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# Influence of high fields and humidity on the spatio-temporal evolutions of rotational and vibrational temperatures of N<sub>2</sub> and O<sub>2</sub> of a corona discharge in atmospheric air by spontaneous Raman scattering

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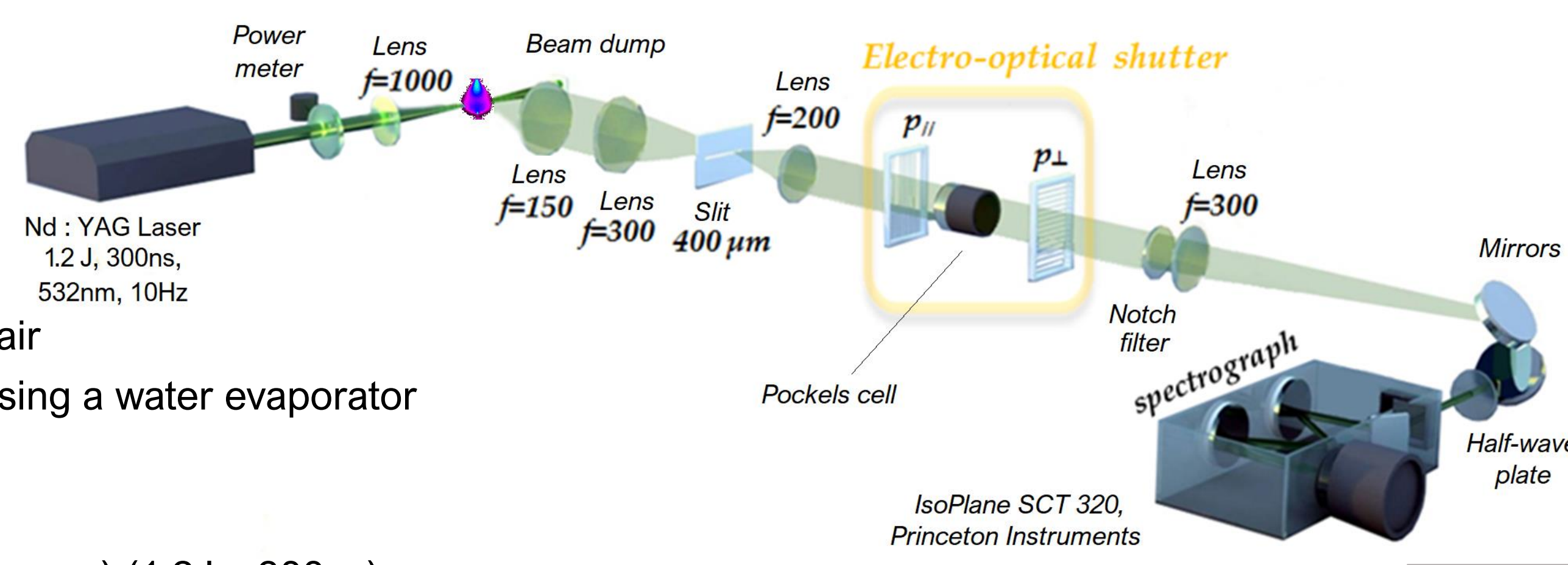
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**Summary:** We report results on the influence of humidity on the energy relaxation and heating mechanisms of a high fields nanosecond corona discharge in atmospheric air. At 85kV, for both dry and humid air, high non-equilibrium vibrational excitation of N<sub>2</sub> 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<sub>2</sub>O. 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.

