Chemical Energy storage by CO_2 Plasmolysis

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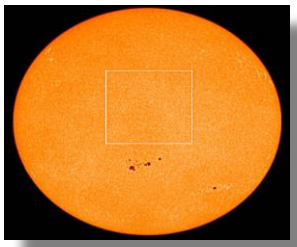
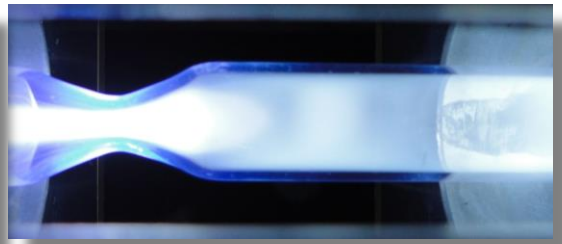
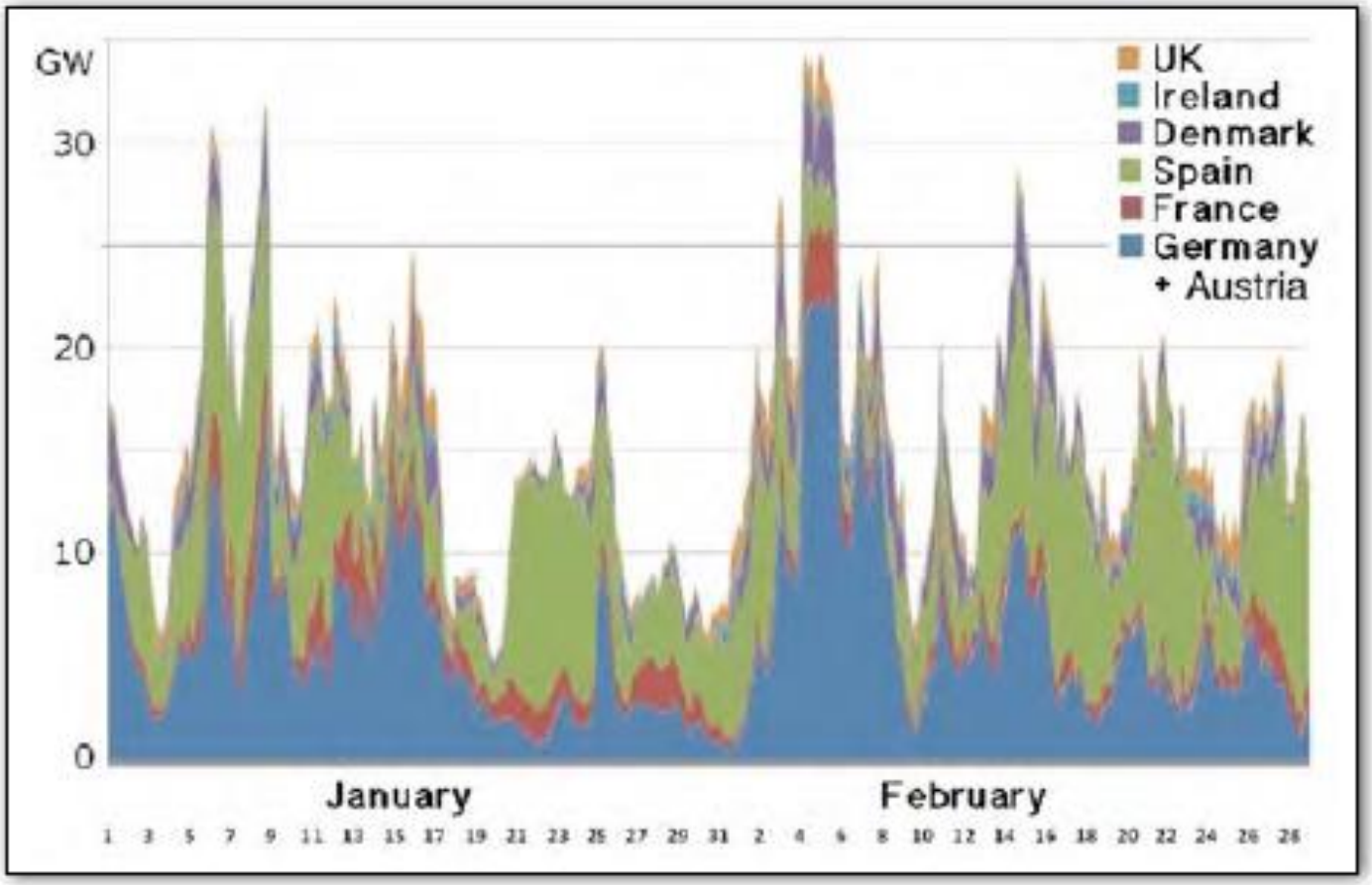



Why Chemical Storage

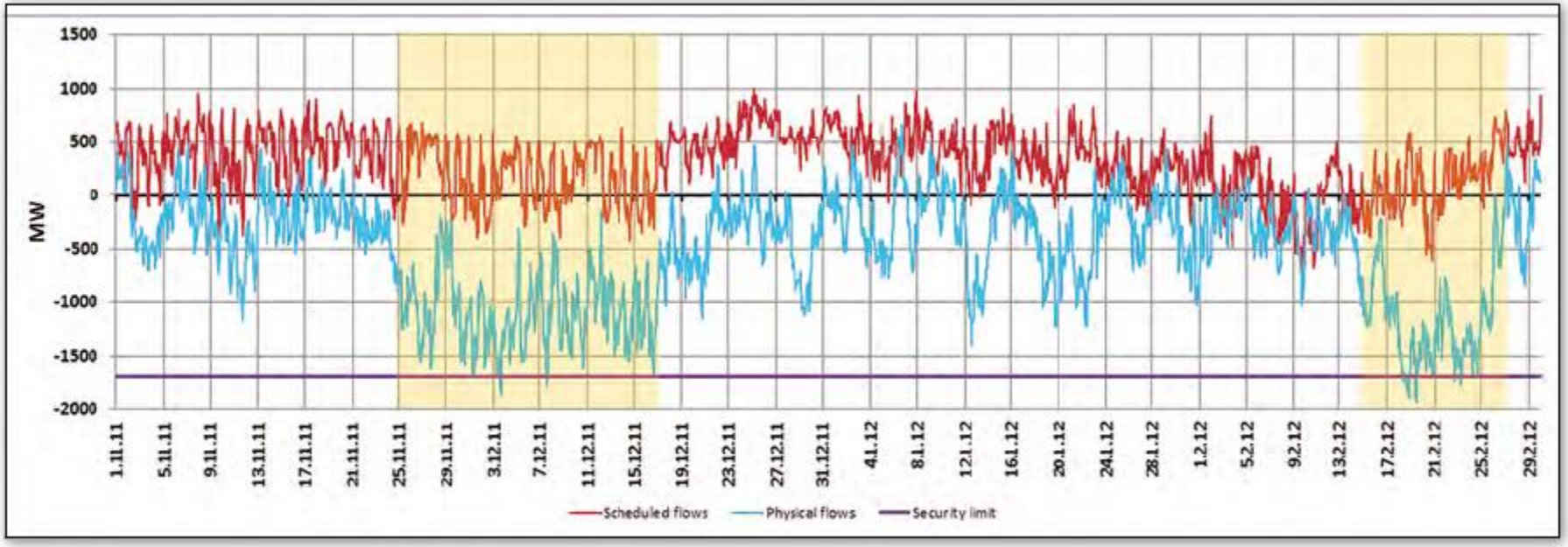
- **Renewable Energy Sources** (PV, wind, concentrated solar) are limited by ill-matched Supply-Demand character
  - Intermittent peak power flow requires over capacity on grid
  - Installed capacity to provide base load is vastly under-employed
- **Storage** capacity to bridge one day EU electrical power requirement ~ 10TWh. EU hydro storage capacity 15TWh.
- EU storage requirements over several days can only be met by **chemical storage**

Which Energy policy for France 2010-2050
Jean Louis Bobin, EuroPhysNews 44/1 2013



Wind power over Western Europe Jan-Feb 2011 by H.Flocard, J.P.Pervès)
Peaks and troughs are correlated due to size of low pressure areas
Installed wind capacity Europe 96 GW (2011)

Zbyněck Boldiš, EurPhysNews 44/4 2013
Chech electricity grid challenged by German Wind



Power (MW) vs. time period Nov 2011 to Feb 2012

- red: ČEPS scheduled flow (~ 500MW generated)
- blue: Physical flow (German RES import)
- violet: Max safe operation limit 1700MW exceeded

Power to Gas & Carbon Capture and Usage

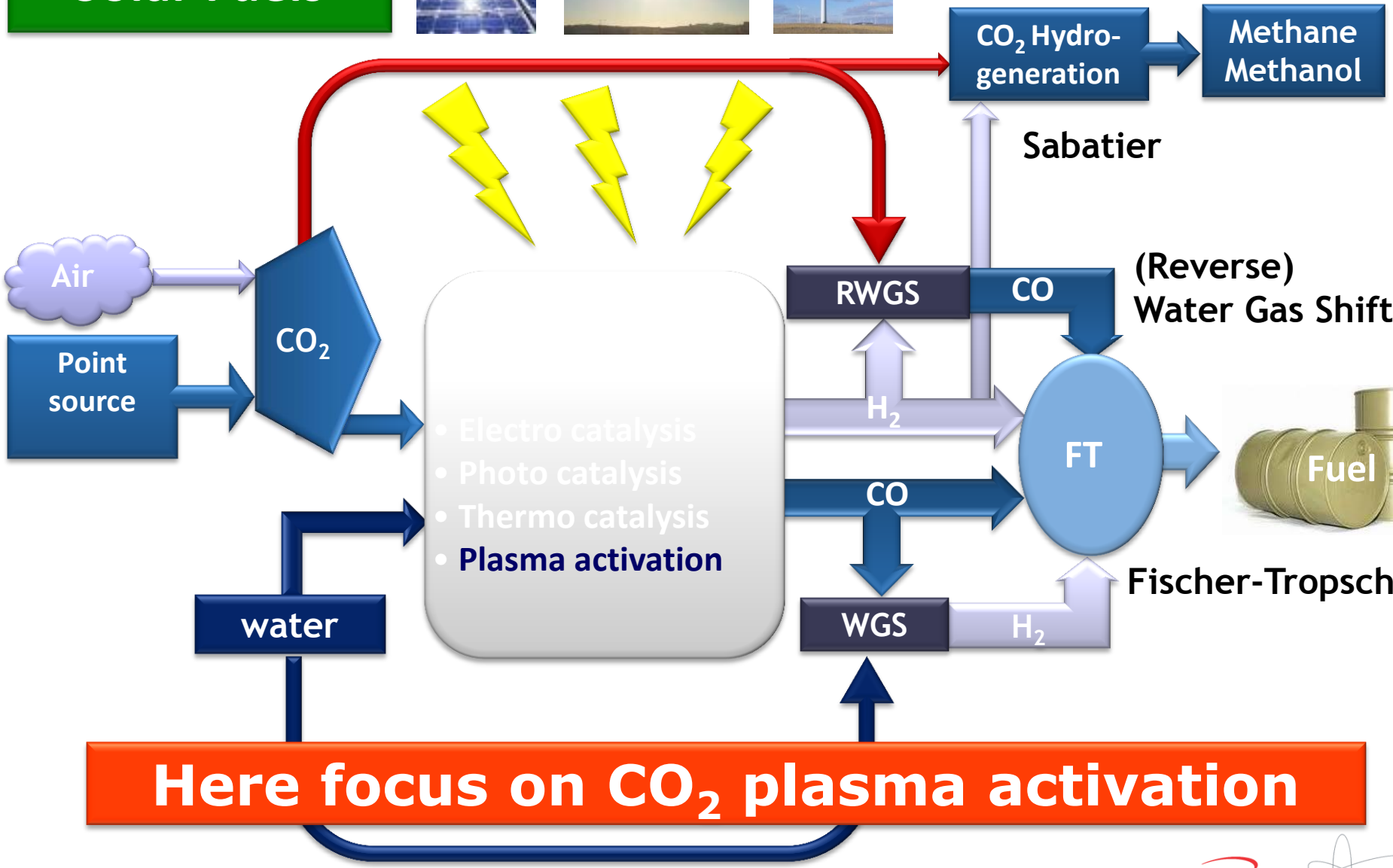
One way to cope with intermittent supply

and to enhance useful capacity

- Power to Gas **(P2G)** to convert excess **electricity** generated by wind/solar power **into hydro-carbon-based (solar) fuels** by splitting CO_2 and or H_2O and forming syngas
- CO_2 neutral power generation possible when **CO_2** emitted by burning these fuels is **recaptured and reused (CCU)**
- Advantage: **Existing infra structure** for gas and oil storage, transport and distribution can be employed and enhanced

Grand Scheme Solar Fuels





Here focus on CO_2 plasma activation

Courtesy Wim Haije (ECN)

Why Plasma?

Low temperature (T_e~1eV, T_i~0.1eV) weakly ionised (10^{-5}-10^{-6}) gas to ease conditions for splitting CO_2 by vibrational excitation of CO_2, which lowers activation energy.

Conditions far from thermo-dynamic equilibrium T_{vib}>>T_{gas}

Compared with electrolysis

- High energy efficiency (~60% demonstrated)
- High power density (45W/cm^3, CO 20A/cm^2 equivalent)
- Rapid ramping up and down (wrt high temperature SOEC)
- No scarce materials employed (Pt catalyst in PEM)

NWO FOM

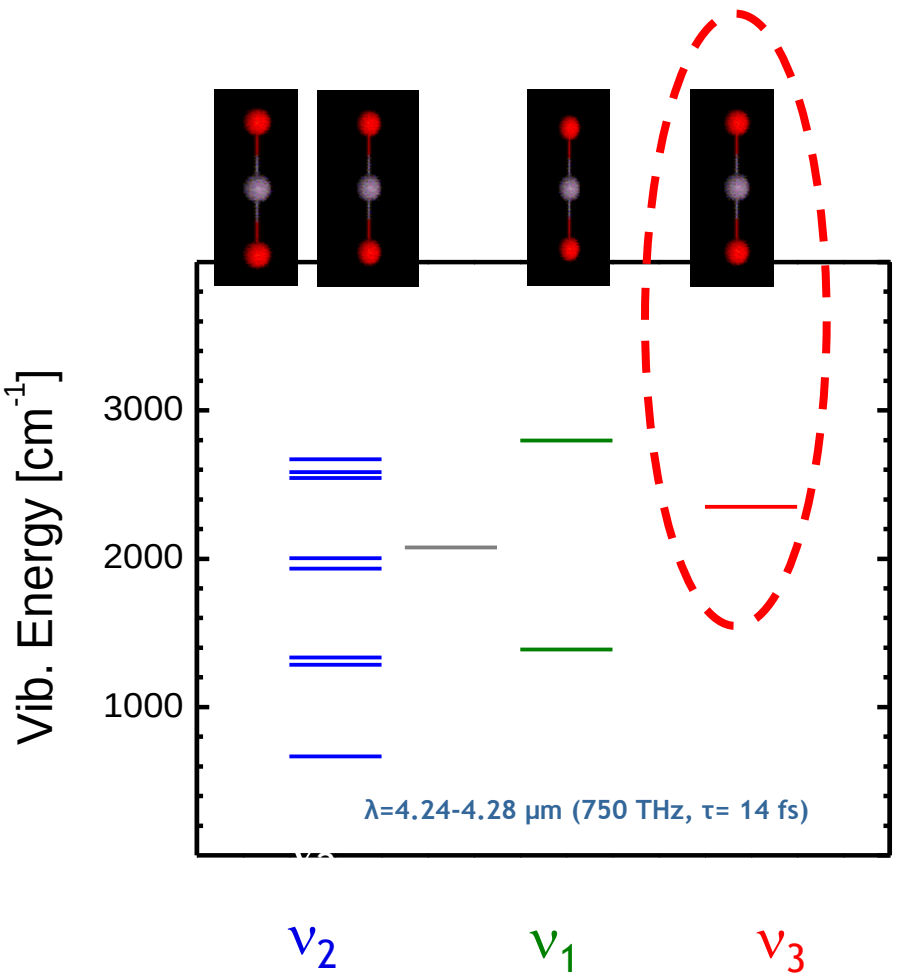
Out of equilibrium $T_{vib} > T_0$ chemistry

