Influence of high fields and humidity on the spatio-temporal evolutions of rotational and vibrational temperatures of N_2 and O_2 of a corona discharge in atmospheric air by spontaneous Raman scattering

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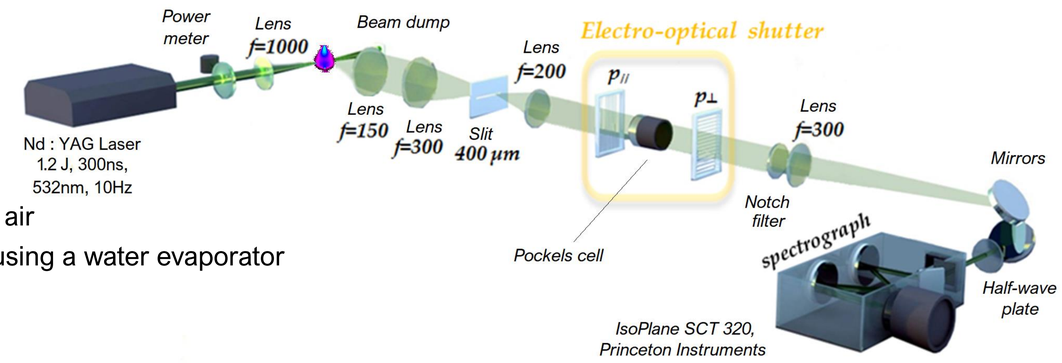
Summary: We report results on the influence of **humidity on the energy relaxation and heating mechanisms** of a high fields nanosecond corona discharge in atmospheric air. At 85kV, for both dry and humid air, **high non-equilibrium vibrational excitation of N_2** is observed in the first hundreds of nanoseconds of the post-discharge. Below 1% of water vapor concentration, the gas temperature reaches ~550K at the pin due to fast heating mechanisms. Above 1% of water vapor concentration, 800K is reached due to **OH formation** and **fast vibration-translation transfers of H_2O**. Then, vibrational-vibrational transfers dominate until 10µs for any water vapor concentration up to 2%. Until 500µs, vibrational-translational transfers participate to moderate heating of the gas, about 1000K. Thermal equilibrium is reached within 10 to 50ms.

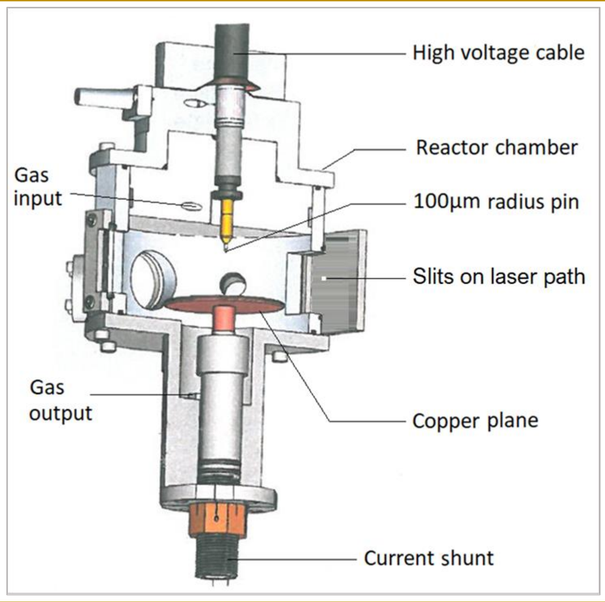
Introduction: This work comes within a research on the fundamental mechanisms of **diffuse electric discharges under very high electric fields** and the associated non-equilibrium plasmas in atmospheric air. Such discharges are created at very high over-voltages, several tens of kilovolts, with **sub-nanosecond 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.

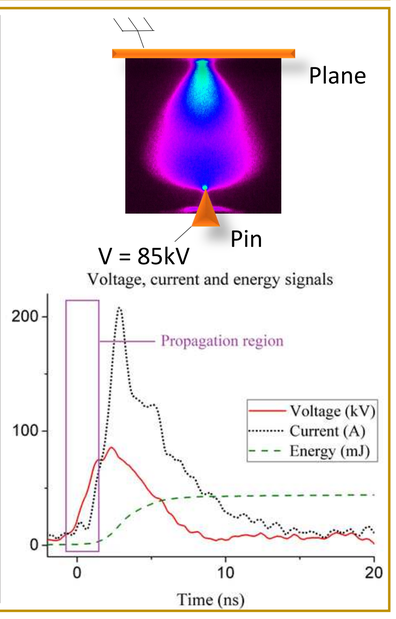
Experimental setup:

- Pin-plane geometry, 18mm gap
- ~100 µm pin radius
- Voltage peak: 85kV
- Repetition frequency: 5Hz
- P=1atm, 1 L/min flow of synthetic air
- Water vapour up to 2% is added using a water evaporator and dilution system



- Agilite pulsed Nd:YAG laser (Continuum) (1.2J – 300ns)
- 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 state of the gaz:

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 :

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

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

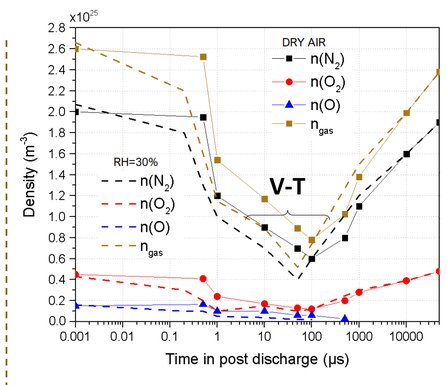
$T_{rot} \neq T_{v=0,1} \neq T_{v>1}$

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

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

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

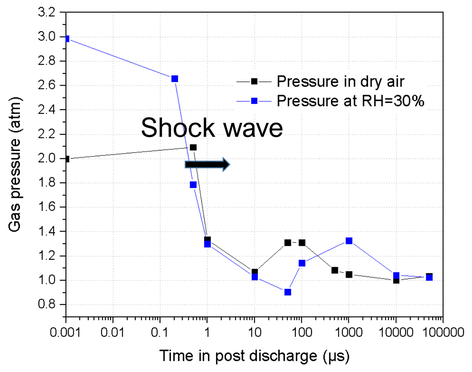
Density temporal profiles:



Just after the discharge:
- Isochoric heating of the gas
- Enhanced T_{gas} and pressure at RH=30%
- Significant dissociation of O_2
- Gas expansion starts

At 1µs:
- Shock wave re-establishes pressure

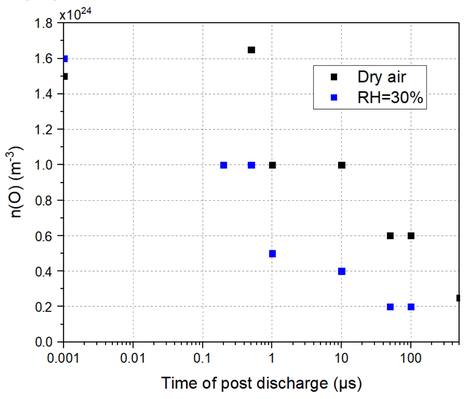
Pressure temporal profiles:



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

From 500µs to 10ms:
- Relaxation by diffusion

n(O) temporal profiles:

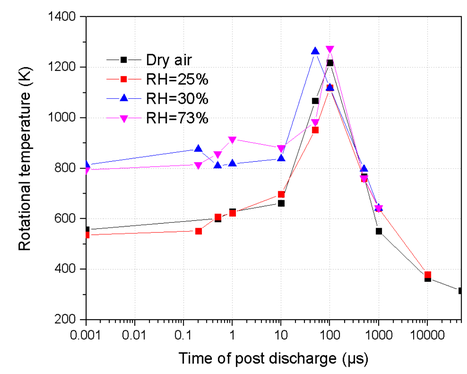


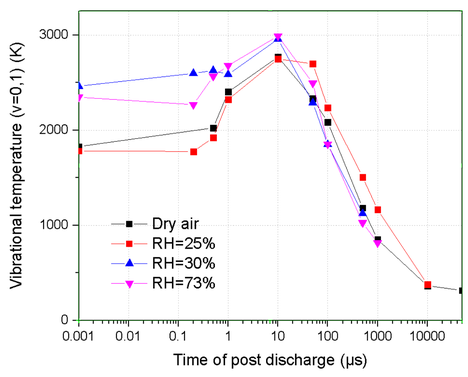
The evolution of the ratio of O_2 and N_2 atoms compared with the equilibrium gives n(O):

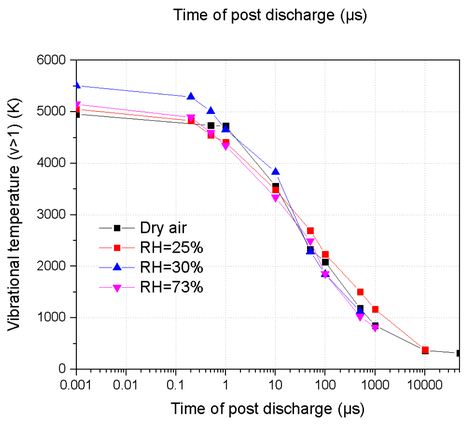
$$\tau_{dissociation}\,(O_2) = \frac{1/2n(O)}{n(O_2)+1/2n(O)}$$