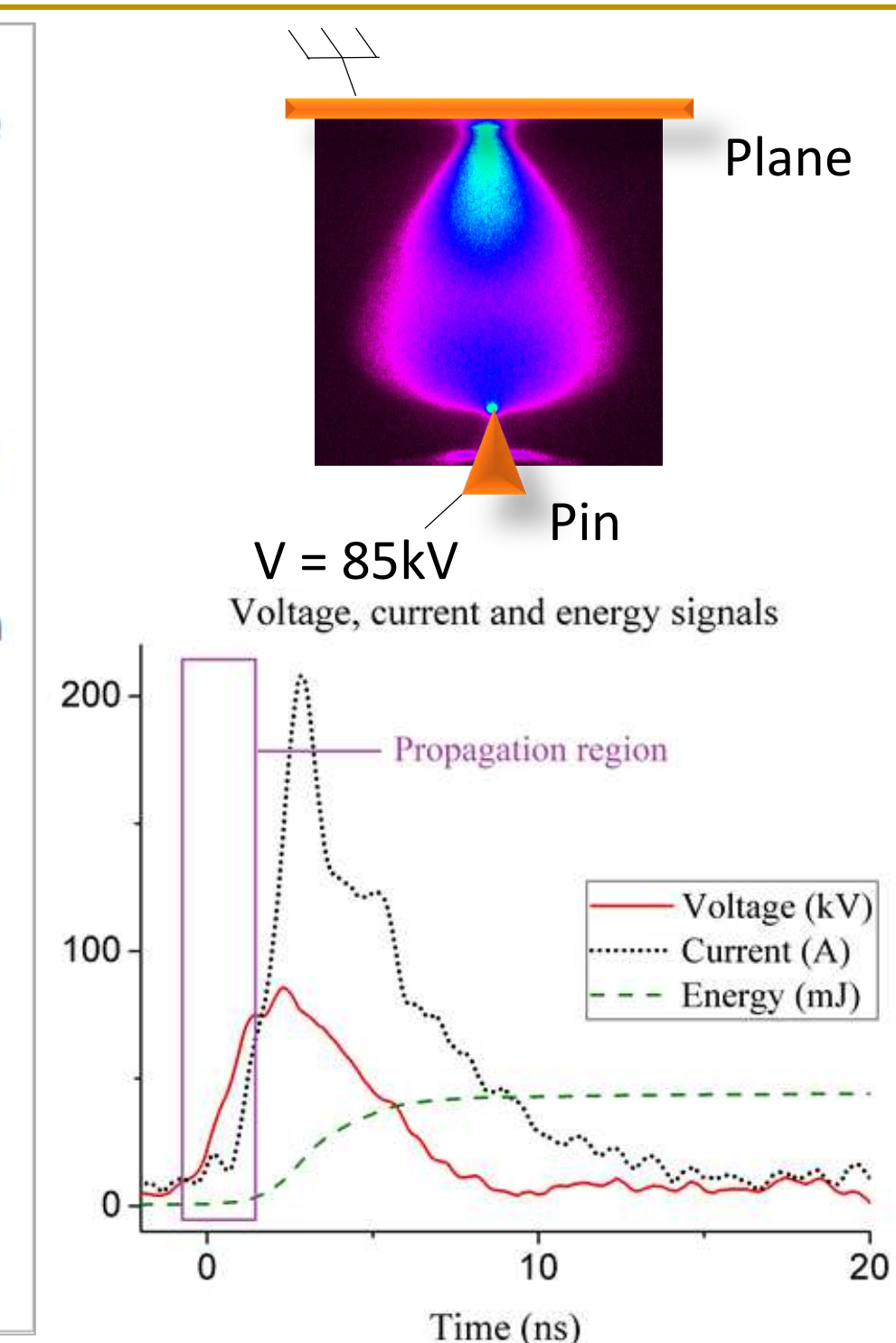
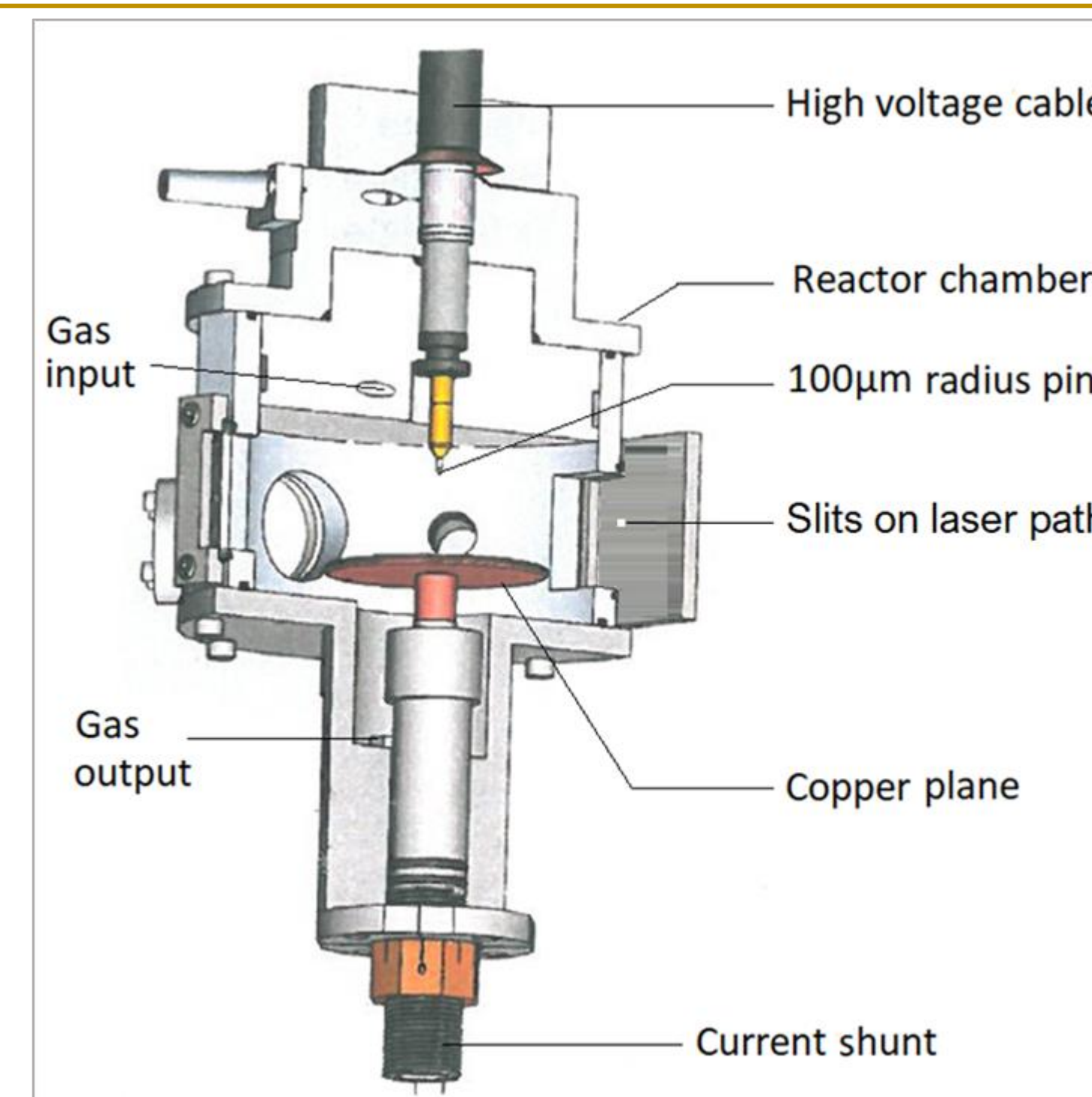
**Introduction:** This work comes within a research on the fundamental mechanisms of diffuse electric discharges under very high electric fields and the associated non-equilibrium plasmas in atmospheric air. Such discharges are created at very high over-voltages, several tens of kilovolts, with sub-nanosecond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