Chemical reaction scheme

CO_2 -> CO + O (ΔH=5.5 eV)
followed by reuse energetic **O** radical
CO_2 + O -> CO+ O_2 (ΔH=0.3 eV)
Net
CO_2 -> CO + ½O2 (ΔH=2.9 eV)

Efficiency to be increased by

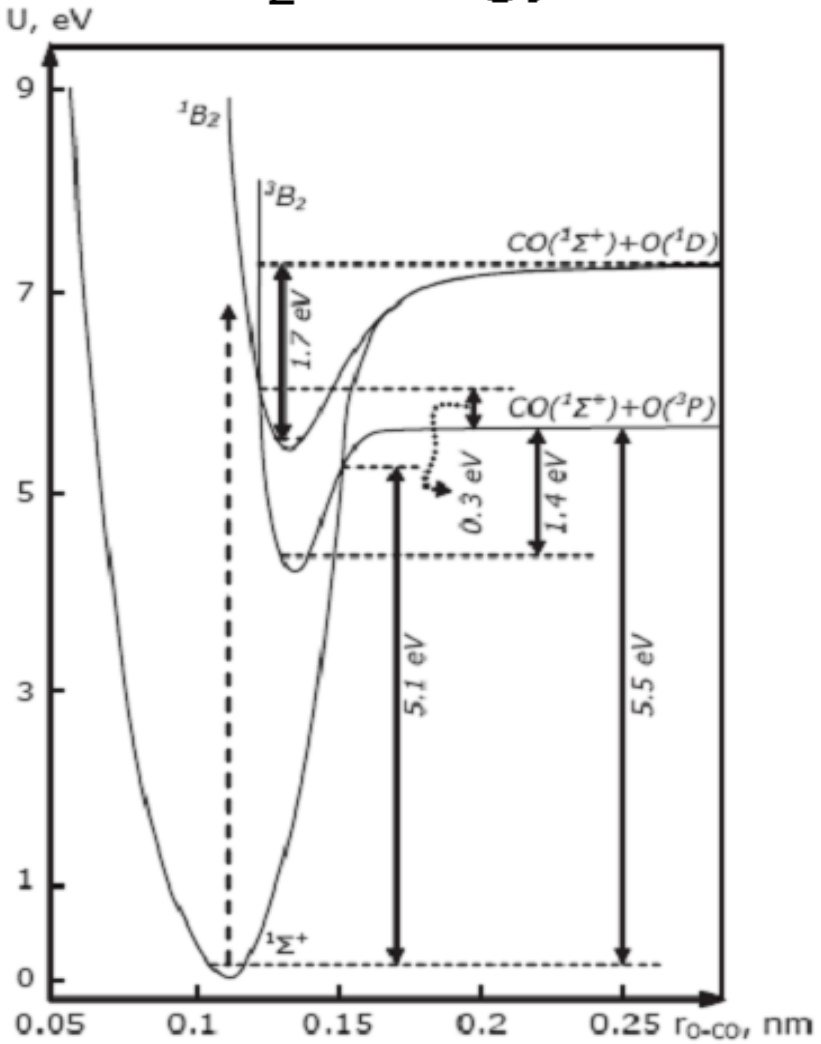
Concentration of electron energy on vibrational excitation of CO_2 in asymmetric stretch mode



Arrhenius/Fridman: Activation energy reduced by vibration energy
k = A exp (αEv-Ea)/kT

CO2 chemistry out of equilibrium Tv > T 0

low CO_2 energy levels



- Direct dissociation via $^1B_2$ vibration mode produces singlet O^1D atomic oxygen requiring ~7.5 eV
- More efficient via $^1B_2$ to $^3B_2$ singlet triplet transition ~5.5 eV producing
- Atomic Oxygen triplet O^3P

cross section CO2 assym vibrational excitation

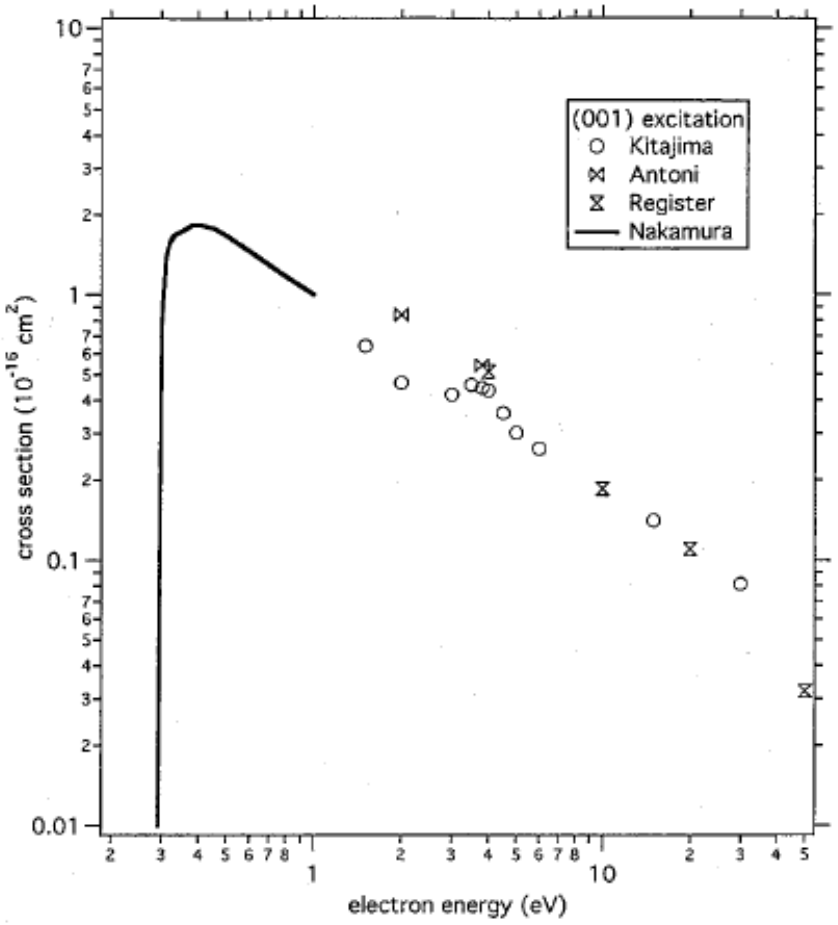
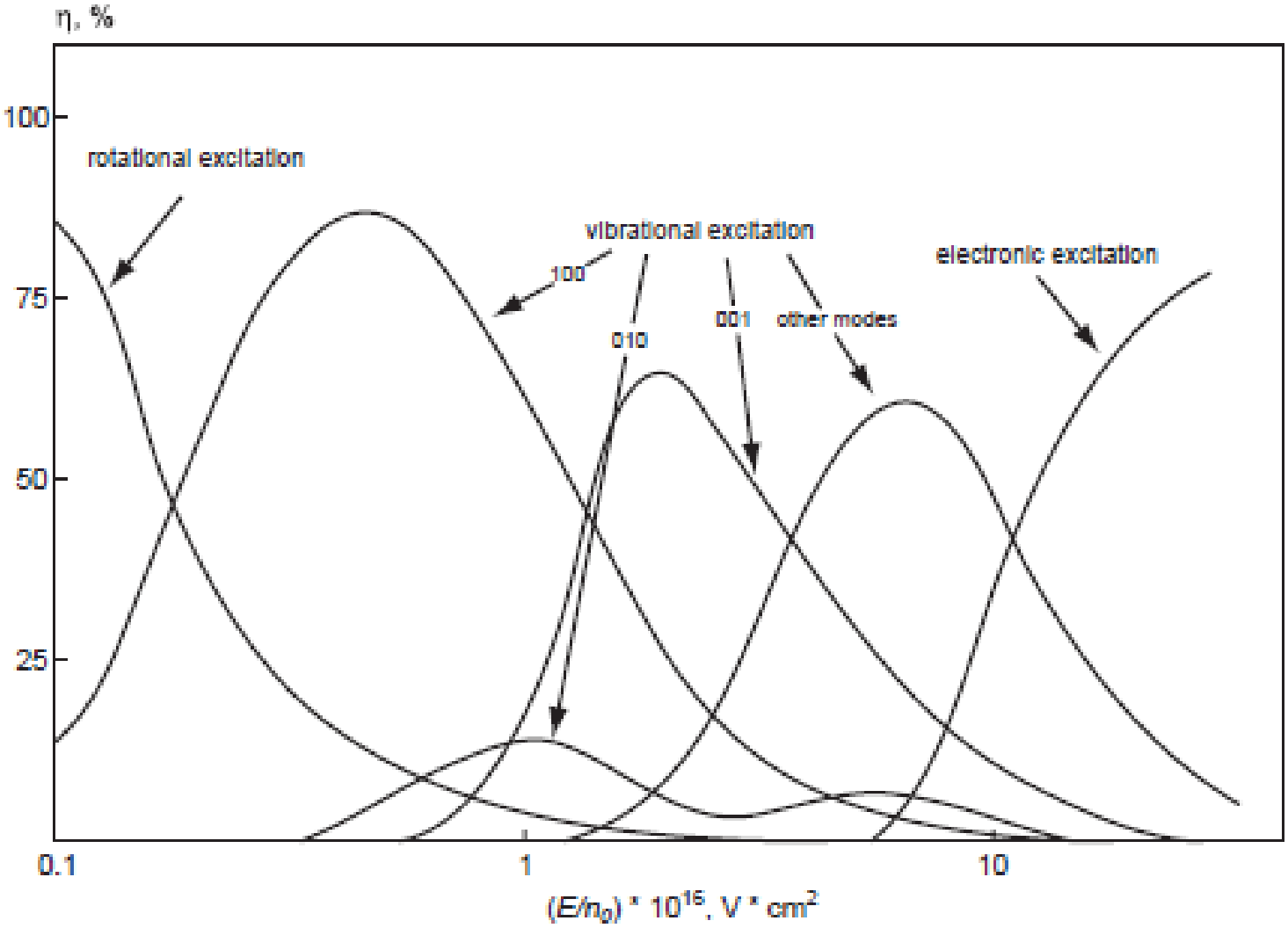


FIG. 7. Cross sections for the electron-impact excitation of the vibrational state (001) of CO_2. Comparison of the beam experiments by Kitajima *et al.*,[32] Antoni *et al.*,[33] and Register *et al.*,[26] and the swarm result of Nakamura[31] is shown.

- Vibration excitation of asymmetric stretch mode reaches maximum at electron energy 0.4 eV
- RF field at 915 MHz is stationary compared with collision processes (<< 1ns)
- Steady electron drift establishes $v_D \sim E/n$
- $E/n\sigma = E\lambda$ equals potential drop an electron experiences in between collisions
- result $E/n = 1.4\ 10^{-16} Vcm^2$

Vibrational excitation as function of reduced electric field E/n



v_3 (001) asymmetric stretch mode @ E/n=2x10^{-16} Vcm^2

Energy Efficiency η against energy per incoming CO_2 molecule E_v

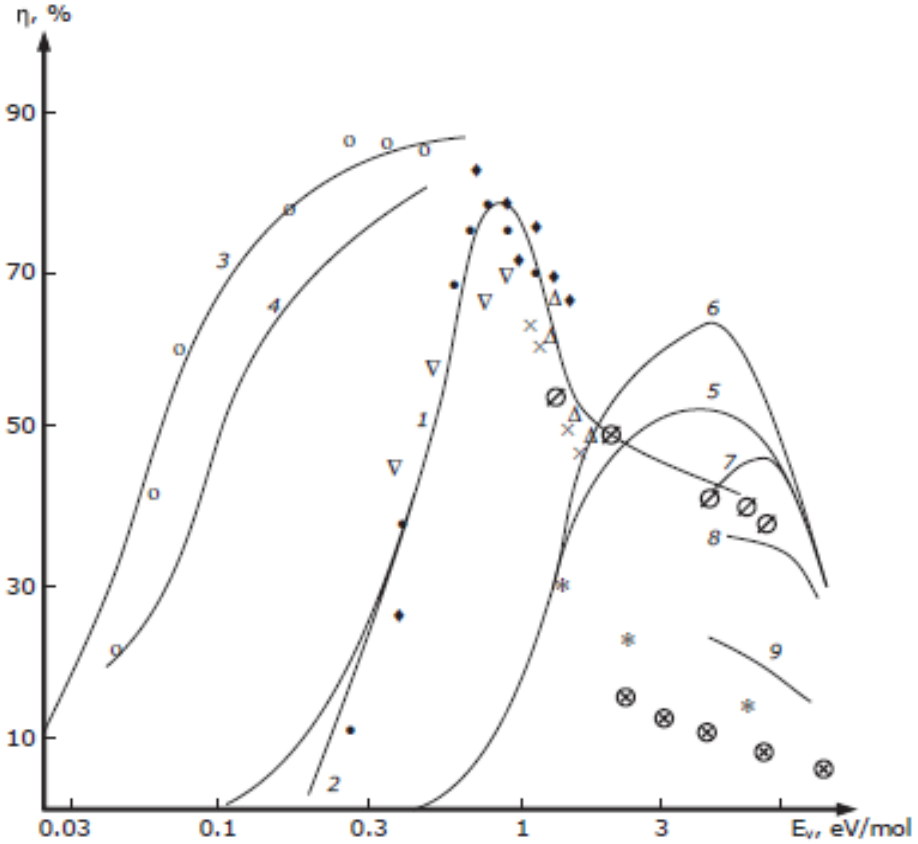


Figure 5–2. Energy efficiency of CO_2 dissociation as a function of specific energy input. (1, 2), non-equilibrium calculations in one- and two-approximations; non-equilibrium calculations for supersonic flows: (3) M = 5; (4) M = 3.5; calculations of thermal dissociation with (5) ideal and (6) super-ideal quenching; (7) thermal dissociation with quenching rates 10^9 K/s, (8) 10^8 K/s, (9) 10^7 K/s. Different experiments in microwave discharges: o, ♦, Δ, ×. Experiments in supersonic microwave discharges: •. Experiments in different RF-CCP discharges: o,∇. Experiments in RF-ICP discharges: ∅. Experiments in different arc discharges: ⊗, *.

