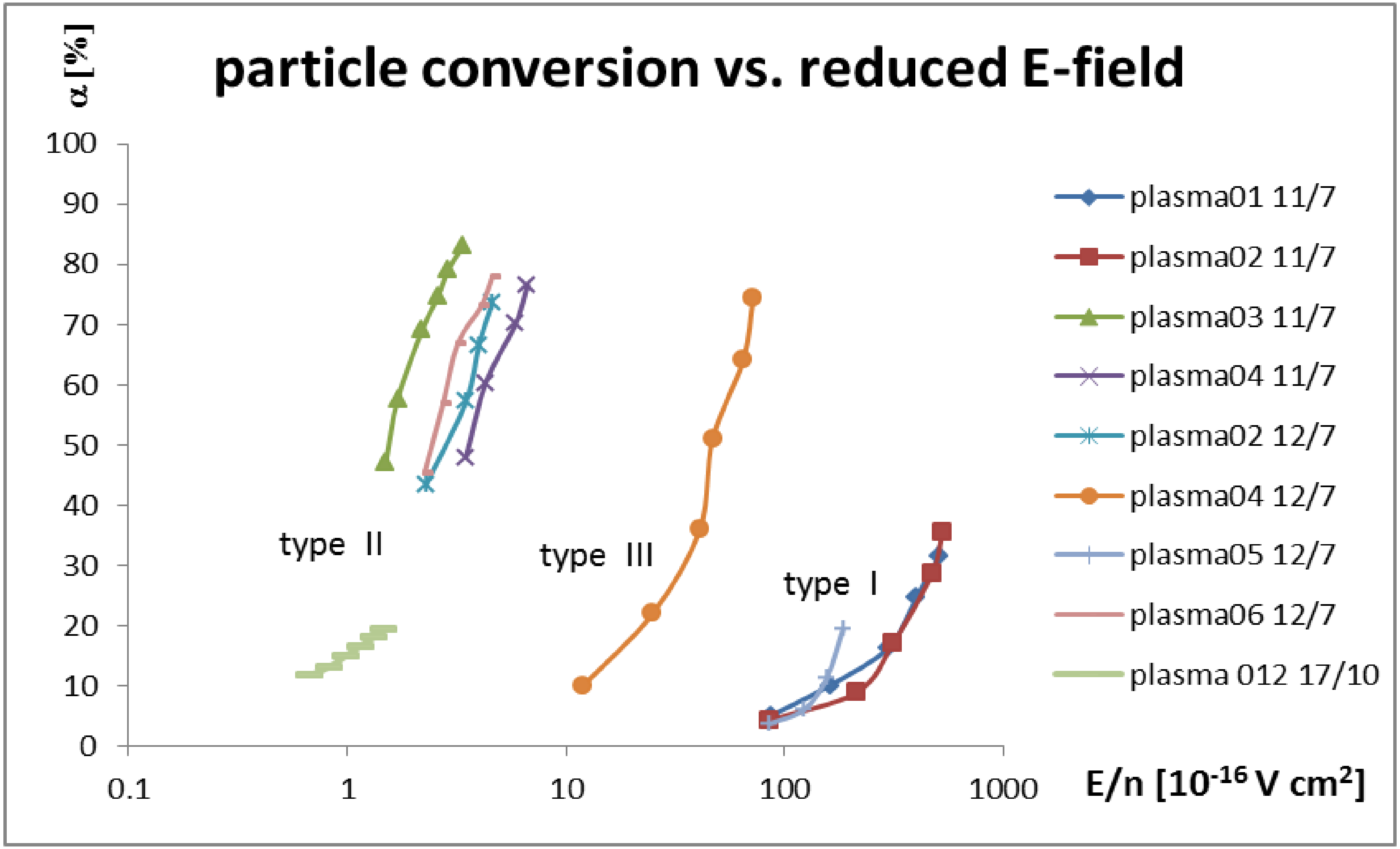
Overview of experimental results



Overview of experimental results



Overview of experimental results



Conclusion

Energy efficiency >50% obtained for 10% CO_2 conversion through low temperature plasma activation.

Next Physics steps:

- Diagnose the plasma: determine reduced electric field (incl. n_e, T_e, n_0, T_0) and vibration state CO_2 (FTIR, Thomson scatter, CARS,..)
- Create super cooled gas stream T_0~100K to lower vibration-translation energy relaxation
- Separate out flow CO from CO_2 (low conversion factor)

Next System steps:

- DIFFER experimental facility (1.3 kW 2.45 GHz) built
- 100 kW 915 MHz DIFFER facility planned
- Design and development of output gas separation system

End of lecture 1

Thank you for your attention!

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