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

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

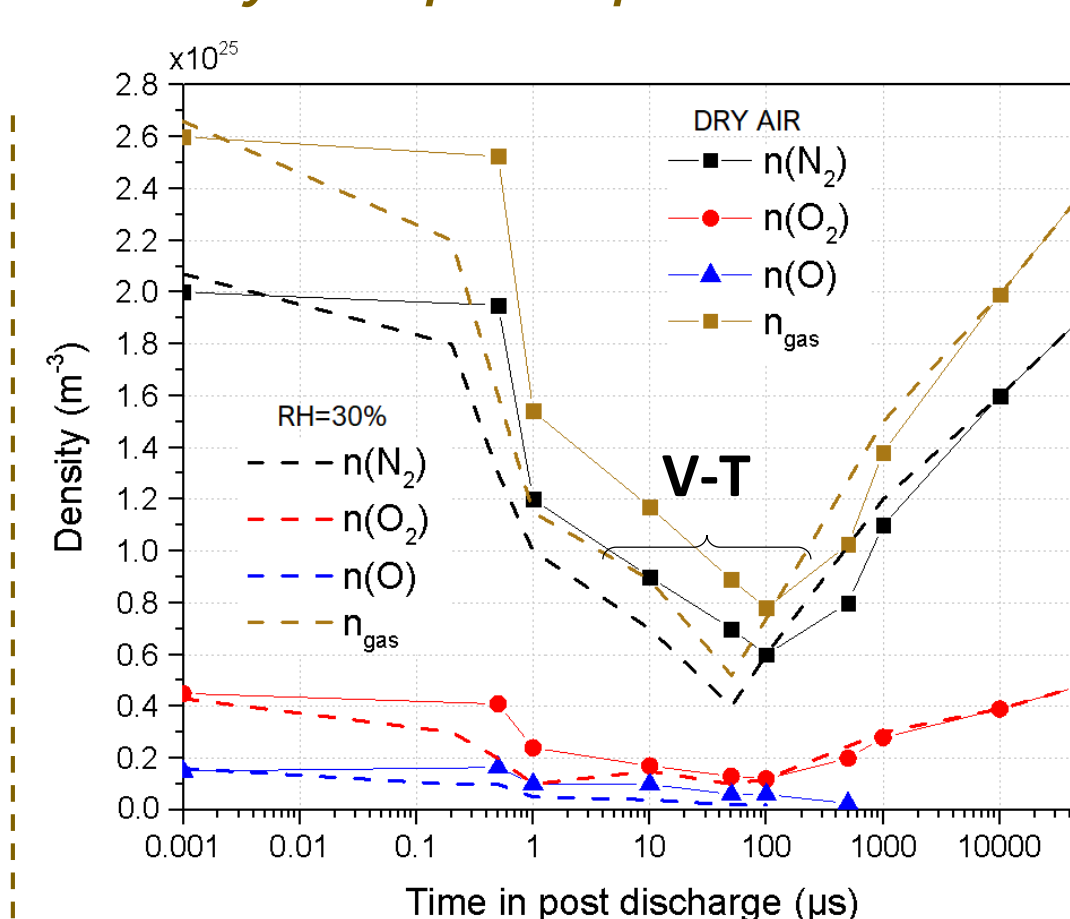
$$N_{v=0,J} = N \frac{(2J+1)g_J \exp\left(-\frac{hc(E_{vib}(v=1) - E_{vib}(v=0)) - hcE_{rot}(0,J)}{kT_{v01}} - \frac{hcE_{vib}(v=1)}{kT_{v1v}} - \frac{hcE_{rot}(0,J)}{kT_{rot}}\right)}{Q_{vib}(T_{v01}, T_{v1v})Q_{rot}(0, T_{rot})}$$

$$N_{v>0,J} = N \frac{(2J+1)g_J \exp\left(-\frac{hcE_{vib}(v)}{kT_{v1v}} - \frac{hcE_{rot}(v,J)}{kT_{rot}}\right)}{Q_{vib}(T_{v01}, T_{v1v})Q_{rot}(v, T_{rot})} \quad T_{rot} \neq T_{v=0,1} \neq T_{v>1}$$