- $\eta = H/E_{co}$
- H = 2.9 eV net enthalpy to produce one CO molecule
- E_{co} energy per CO produced
- The fraction α of CO_2 converted into CO yields
- $E_v = \alpha E_{co} = (\alpha/\eta) H$

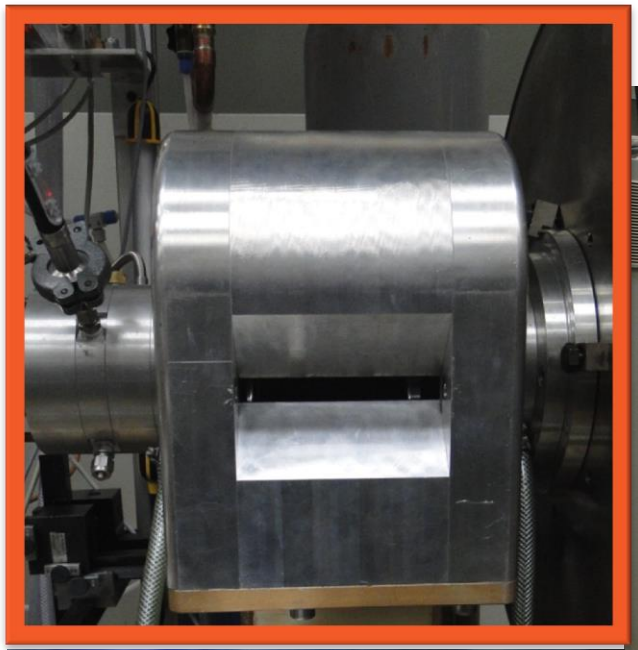
  where E_v = energy per input CO_2 molecule

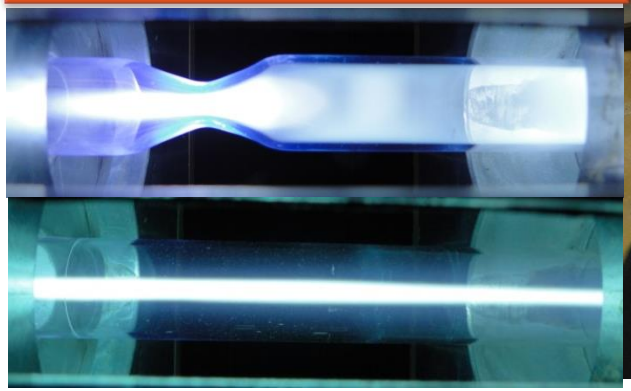
Particle and energy balance

- Particle balance $2v_B=n_0<\sigma v>r$ yields electron temperature through Bohm velocity $v_B=\sqrt{(kT_e/m_i)}$
- Energy balance $P_{RF}=n_e n_0 \Sigma_i <\sigma v> \Delta\varepsilon_i V$ yields electron density and ionisation degree
- Typical ionisation degree $n_e/n_0 \sim 10^{-5}$-10^{-6}
- Typical kT_e~1-3eV,

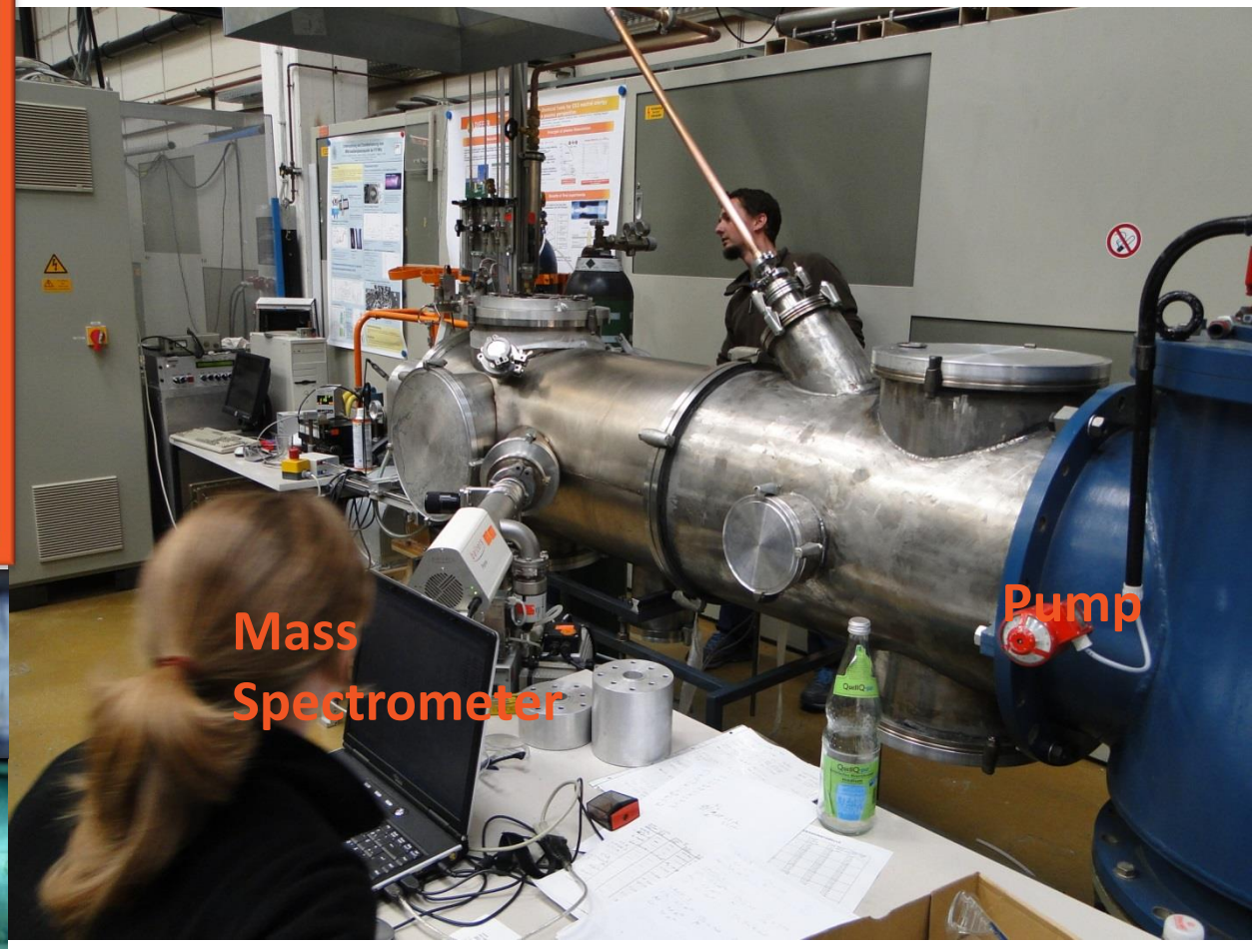
- $T_e \sim E/n$ where $E/n \sim 2\times10^{-16}$ corresponds to $kT_e \sim$ 0.5 eV
- Hence conflicting requirement on ionization ($T_e > 3$eV) vs. vibrational excitation ($T_e < 1$eV)

Experiments at IPF Stuttgart



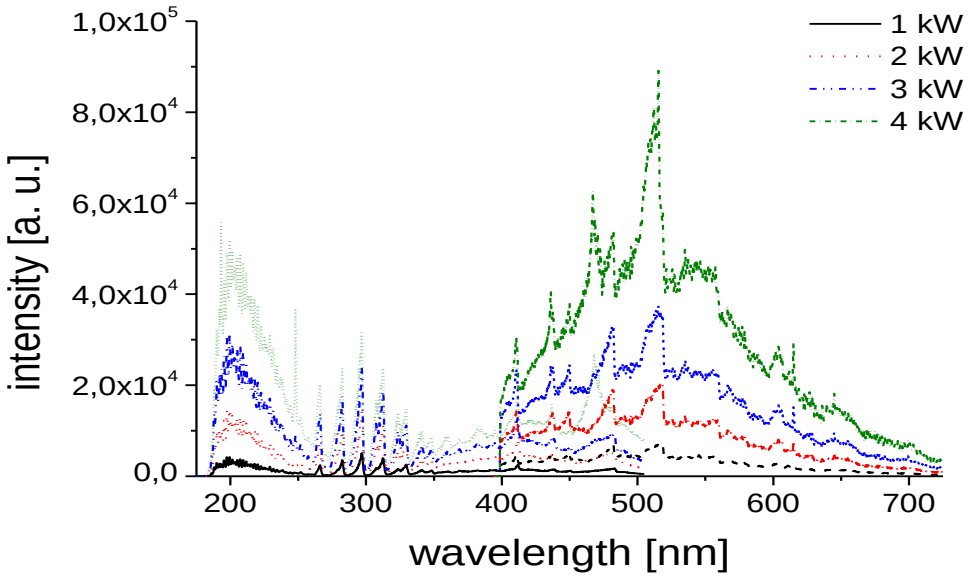


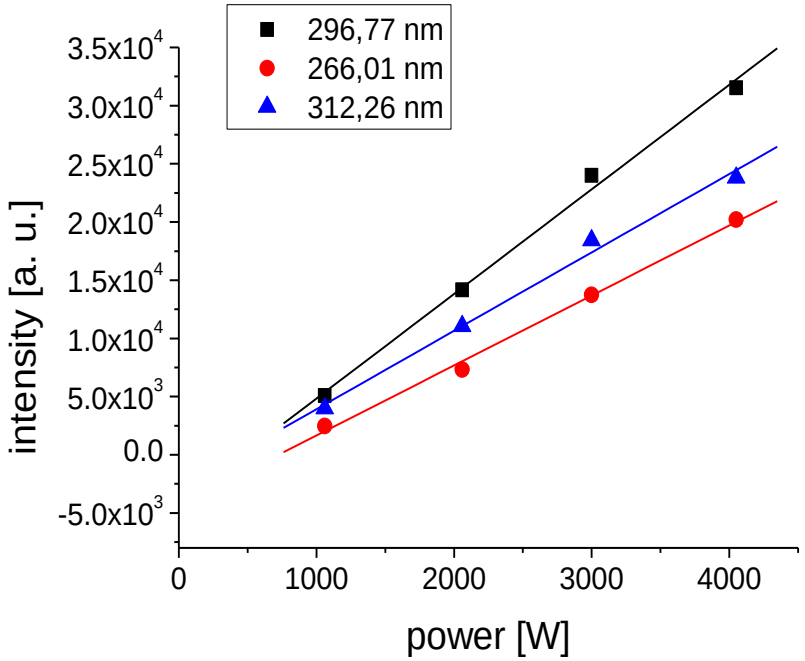
Microwave input 30 kW @ 915 MHz



High and low reduced electric field CO_2 plasma

Type I discharge, Optical emission spectroscopy





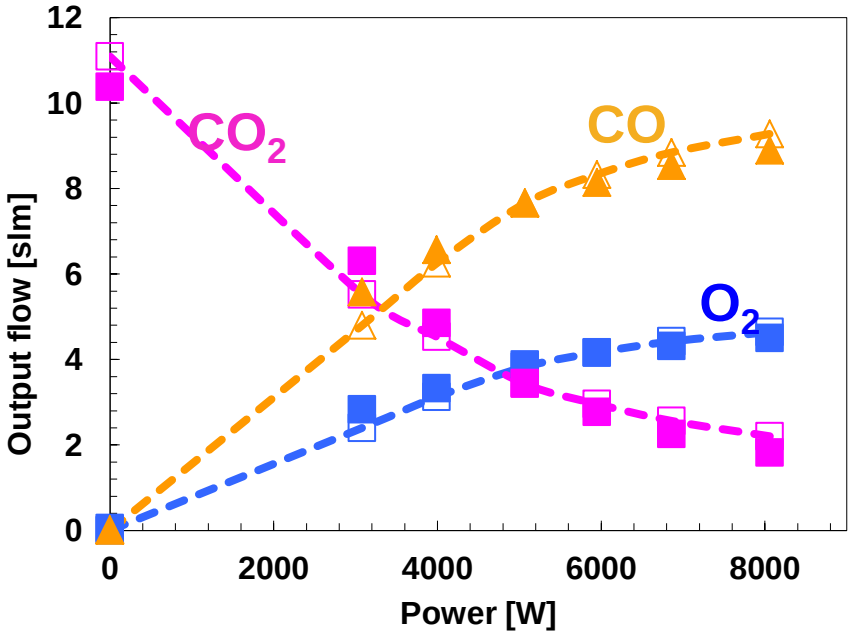
- CO third positives, fourth positives, Angstrom and triplet identified.
- CO line intensity increases linear with power

