Spatio-temporal evolutions of rotational and vibrational temperatures of nitrogen and oxygen of a high field atmospheric discharge in dry air by spontaneous Raman scattering

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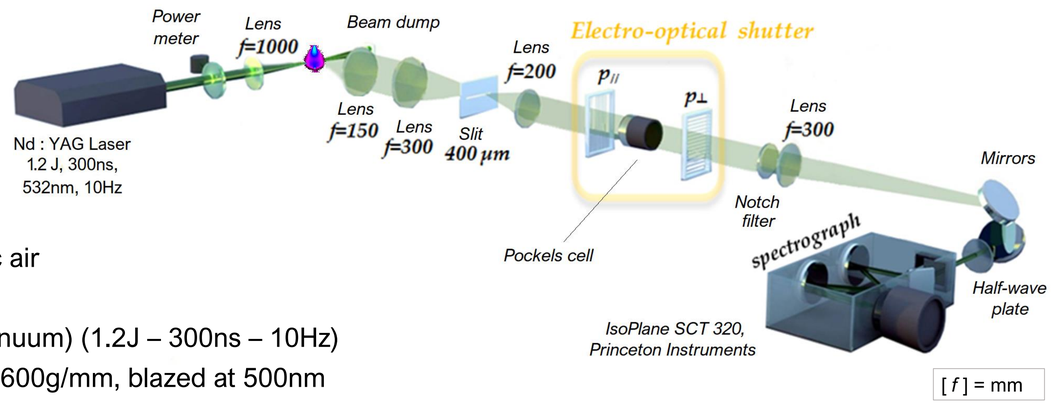
Summary: We report results on the influence of **high electric fields on the energy relaxation and heating mechanisms** of a nanosecond corona discharge in atmospheric air. At 85kV, high non-equilibrium vibrational excitation of nitrogen is observed in the first hundreds of nanoseconds of the post-discharge. **Vibrational-vibrational transfers** dominate until 10µs. Then, **vibrational-translational transfers** participate to **moderate heating of the gas** (about 1000K). **Thermal equilibrium** is reached within 10 to 50ms. At 65kV, energy relaxation time scales are similar but vibrational temperatures are lower and the gas temperature remains below 500K.

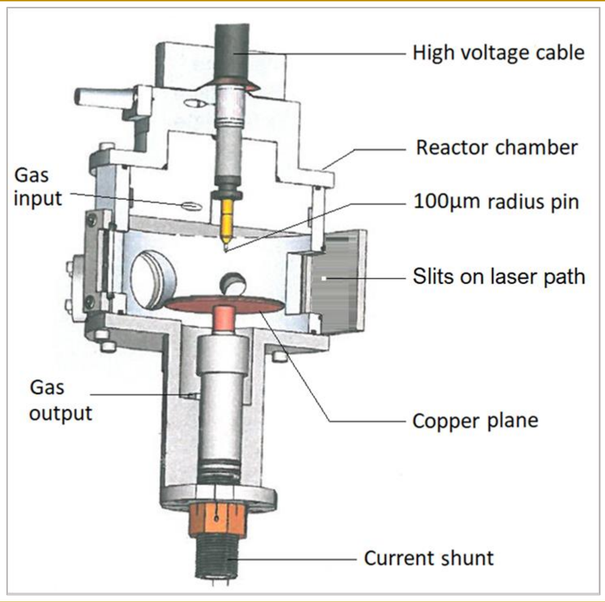
Introduction: This work comes within a research on the fundamental mechanisms of **diffuse electric discharges under very high electric fields** and the associated non-equilibrium plasmas in atmospheric air. Such discharges are created at very high over-voltages, several tens of kilovolts, with **sub-nanosecond rise times** and without any pre-ionizing system [1].
In the context of air treatment research, better understanding of the physical and chemical processes of these discharges helps to develop advanced and high energy efficiency reactors. The **high field** values that make **large volume discharges**, should enable the design of plasma reactors presenting more homogeneous properties than current ones.

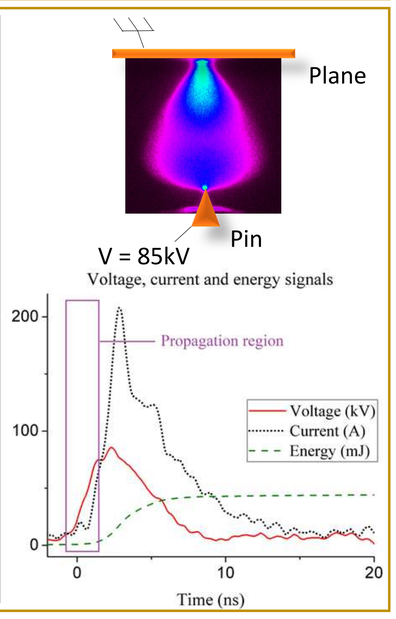
Experimental setup:

- Pin-plane geometry, 18mm gap
- ~100µm pin radius
- Voltage peaks at 65kV or 85kV
- Repetition frequency: 5Hz
- P=1atm, 1 L.min^{-1} flow of synthetic air



- Agilite pulsed Nd:YAG laser (Continuum) (1.2J – 300ns – 10Hz)
- Spectrograph: IsoPlane SCT320 - 600g/mm, blazed at 500nm
  Back-illuminated CCD (Pixis 400B)
- Notch filter at 532nm
- Electro-optical shutter : 2 crossed polarizers + KD*P Pockels cell (LAP-50, Quantum Tech.)





Choice of the fitting model according to the state of the gas [2]:

Various energy distribution functions have to be considered to correctly describe reactive media because of strong energy transfers.

- A **model at thermodynamic equilibrium** for spatial positions out of the discharge and all positions after complete energy relaxation:

$$N_{v,J} = N\frac{\left(2J+1\right)g_J\exp\left(-\frac{hcE_{vib}(v)}{kT}-\frac{hcE_{rot}(v,J)}{kT}\right)}{Q_{vib}(T)Q_{rot}(v,T)}$$

$T_{trans} = T_{rot} = T_{vib}$

- A **three temperatures model** for times before vibrational relaxation:

$$N_{v=0,J} = N\frac{\left(2J+1\right)g_J\exp\left(-\frac{hc\left(E_{vib}(v=1)-E_{vib}(v=0)\right)}{kT_{v_{01}}}-\frac{hcE_{vib}(v=1)}{kT_{v_{1v}}}-\frac{hcE_{rot}(0,J)}{kT_{rot}}\right)}{Q_{vib}(T_{v_{01}},T_{v_{1v}})Q_{rot}(0,T_{rot})}$$

$$N_{v>0,J} = N\frac{\left(2J+1\right)g_J\exp\left(-\frac{hcE_{vib}(v)}{kT_{v_{1v}}}-\frac{hcE_{rot}(v,J)}{kT_{rot}}\right)}{Q_{vib}(T_{v_{01}},T_{v_{1v}})Q_{rot}(v,T_{rot})}$$

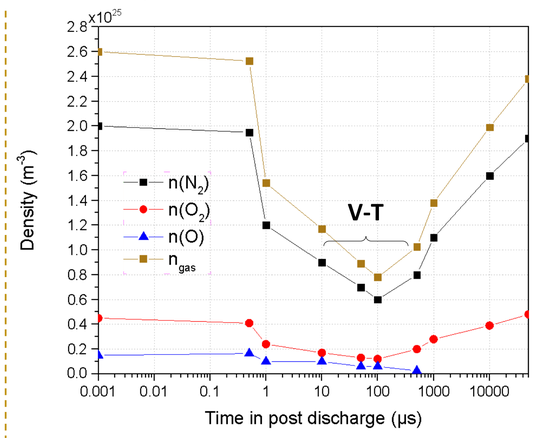
$T_{rot} \neq T_{v=0,1} \neq T_{v>1}$

- A **two temperatures model** for times after vibrational relaxation:

$$N_{v,J} = N\frac{(2J+1)g_J\exp\left(-\frac{hcE_{vib}(v)}{kT_v}-\frac{hcE_{rot}(v,J)}{kT_{rot}}\right)}{Q_{vib}(T_v)Q_{rot}(v,T_{rot})}$$

$T_{rot} \neq T_{vib}$

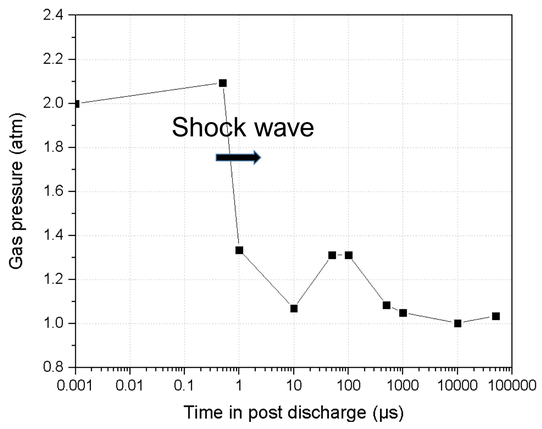
Density temporal profiles:



Just after the discharge:
- Isochoric heating of the gas
- Significant dissociation of oxygen molecules
- Gas expansion starts

At 1µs:
- Shock wave re-establishes pressure

Pressure temporal profiles:



From 10µs to 500µs:
- Enhanced gas expansion with heating due to V-T transfers

From 500µs to 10ms:
- Relaxation by diffusion

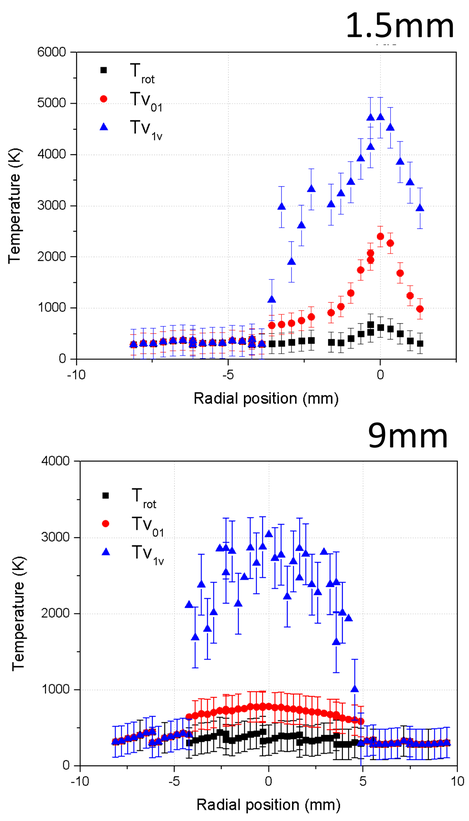
O_2 dissociation model:

n(O) is determined with the evolution of the ratio of O_2 and N_2 atoms compared with the equilibrium ratio 1:4

$$\tau_{dissociation}\,(O_2) = \frac{1/2n(O)}{n(O_2)+1/2n(O)}$$

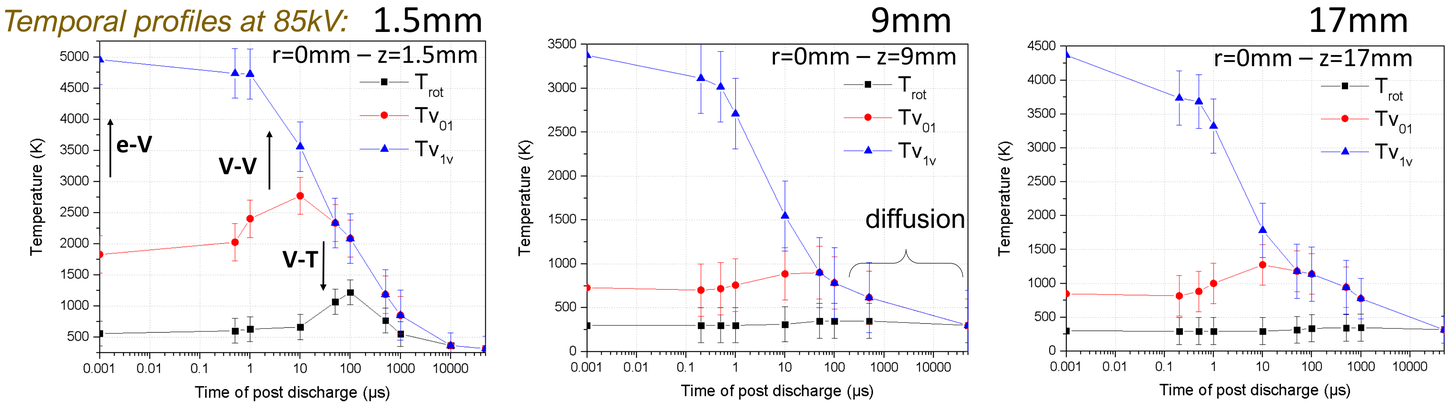
85kV – dry air – at the pin :
- Just after the discharge, ~15% of O_2 are dissociated.
- Density of O atoms is divided by two in 100µs.
- O atoms are recombined in 500µs.

Radial profiles at 85kV – 1µs:

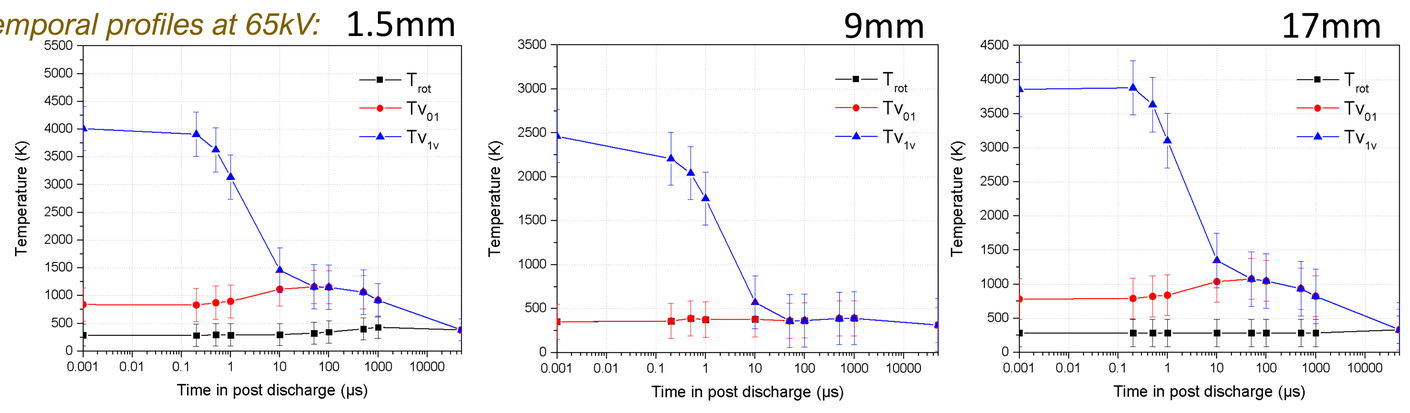


- **Radial temperature extent** depends on the vibrational level considered.
- The radial extent is **coherent with the light emission profiles**.
- The rotational temperature can only be determined with **good sensitivity over 500K**. Below, it is influenced by the accuracy of the instrumental function for each region of interest.

Temporal profiles at 85kV:



Temporal profiles at 65kV:



At 1.5mm:
- **Gas heating requires strong non-equilibrium** induced by very high voltages.
- Voltage impact on vibrational non-equilibrium and induced V-T gas heating processes is mostly **localised at the pin**.

At 9mm:
- **Close to equilibrium** between vibrational and rotational levels at low voltage.
- Excitation of v=0,1 **under detector sensitivity at 65kV.**

→ **Almost no heating** of the gas in most of the discharge volume up to 85kV.

At 17mm:
- **Low effect of voltage** between 65kV and 85kV.
- Gas heating at the limit of detection sensitivity.

❖ Relaxation time scales are similar whatever the position and voltage. The same mechanisms prevail.

Just after the discharge:
- **e-V transfers** during the discharge

=> high non-equilibrium vibrational distribution.
- **Fast heating** dominantly due to [3]:
  - Quenching of $N_2(C,B)$ states by O_2
  - Dissociation of O_2 and N_2 by electronic impact
  - Quenching of $O(^1D)$ with N_2 and O_2
  - Reactions involving charged particles

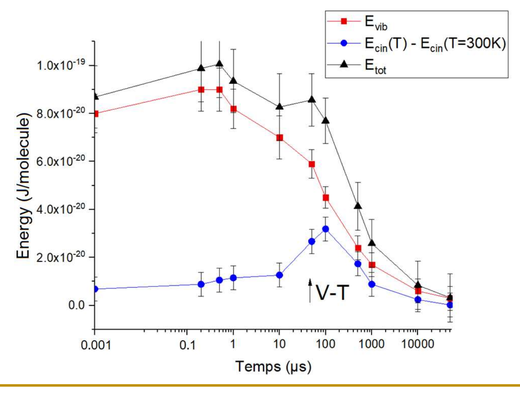
Up to 10µs:
- **V-V transfers** dominate from high to low vibrational levels
- Vibrational equilibrium is reached between **10 and 50µs**
- Low V-T transfers
- Ongoing chemical heating balanced by adiabatic cooling → +100K at the pin

10µs to 500µs:
- V-T transfers dominate: gas heating

500µs to 1ms:
- Cooling by gas diffusion and convection

Energy per molecule of $N_2(X)$:

- ~ 90% E_{vib} at t=100ns
- E_{cin} constant over 10µs: low V-T transfers
- E_{vib} decrease slowly from 1µs: choc wave
- Heating: V-T transfers
- E_{vib} fall, E_{cin} fall: relaxation by diffusion



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Conclusion: Highly non-equilibrium discharge shows ~90% of the energy of N_2 molecules is stored in vibrational excitation at the end of the discharge and up to ~15% of O_2 molecules are dissociated. In dry air, fast heating is low and very localised at the pin. A shock wave re-establishes pressure at 1µs. V-V transfers dominate from 1 to 50µs, followed by V-T transfers. Significant induced heating is localised at the pin and reaches no more than 1000K and requires high voltages. Voltage impacts the energy share between vibrational levels: excitation of levels 0 and 1 in the volume requires voltages >65kV. High temperatures maintained over more than 100µs on mm scale regions at the pin can compete with spark discharges for combustion and high vibrational excitation on large radial extent promotes reactivity.

References:

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