Just after the discharge, $\tau_{dissociation}\,(O_2)$ ~ 15%
O atoms loss is in humid air is dominantly due to reaction **c.**

Temperature profiles of N_2 for different relative humidities (85kV - r=0mm - z=1.5mm):







In dry air:
Fast heating (+250K) dominantly due to [2]:
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

In humid air:
Increased fast heating (+500K) in less than 300ns [3,4]:
- Exothermic OH formation, during the discharge
  - By electronic impact from H_2O:
    $H_2O + e^- \rightarrow H + OH + e^-$
    $H_2O + e^- \rightarrow OH^- + H$
    $H_2O + e^- \rightarrow H^- + OH$
    a *Fast process during the discharge*
  - Other reactions:
    $H + O_2 + M \rightarrow HO_2 + M$, M Є [$O_2$(v), N_2(v)]
    $O(^3P) + HO_2 \rightarrow OH + O_2(v)$
    b *Three step process*
    $O(^3P)$ is decreased by $OH + O(^3P) \rightarrow O_2(v) + H$ and,
    by loss of $O(^1D)$ through **c** in quenching reactions with O_2 and N_2
    $O(^1D) + H_2O \rightarrow 2\,OH$ **c**
    $N_2(a) + H_2O \rightarrow N_2(v) + OH + H$ **d**
- Fast V-T transfers with H_2O(v):
  $H_2O(v_2) \rightarrow H_2O(T)$ τ = 40ns
  $H_2O(v_1,v_3) \rightarrow H_2O(T)$ τ = 100ns *(independent of temperature)* **e**
  - H_2O(v) created by electronic impact:
    $H_2O + e^- \rightarrow H_2O(v_2=1) + e^-$
    $H_2O + e^- \rightarrow H_2O(v_1=1) + e^-$
    $H_2O + e^- \rightarrow H_2O(v_3=1) + e^-$
    f *Fast process during the discharge*
  - H_2O(v) created by quenching with O_2 and N_2:
    $O_2(v) + H_2O \rightarrow O_2(v\text{-}1) + H_2O(v)$ τ ≈ 3µs
    $N_2(v) + H_2O \rightarrow N_2(v\text{-}1) + H_2O(v)$ τ ≈ 100µs (300K)
    τ ≈ 15µs (1000K)
    g *Slow process*

Increased heating of low vibrational levels of N_2 not yet described.

Discussion:

- The large majority of the additional heating due to water vapour probably comes from **fast discharge processes** involving OH or H_2O(v) (reactions (**a**, **c**, **d** and **f** followed by **e**)).
- Contrary to [4], no strong increase of temperature is observed at 10µs due to reactions **g** followed by **e**. The low efficiency of H_2O(v) quenching with O_2 probably comes from:
  - **low vibrational excitation of O_2 in dry air**

Vibrational excitation of O_2 by electron impact is weak due to **low cross sections** contrary to N_2.

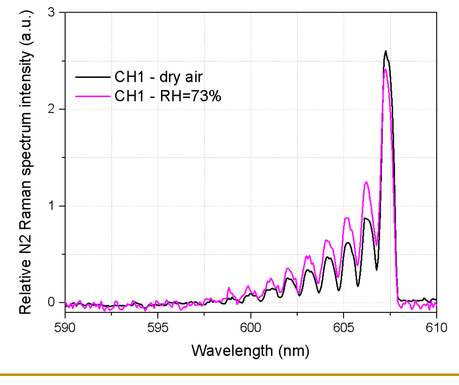
Also O_2(v) experiences vibrational relaxation by **quenching with O**.

In humid air, vibrational excitation of O_2 is enhanced by reactions involving OH and O (reactions **b**, $OH + O(^3P) \rightarrow O_2(v) + H$) and the quenching with O is much less efficient due to reaction **c.**

  - **high O_2 dissociation**

Vibrational excitation of N_2:

- Vibrational levels up to v=11 are populated
- Population of low vibrational levels increased in humid air



Conclusion at the pin at 85kV:

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.
Below 1% of water content, fast heating is low and very localised at the pin with only 550K. Above 1% of water vapor concentration, 800K is reached due to OH formation and fast vibration-translation transfers of H_2O. Then, V-V transfers dominate from 1 to 50µs, After 10µs, humidity effects are not observed anymore. From 50µs to 500µs, significant heating due to V-T transfers is localised at the pin and reaches no more than 1000K. High temperatures maintained over more than 100µs on mm scale regions at the pin can compete with spark discharges to support combustion.

References:

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[3] A. Komuro, R. Ono, J. Phys. D: Appl. Phys. **47** (2014) 155202 (13pp)
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