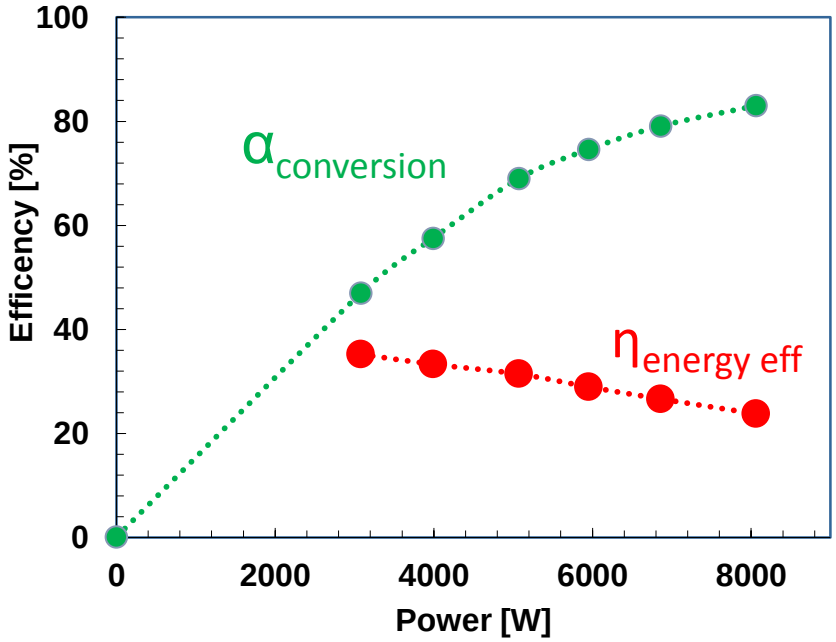
Mass spectrometry

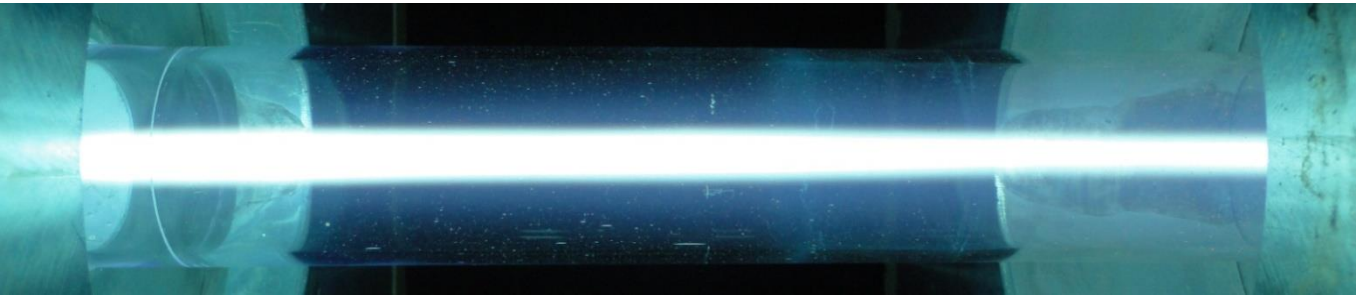
CO produced at expense of CO_2

CO_2 flow 11.1 slm

$CO_2 > CO + ½O_2$

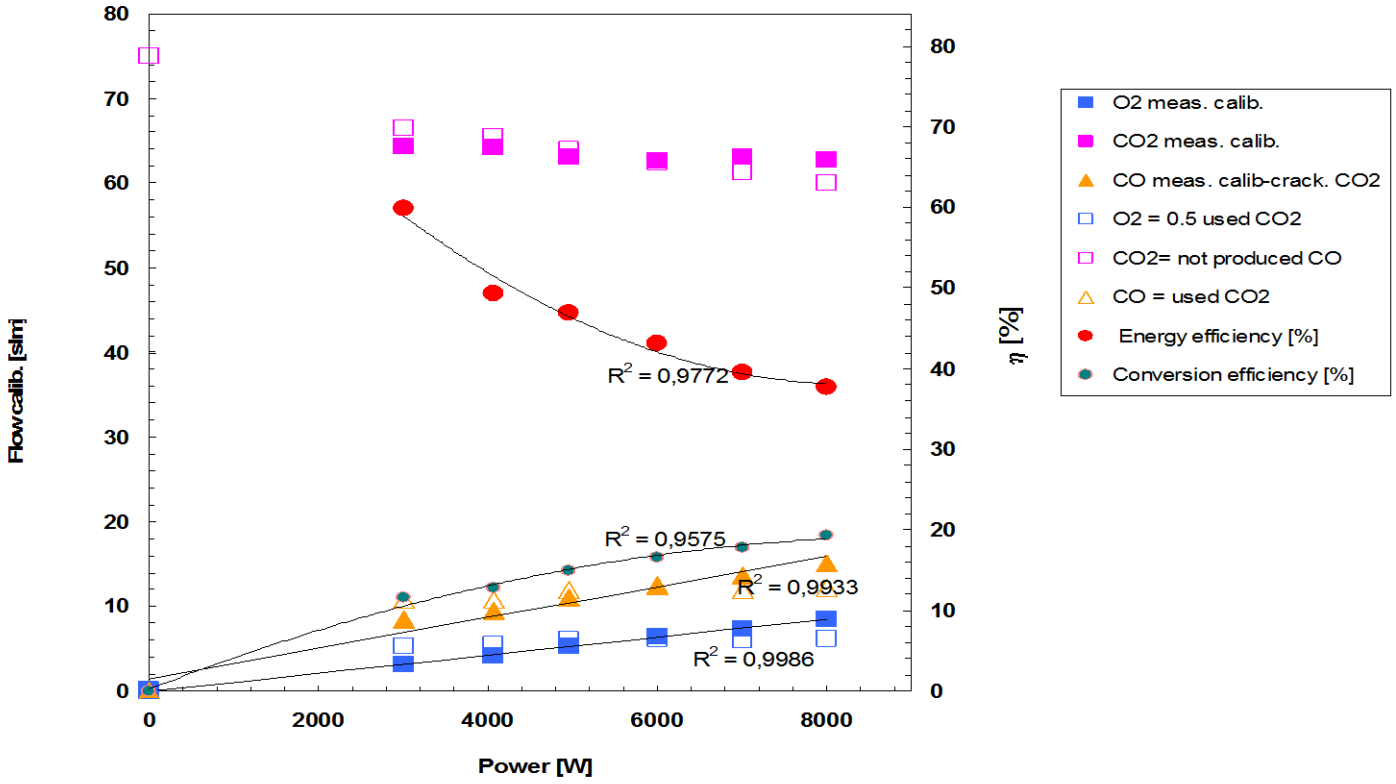




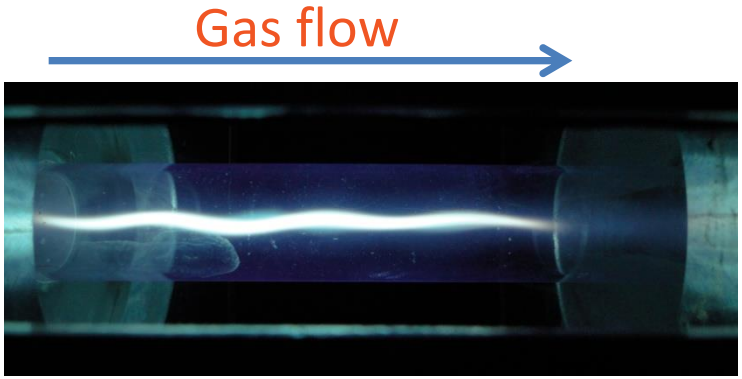


$\eta = \Delta H / E_{CO}$

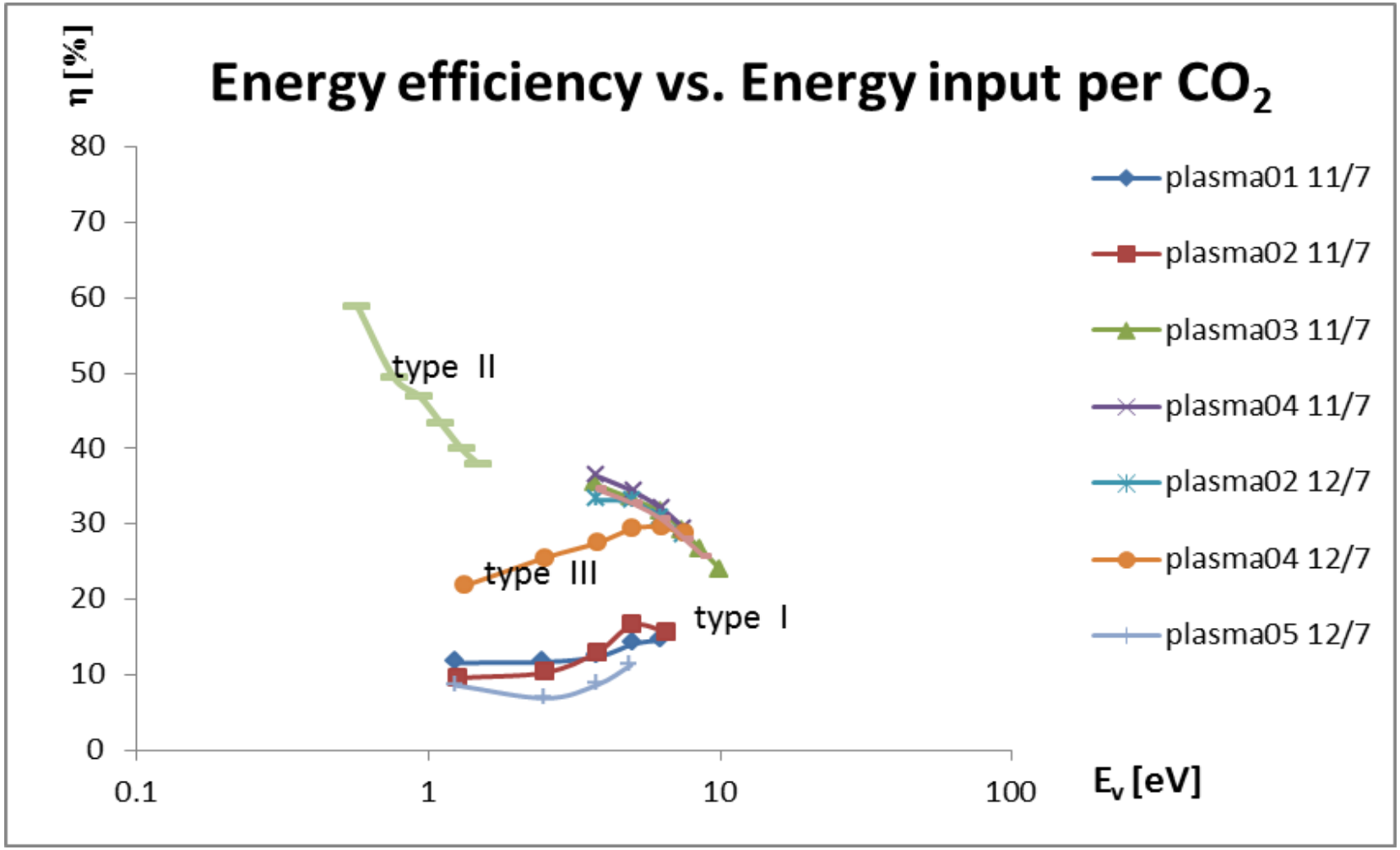
Lower reduced E field to enhance efficiency



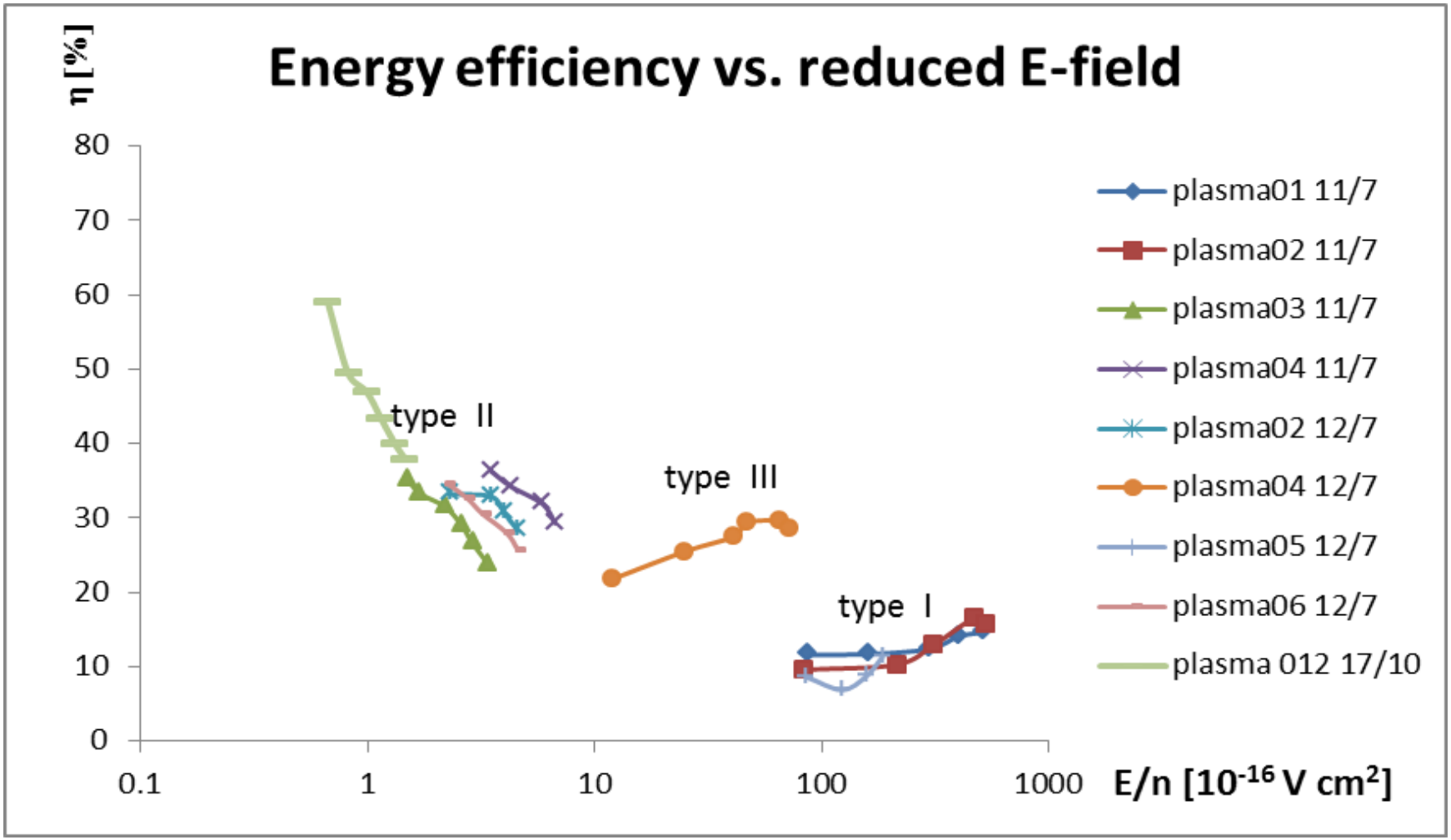
- 10 mm symmetric nozzle at exit of RF cavity
- RF input power 3020-8010 W
- Gas pressure reaction chamber 190-250 mbar
- Expansion chamber 0.3..0.4 mbar
- Gas flow 75 slm CO_2
- **Energy spent per CO_2 molecule 0.56..1.49 eV**



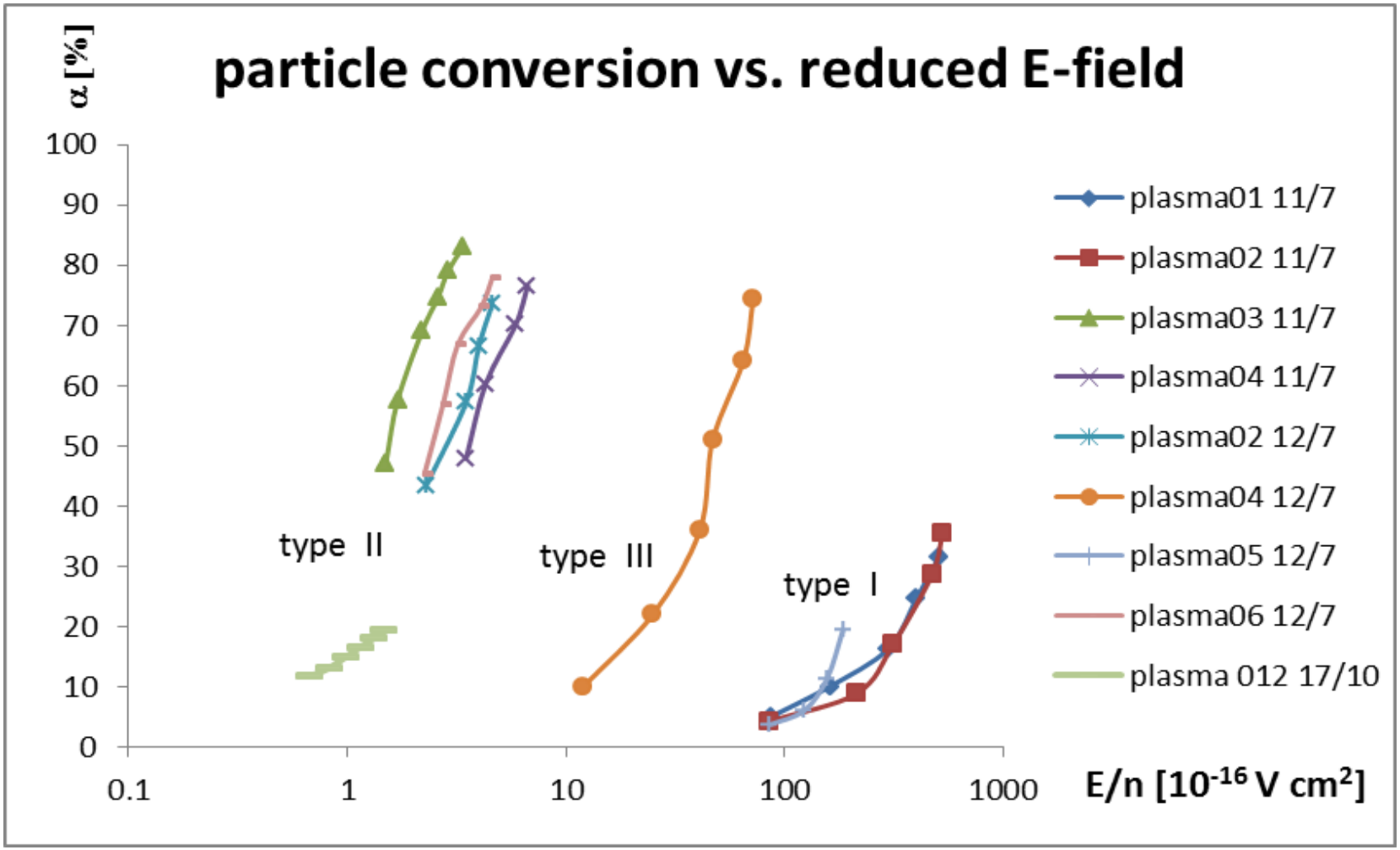
Overview of experimental results



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 de-excitation**
- **Separate out flow CO from CO_2 (low conversion factor)**

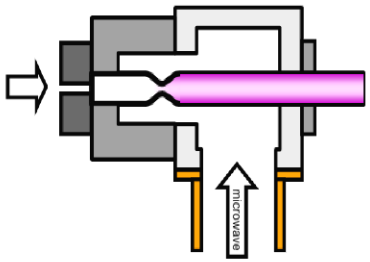
Next System steps:

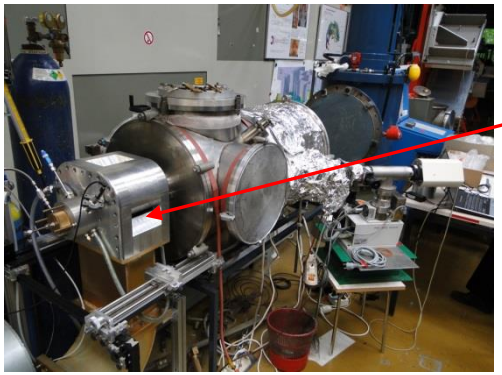
- **DIFFER experimental facility (1.3 kW 2.45 GHz) built**
- **100 kW 915 MHz DIFFER facility planned**
- **Design and development of output gas separation system**

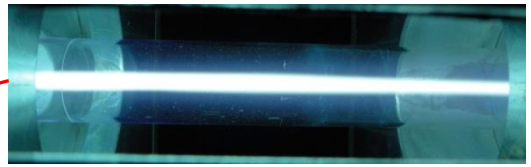
Outlook

- **System approach, including**
  - carbon capture serving as input
  - Separation of CO and H_2 at output
  - processing to gaseous (S) or liquid fuel (F-T)
  - System engineering
  - Economic and social assessment

Flying start by DIFFER & IPF Cooperation

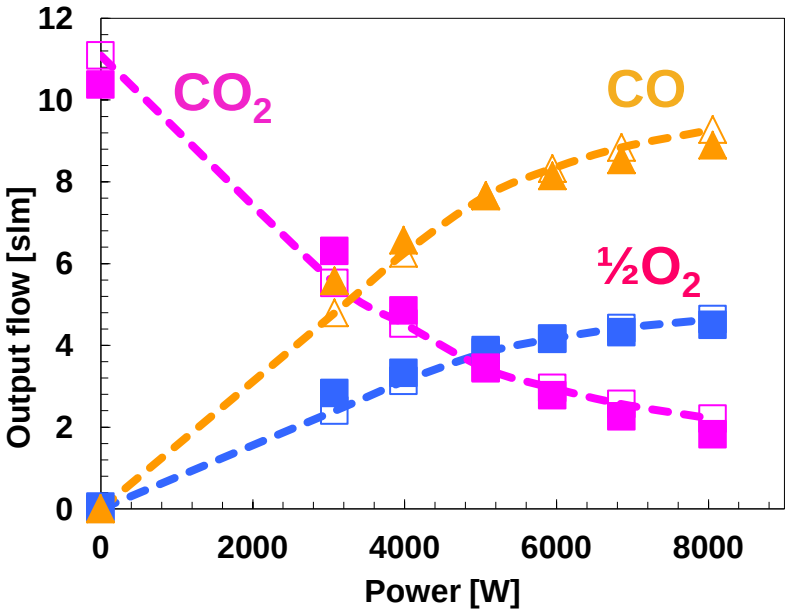


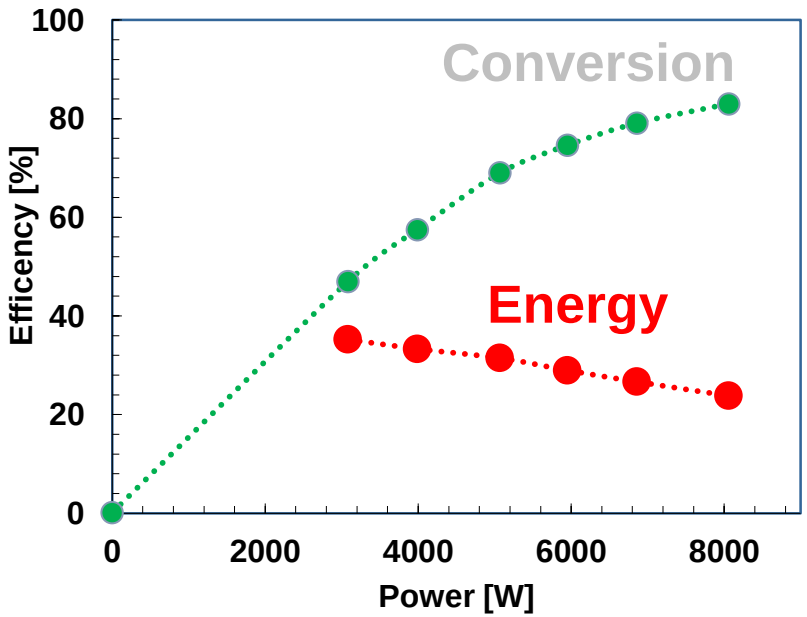




Plasma by
915 MHz microwaves
max 30 kW

✓CO produced at expense of CO_2

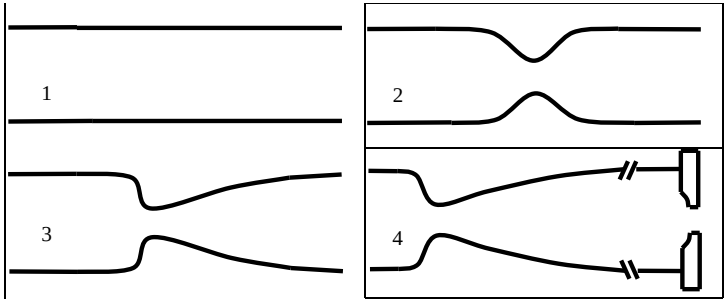




✓Measurements (solid) by mass spectrometry

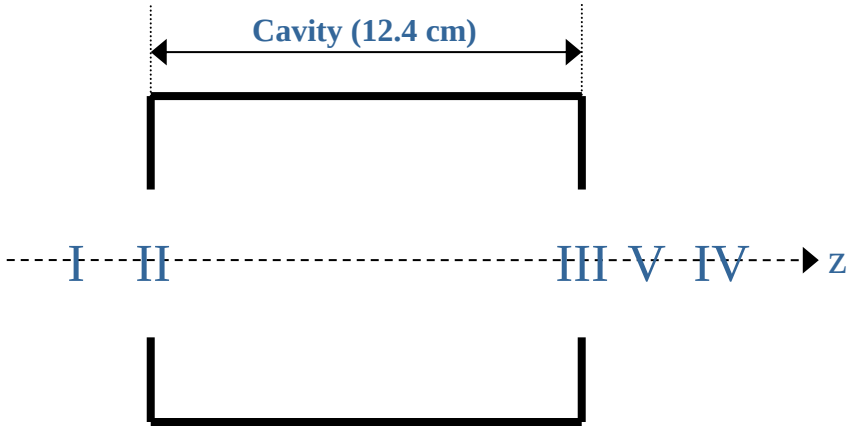
Constant CO_2 flow of 11.1 SLM(2.3 kW@100% Energy efficiency)

Various nozzle positions/types explored



Nozzle configurations/types:

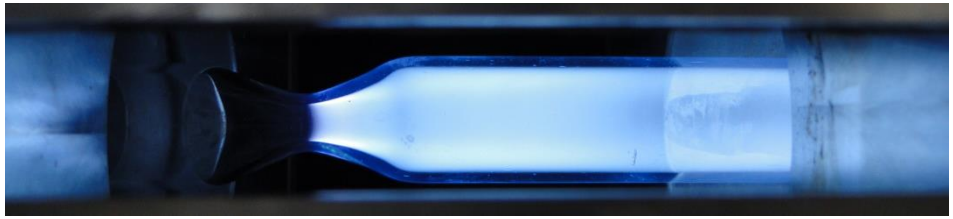
1. Straight (∅ 26 mm)
2. Symmetric (∅ 26 mm with ∅5 mm and ∅10 mm throat)
3. Laval (∅ 26 mm with ∅5 mm throat)
4. Double nozzle (Laval combined with copper exit nozzle of ∅5 mm)

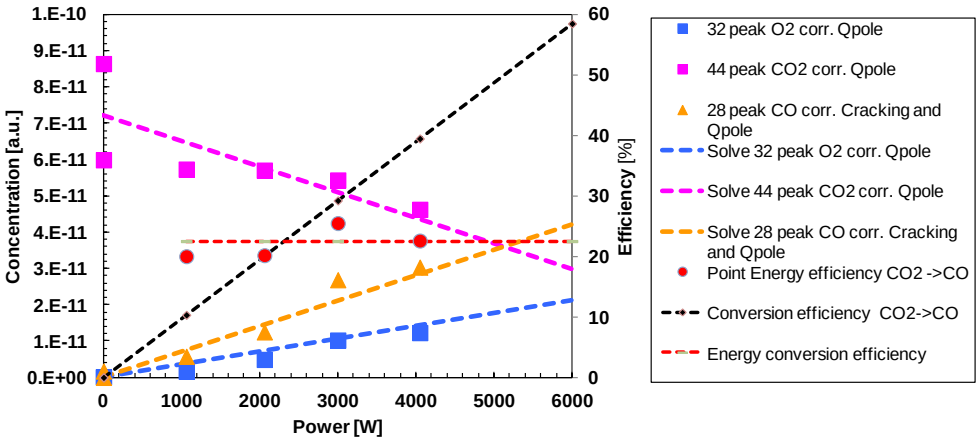


Nozzle Positions

- I z = -3 cm
- II z = 0 cm
- III z = 12.4 + 0 cm
- IV z = 12.4 + 5 cm
- V z = 12.4 + 3 cm

Particle conversion α and energy efficiency η





- α = COout/CO2in = CO/(CO+CO2)
- W= NF/60x22.4 (eEv) [eV/s] = C (Ev/H) F [W] [1]
- Ico = aW; Ico2 = -aW + b and Io2 = ½ aW, yielding: [2]
- α = a/b W at fixed F [3]

$$n_E = H/Eco = H/(E_v/a) = a\, H/E_v = [Eq.3] = a/b\ W\ H/E_v = [Eq.1] = a/b\ CF$$

$$E_v = (a/n_E)\ H = 2.9\ (a\ /n_E)\ [eV]$$

Electron energy loss in CO_2 plasma

electrons

⇩

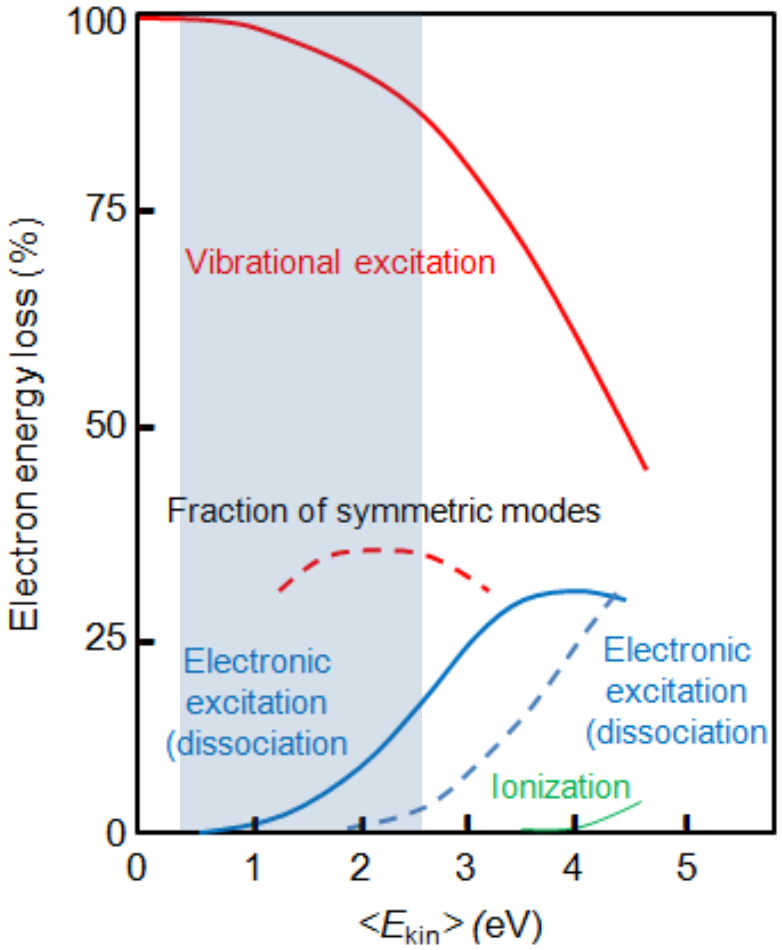
electric field

⇩

collisions

⇩

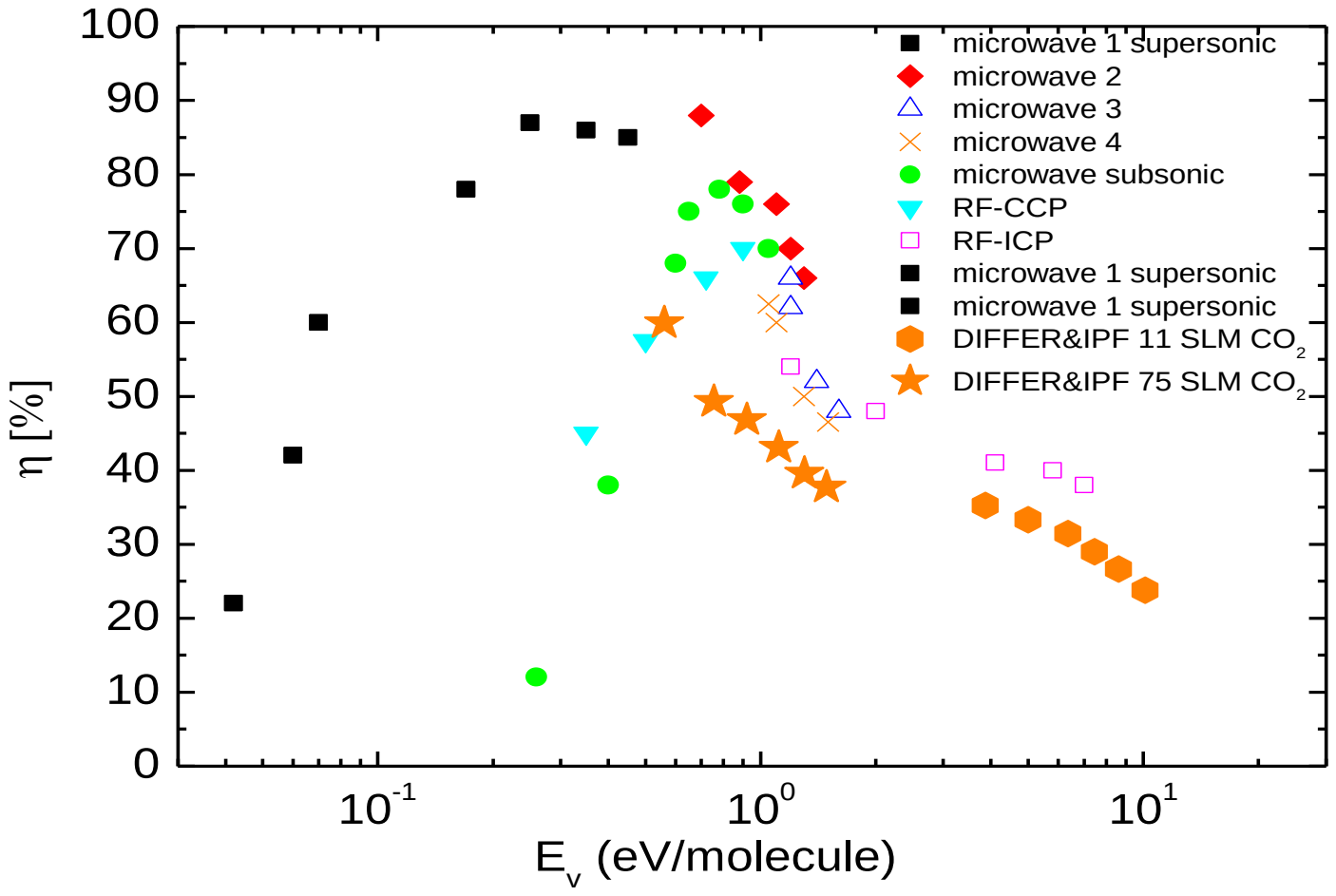
vibrational excitation



Electron energy loss depends on reduced electric field → depends on average electron energy

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

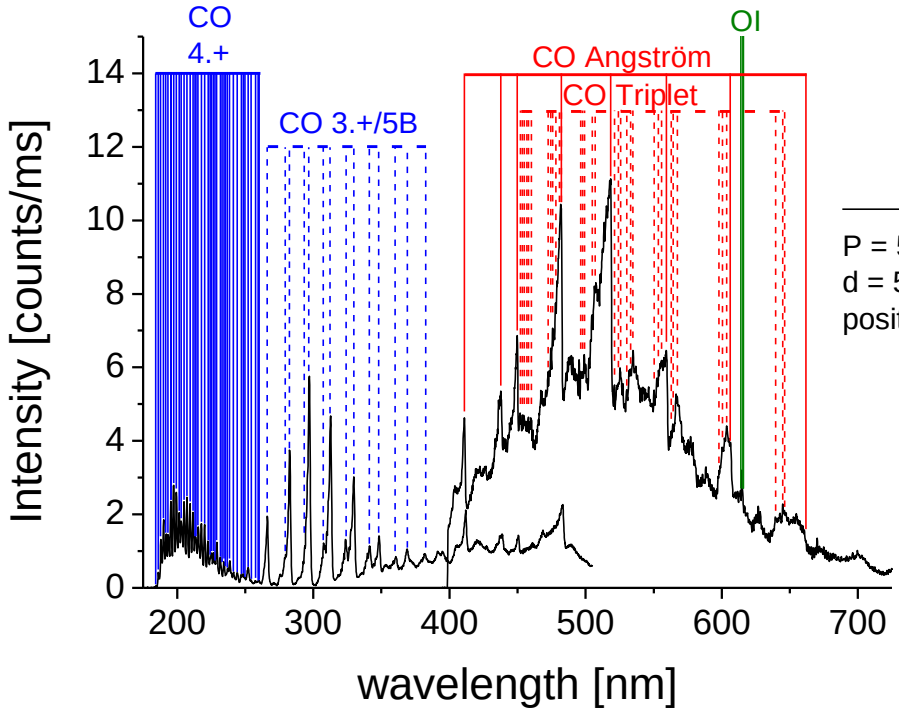
Energy per incoming CO_2 molecule to be around 0.4 eV



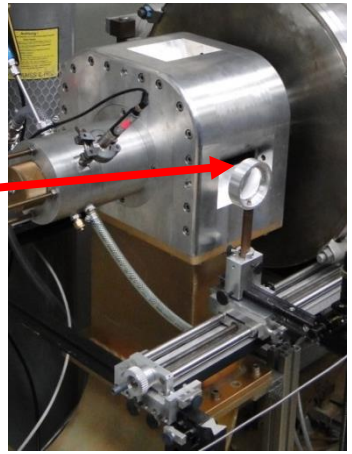
Russian Experimental Results and recent DIFFER results

Optical Emission Spectroscopy

- electronic transitions CO and C2 observed
- Insight in vibrational excitation CO (and CO_2)



—— spectrum
P = 5 kW,
d = 5 mm asymm,
position I

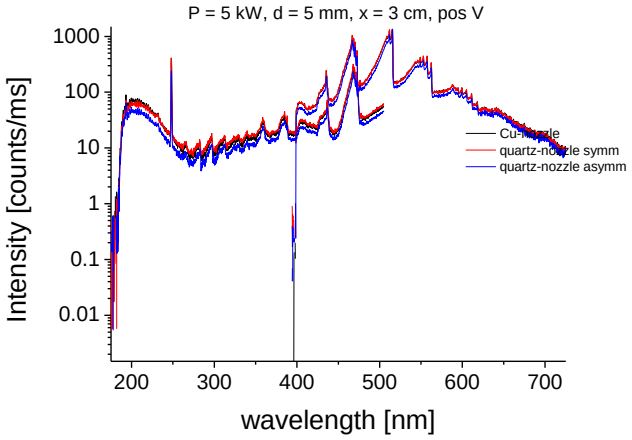


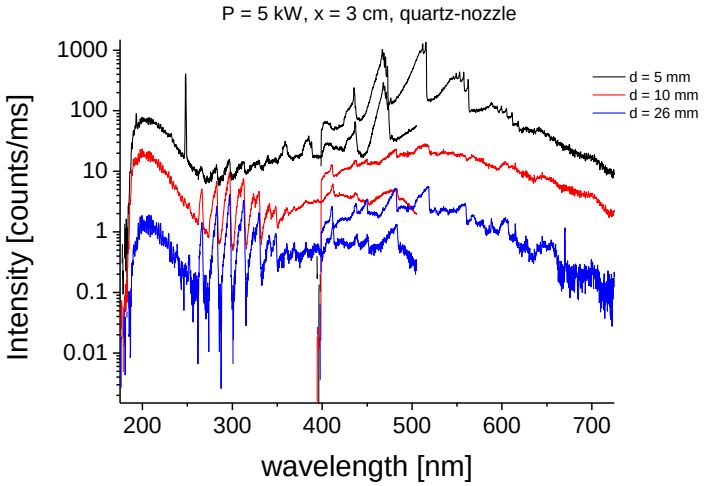
Expanding plasma at 0.8 mbar plasma pressure, high reduced E field

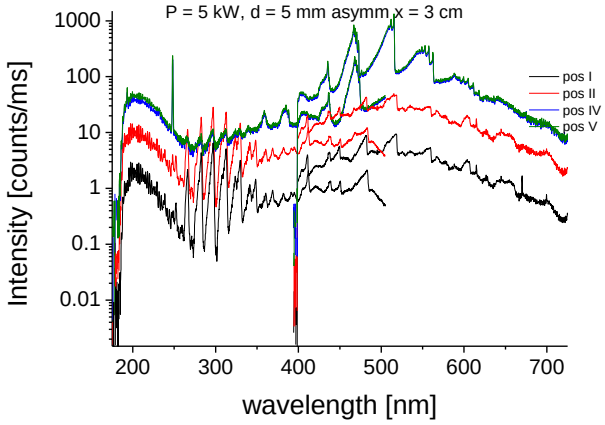
CO **4th positive** system, singlet transition $A^1\Pi > X^1\Sigma$
CO **3th positive** system, triplet transition $b^3\Sigma+ \rightarrow a^3\Pi$
CO **Ångström** $B^1S^+ \rightarrow A^1P$
C2 Swan band of C2 $A^3\Pi_g > X^3\Pi_u$
CO **Triplet** System $d^3\Delta > a^3\Pi$
CO2-, CO2+-, and CO+-bands as well as atomic carbon lines are not observed

[Pearse and Gaydon]

Overview CO Spectra in UV and visible

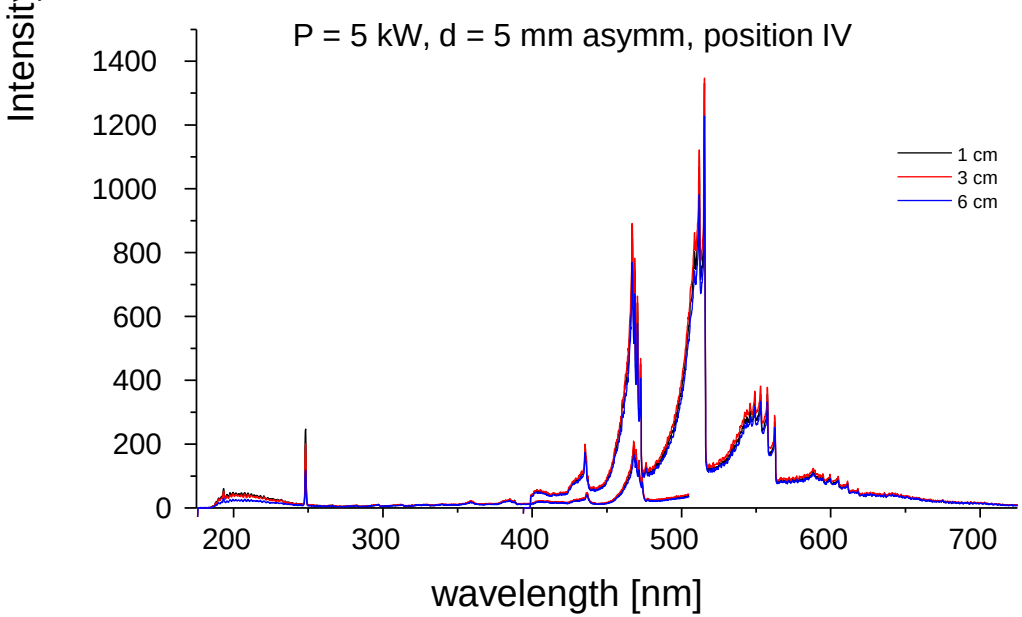






- Nozzle shape: hardly any difference observed
- Nozzle dia. change: transition from type I to type II discharge, intensity x 100
- Nozzle position at entrance or exit, dramatic change in efficiency observed

Spectra type II discharge



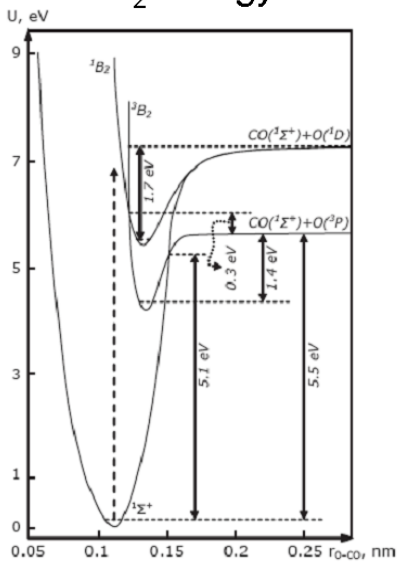
- Spectra dominated by Swan C2 band
- Some atomic Oxygen and atomic carbon
- Intensity factor 100 increase

C2 Swan band $A^3\Pi_g > X^3\Pi_u$

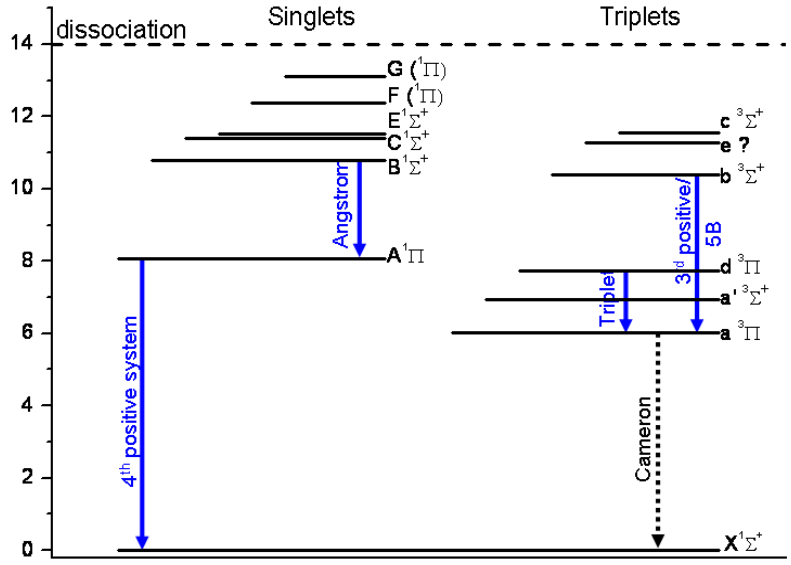
λ [nm]	438.3 (2.0)	473.7 (1.0)	516.5 (0,0)	563.6 (0.1)	619.1 (0.2).
I [au]	2	9	10	8	3
λ measured	436	468/469	516	567/568	614/617

Energy diagram of CO2 and term levels CO and O

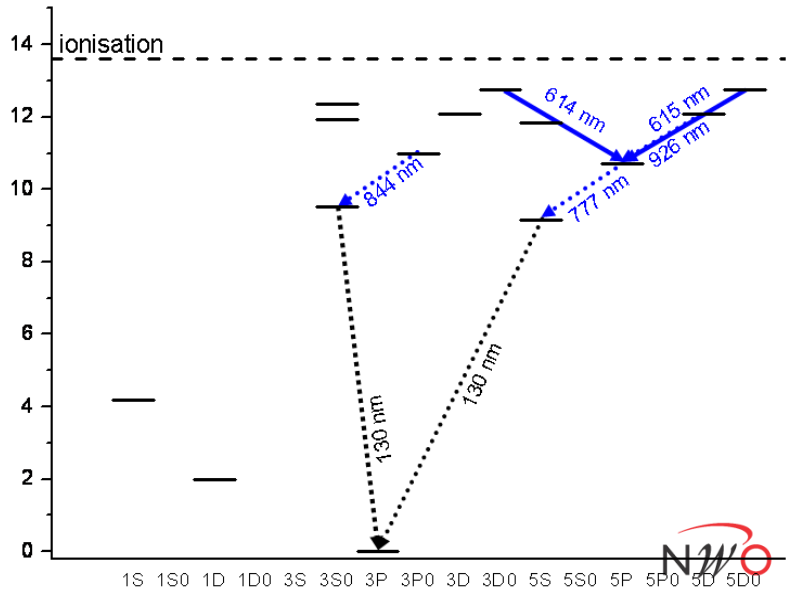
low CO_2 energy levels



CO energy levels



some important O energy levels



Identification CO spectral lines in UV-visible

λ[nm] 3rd pos P&G pg110	283.31	297.7	313.4	330.5	349.3	369.9
λ[nm ±2 nm] measured	281	295	311	329	347	367
I [au]	10	9	8	7	6	2

5B band CO P&G λ[nm]	I [au]	spectrum measured [nm ±2 nm]	E [eV] calculated	ΔE [eV]
266.5 (1.0)	8	264	4.69	0.236
279.3	2	278	4.453	0.214
293	1	292	4.24	0.194
307.9	5	307	4.046	0.177
324.2	6	320	3.869	0.195
341.9	5	337	3.674	
361.27	5	367		
382.51	2	381		

λ [nm]	412.36	439.31	451.09	483.53	519.82	561.02	607.99	662.03
λ measured	411	437	450	482	518	560		
I [au]	7	8	10	10	10	10	9	7

λ [nm]	480.67	497.9	505.27	523.84	601.05	643.31
λ measured			506	525	603	645
I [au]	8	6	8	5	8	10

Cross sections Itikawa

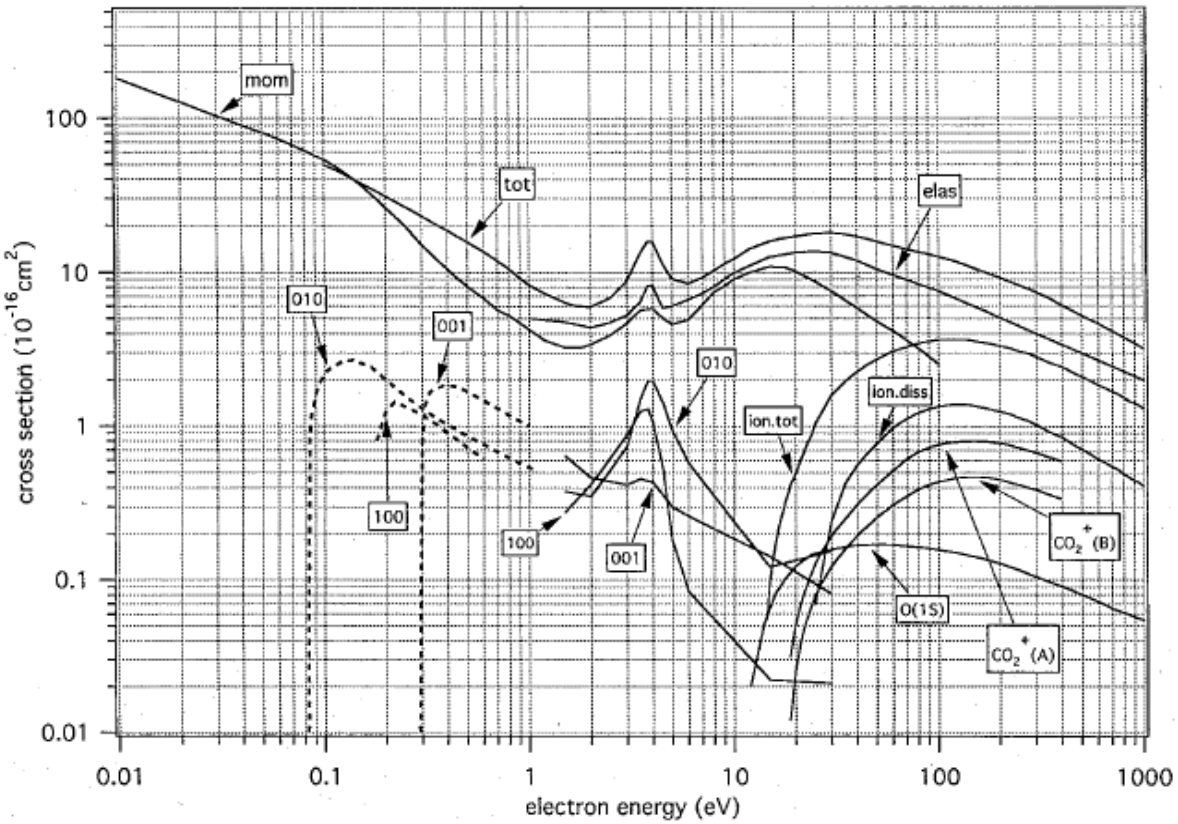


FIG. 20. Summary of the recommended electron collision cross sections for CO_2.

Sub-sonic and supersonic flow

- Theoretically, V-T relaxation decreases exponentially with gas temperature.
- Gas expansion by nozzle to lower gas temperature.
- Choked flow (M=1) obtained in discharge region
- Transition sub-sonic to super-sonic obtained by increase power at constant flow (gas temperature)
- For choked flow $v_F = c_s$, the relation between temperature and pressure becomes: $kT = \gamma/m_i \{pO/F\}^2$

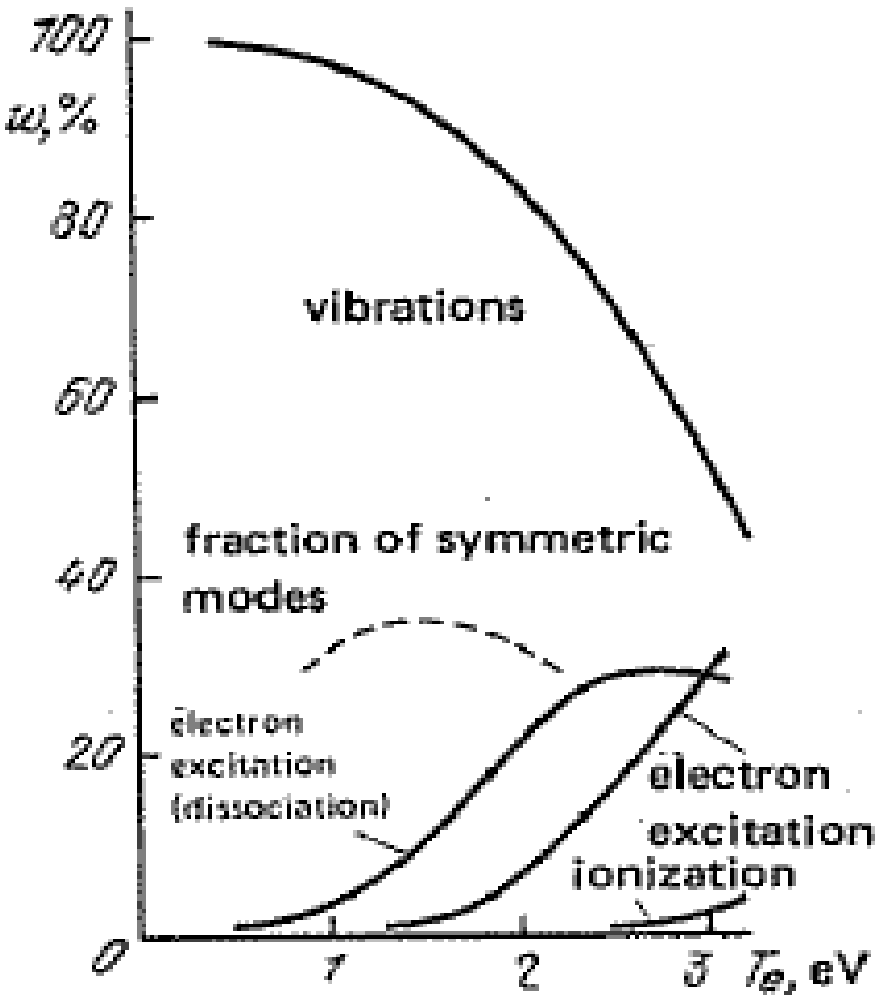
Understanding CO2 dissociation by plasma activation

- How to make sense out of these experiments?

Answer:

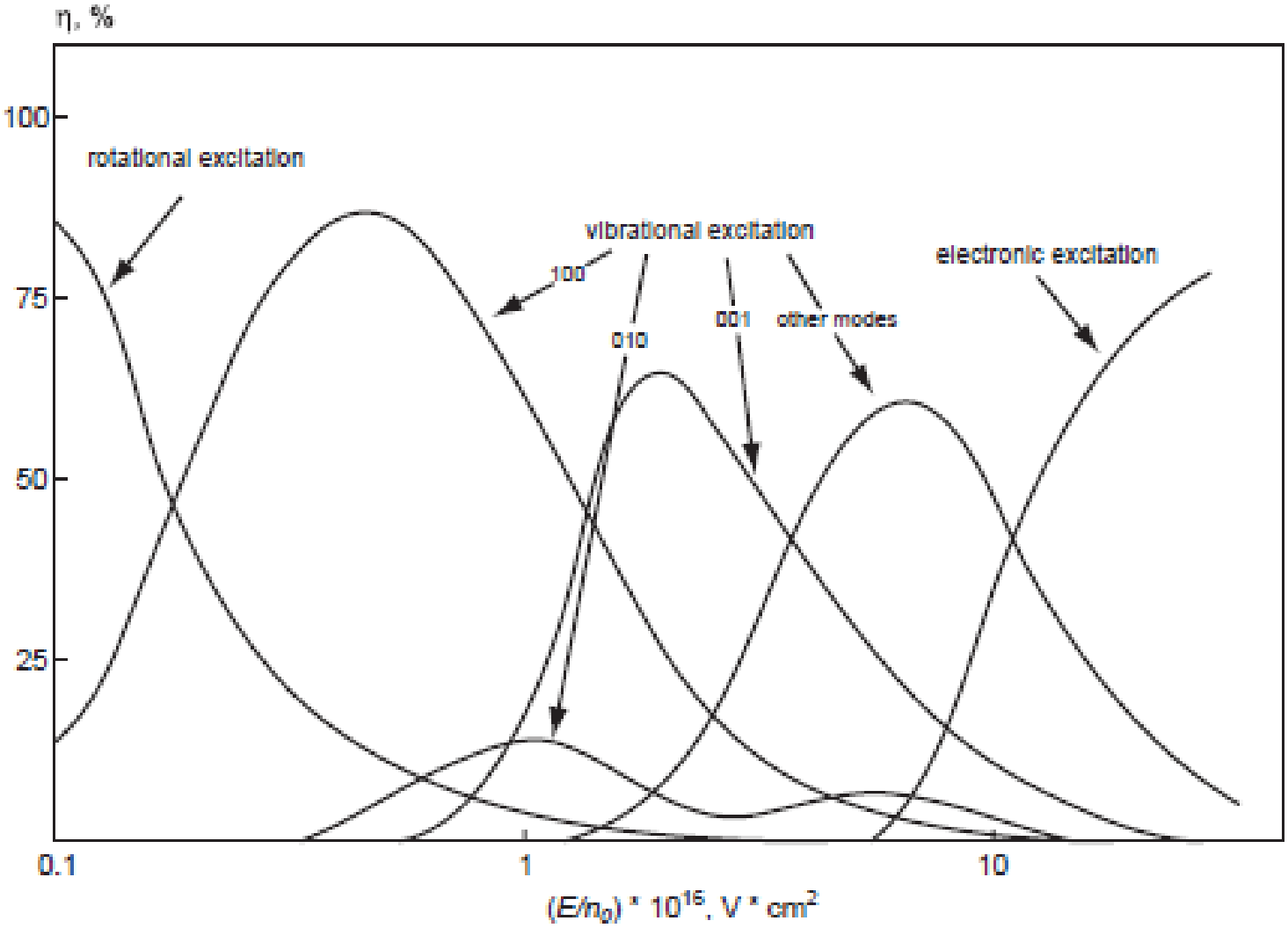
- Reduced electric field E_r=E/n turns out to be key
- One century old concept, yet not appreciated

Electron excitation CO2 vs electron energy



- vibrations excitation requires electron energy T_e< 1eV
- Ionisation starts at T_e> 2 eV
- These two requirements cannot be optimally fulfilled simultaneously

Electron excitation CO2 vs reduced E field



v_3 (001) asymmetric stretch mode @ $E/n=2\times10^{-16}$ Vcm^2

50% mixture CO2-CO

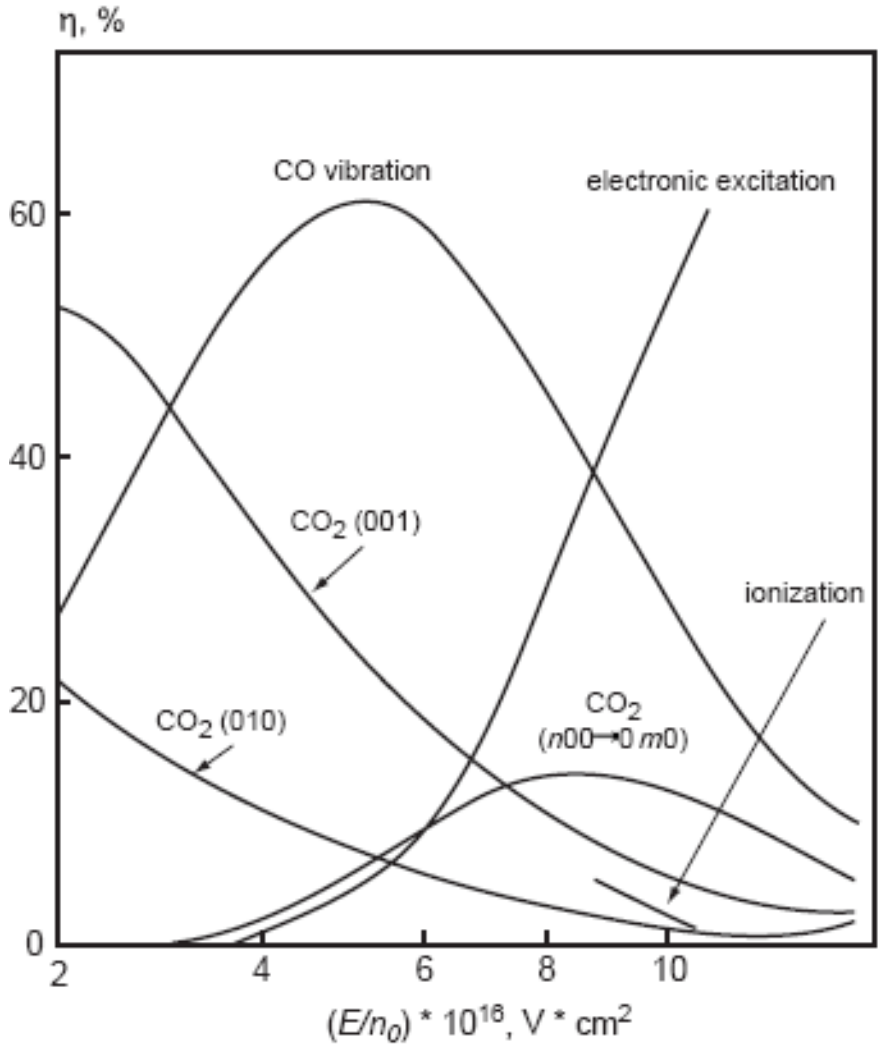


Figure 2–33. Electron energy distribution between different excitation and ionization channels in CO_2(50%)–CO(50%) mixture.

Characteristic time scales and lengths

- typical electric field strength on axis RF cavity E=27kV/m @ 915MHz (P_{RF}=3kW) Half cycle time τ=0.546 ns
- distance travelled by an electron in vacuum accelerated in this E-field during a half cycle $s=½(eE/m)t^2$ ~ 720 μm
- In contrast, CO2 ions move only 9 nm, remaining essentially stationary
- The speed acquired by electrons in this half cycle v=at becomes v= 2.6 10^6 m/s, i.e. an energy of ~20eV
- At this energy De Broglie wavelength λ=h/p is 0.28 nm, hence of the size of the CO2 diameter, i.e. ineffective in vibrational excitation
- The electron neutral collision times follow from the cross section data Itikawa
- At low pressure (1 mbar) λ_{tot} ~ 370 μm, i.e. λ_{tot}~s and electron gains energy
- At high pressure (100 mbar) λ_{tot} ~ 4μm, i.e at 1/100 of RF cycle electron is knocked off-course, not able to gain speed
- interaction time electron - CO2 molecule $\tau_{exc} = 2a_0/v_e$ = 0.39 fs for a 1eV electron, much faster than vibration time τ_{vib} = 14 fs, ie CO2 frozen during interaction
- CO2 - CO2 collision time $\tau_{int} = 4a_0/v_{th}$ = 1.2 ps ie molecules locked during 100 oscillations

Electron - CO2 interaction times

Table II Characteristic time scales and dimensions of the CO_2 plasma

p mbar	τ_{exc} fs	τ_{vib} fs	τ_{etot} ps	τ_{ev} ps	τ_{nn} ns	λ_{nn} µm	λ_{ev} µm	λ_{tot} µm	s µm
1	0.39	14 @	62	12E3	130	50	74E3	370	720 @
100		λ=4.2µm	6	62	1.3	0.5	37	3.7	E=27kV/m

$$\tau_{exc} << \tau_{vib} << \tau_{int} << \tau_{etot} << \tau_{ev} << \tau_{nn} \sim \tau_{RF} \text{ @ 100mbar}$$

CO2 molecule is vibration excited in the ground state $^1\Sigma^+$ by high rate electron impact

VV exchange process populates the higher $^1B_2$ vibration energy levels of the CO2 molecule

Plasma parameters

- In general plasma collision times much longer than neutral collision times. However, at extremely low electron temperature and high density prevailing in our experimental situation, these times become near neutral collision times. Hence, Coulomb collisions play some role in thermalisation.
- $T_{ee} < T_{ei} << T_{ii} < T_{ie}$

n_i	Te=0.1 eV	Te= 1 eV	Te=10eV	Te=100eV
10^{18} m-3	1.3 ns	32 ns	0.84 μs	23 μs
10^{19} m-3	0.15 ns	3.6 ns	0.092 μs	2.5μs

Debye length and number of particles Debye sphere

ne	0.1 eV	1 eV	10 eV
10^{18} m-3	2.35 μm	7.45 μm	23.5 μm
10^{19} m-3	0.75 μm	2.35 μm	7.45 μm

- Debye length small compared with plasma dimension
- Number of particles in Debye sphere is unusually small

$N_{\lambda D}$	0.1 eV	1 eV
10^{18} m-3	54	1720
10^{19} m-3	17	550

V-T Relaxation efficiency is function ionisation degree

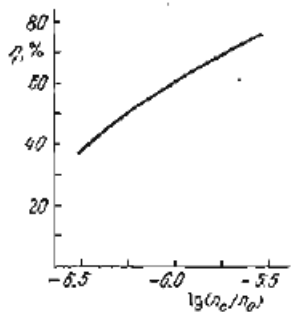


FIG. 10. Relaxation efficiency of CO_2 dissociation vs degree of ionization ($E_V = 0.5$ eV/molecule).

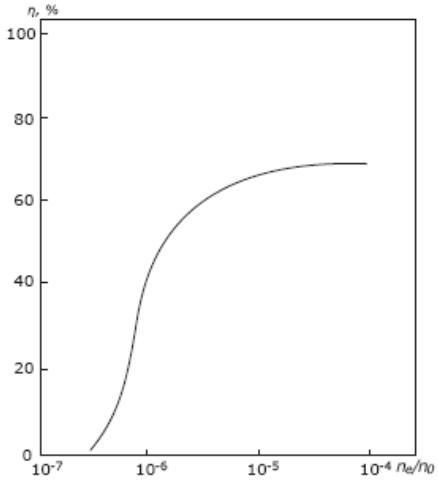


Figure 5–17. Energy efficiency of CO_2 dissociation in plasma at the specific energy input $E_v = 0.5$ eV/mol as a function of plasma ionization degree n_e/n_0.

η_{VT} is the fraction of vibration energy going into dissociation over the fraction going into translation energy. This η_{VT} turns out to be a function of ionisation degree.

Here comes the plasma!

At a pressure of 200mbar (n_o=5.38E^{18}cm-3), a relaxation efficiency η_{VT} = 80% is reached at an electron density n_e=1.7E^{13}cm^{-3}, i.e. quite high!

Plasma frequency as function of density

ne	$N = 8.967 ? n_e$
10^{18} m-3	~9 GHz
10^{19} m-3	~28 GHz

The RF frequency (915 MHz) is lower than the plasma frequency. Hence, the wave cannot propagate. With collisions included, the wave can propagate, but the RF field is essentially stationary for the processes considered.

Vibration energy loss

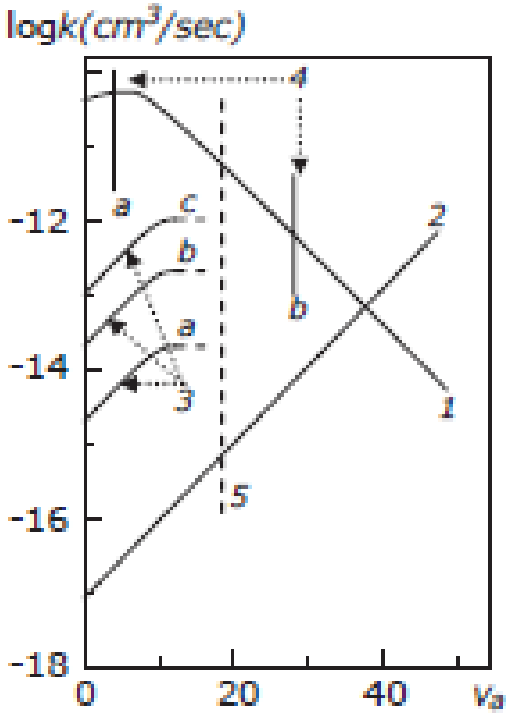


Figure 5–13. Rate coefficients of relaxation processes related to asymmetric mode of CO_2 vibrations at room temperature $T_0 = 300$ K as functions of number of quanta on the mode: (1) VV relaxation; (2) VT relaxation; (3) intermode VV′ relaxation (assuming symmetric vibrational temperature [3a] $T_{vs} = 1000$ K, [3b] $T_{vs} = 2000$ K, [3c] $T_{vs} = 3000$ K); (4) intramolecule VV′ relaxation, transition to vibrational quasi-continuum (assuming [4a] equal excitation of all vibrational modes; [4b] predominant excitation of asymmetric vibrations); (5) CO_2 dissociation energy.

$$k_{VT} \approx 10^{-10} \exp\left(-72/T_0^{1/3}\right), \text{ cm}^3/\text{s},$$

- At vibration levels up to 20, the dissociation energy, the vibration pumping exceeds the translation loss

Vibration Excitation CO_2 vs. Reduced E-Field

Few electrons

⇩

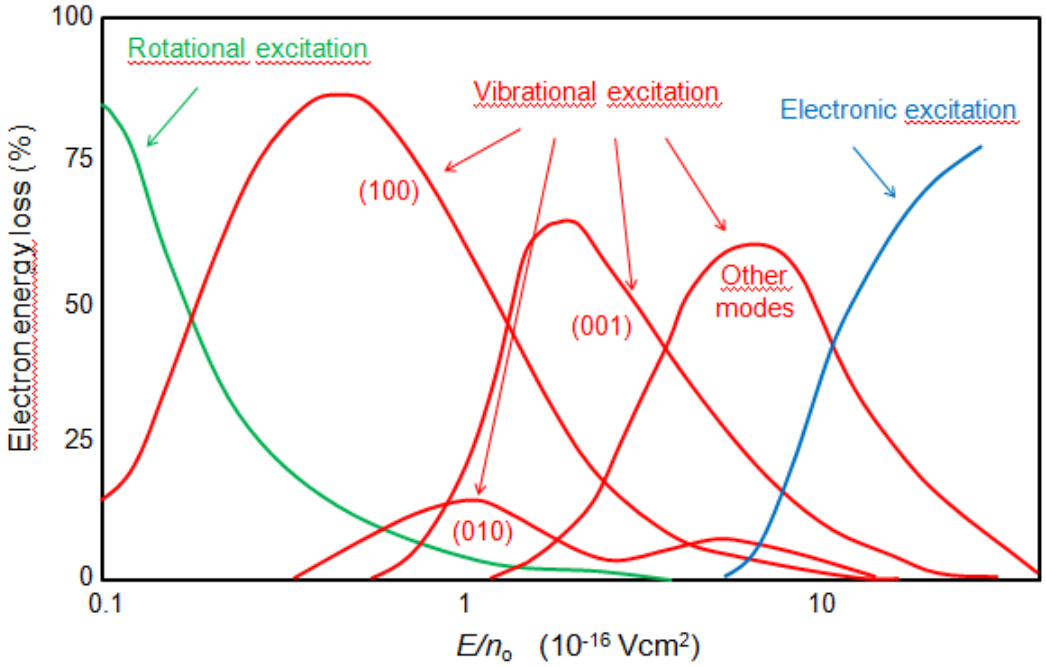
Low reduced electric field

⇩

Electron-neutral collisions

⇩

vibrational excitation



v_3 (001) = CO2 asymmetric stretch mode

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

Nonequilibrium effects: Treanor distribution

electrons

⇩

electric field

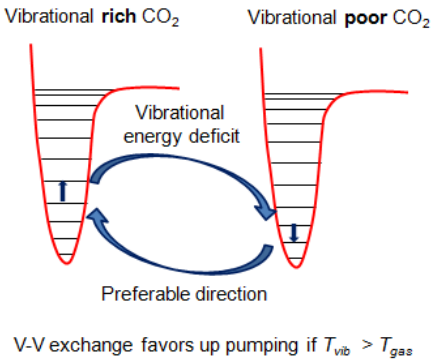
⇩

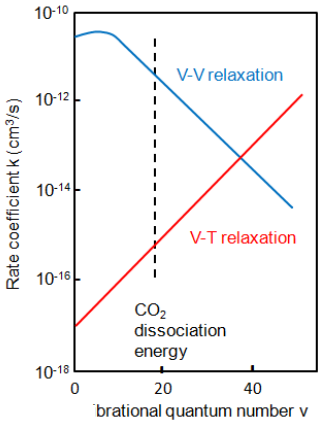
collisions

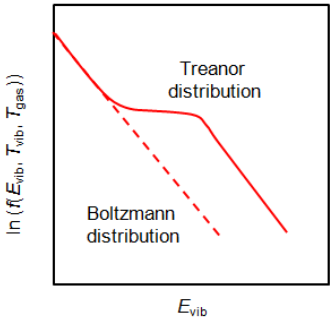
⇩

vibrational excitation

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







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

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

The Energy problem

Why Solar Fuels?

Fossil fuels, albeit finite, are still abundant in terms of world energy reserves:

- Coal reserves 300 yrs (China)
- Gas expanded from 50 to 200 yrs due to fracking shale beds
- Oil demand has peaked in rich world
  - increased efficiency in petrol/diesel engines and emergence of hybrid and electric cars
  - switch to gas to power lorries, buses, ships and domestic/industrial heating systems

What problem?

The Climate problem: IPCC 5th Assessment

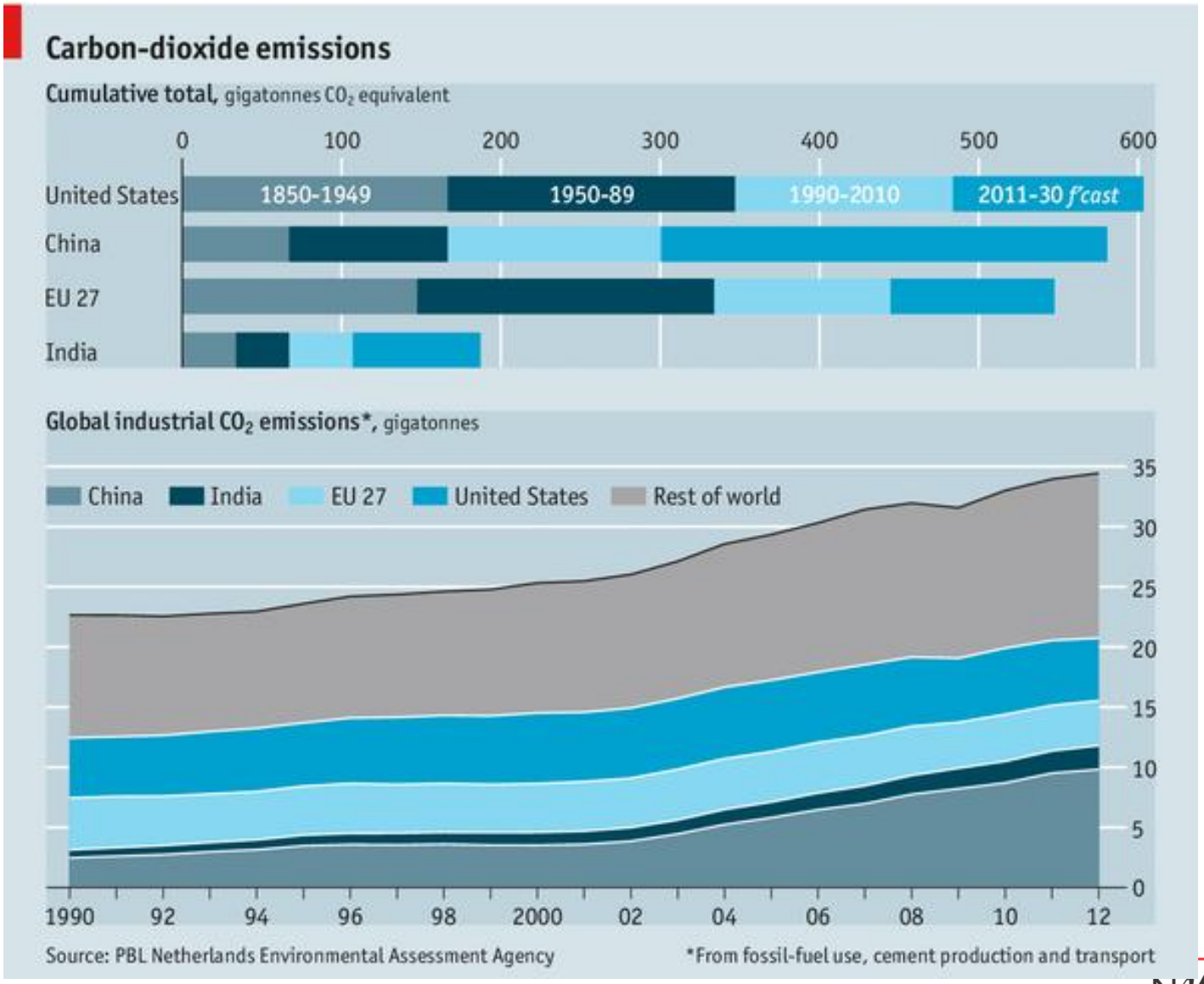
Problem is the CO_2 emission from burning fossil fuel

- Atmospheric concentration increased from 280ppm to 400ppm this year,
- increased radiative forcing from 0.57 to 2.29 W/m^2 since industrialisation
- Result 0.5°C global average surface temperature rise
- + 0.5°C due to climate inertia expected later this century

- Most scientists & governments place 2°C limit on temp. rise
- IPCC defines Carbon budget **1800 Gton CO_2** emission (until 2011 539Gt, yearly 37 Gton global emission)
- Budget will be spent by **2047 ±14yr** (business as usual)
- By **2069 ±18yr** emission stabilisation (Nature 10 Oct 2013)

NWO FOM

Carbon dioxide emissions past and projection 2030



EU plus Aus only 13% share in CO2 emission

What happens in rich countries matters much less than it did.

Developing economies now account for over half the world's emissions, and their share will keep rising. In China, they rose less quickly last year—just 3%, rather than the 10% that has been the recent norm—and the amount of carbon emitted per unit of GDP is falling quite fast. Other nations are not making such progress. India emits much less carbon dioxide than China; but it is a bigger source than Russia, and last year its emissions rose by 7%. Soon more than half of all the carbon ever emitted by human industry and land use will have come from developing countries.

Industrial emissions of carbon dioxide continued to rise in 2012, pushing the atmospheric level ever higher, but they did so at a lower rate than in many recent years. Indeed in big developed economies they dropped—by 4% in America, where utilities were switching from coal to gas, and by 1.3% in recession-hit Europe.

Source Economist 9 November 2013

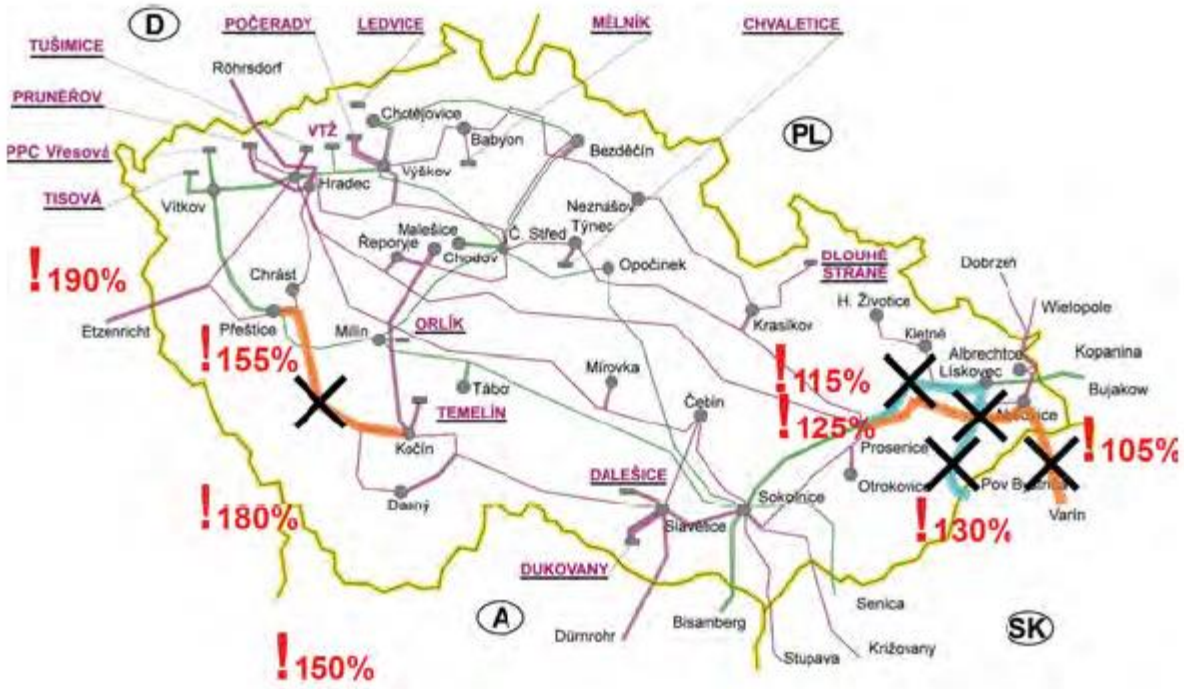
EU energy & climate policy

- 2020 renewable share 20%, GHG emission reduction 20%
- 2050 Roadmap GHG emission reduction 80-95%
- To date 80% fossil fuel in EU energy mix

Gas will play important role in energy transition (IEA 2011)

- CO_2 emission 80% reduced compared with coal
- Gas turbine allows rapid ramping up and down to compensate for intermittent supply by renewables
- Gas storage provides reliable and flexible means to provide back-up power to compensate for low intermittent supply
- Gas transport is factor 10 cheaper than electricity transport

Overloading of Chech electricity grid



- Black crosses indicate tripping of lines in Nov 2011-Feb 2012