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

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

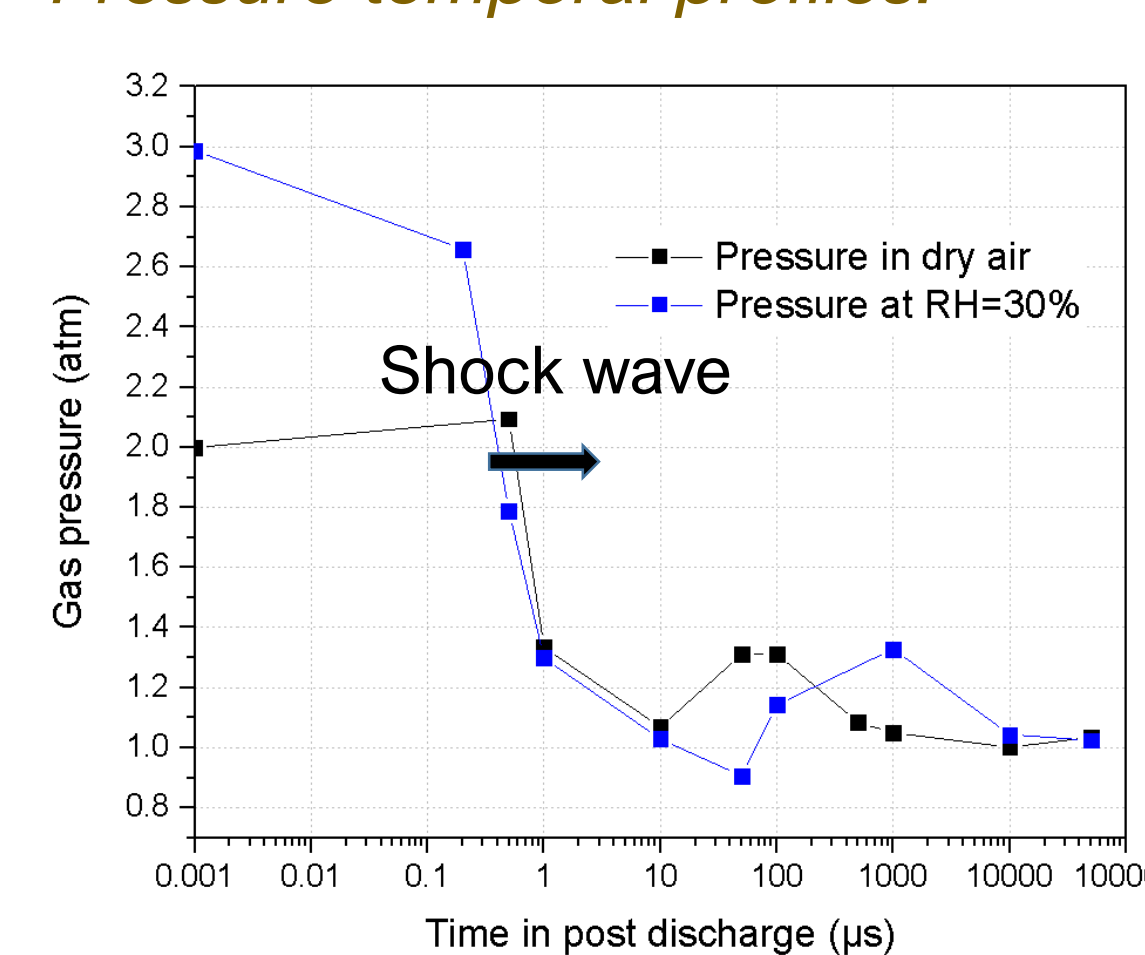
## Density temporal profiles:



### Just after the discharge:

- Isochoric heating of the gas
  - Enhanced T<sub>gas</sub> and pressure at RH=30%
  - Significant dissociation of O<sub>2</sub>
  - Gas expansion starts
- At 1μs:**
- Shock wave re-establishes pressure

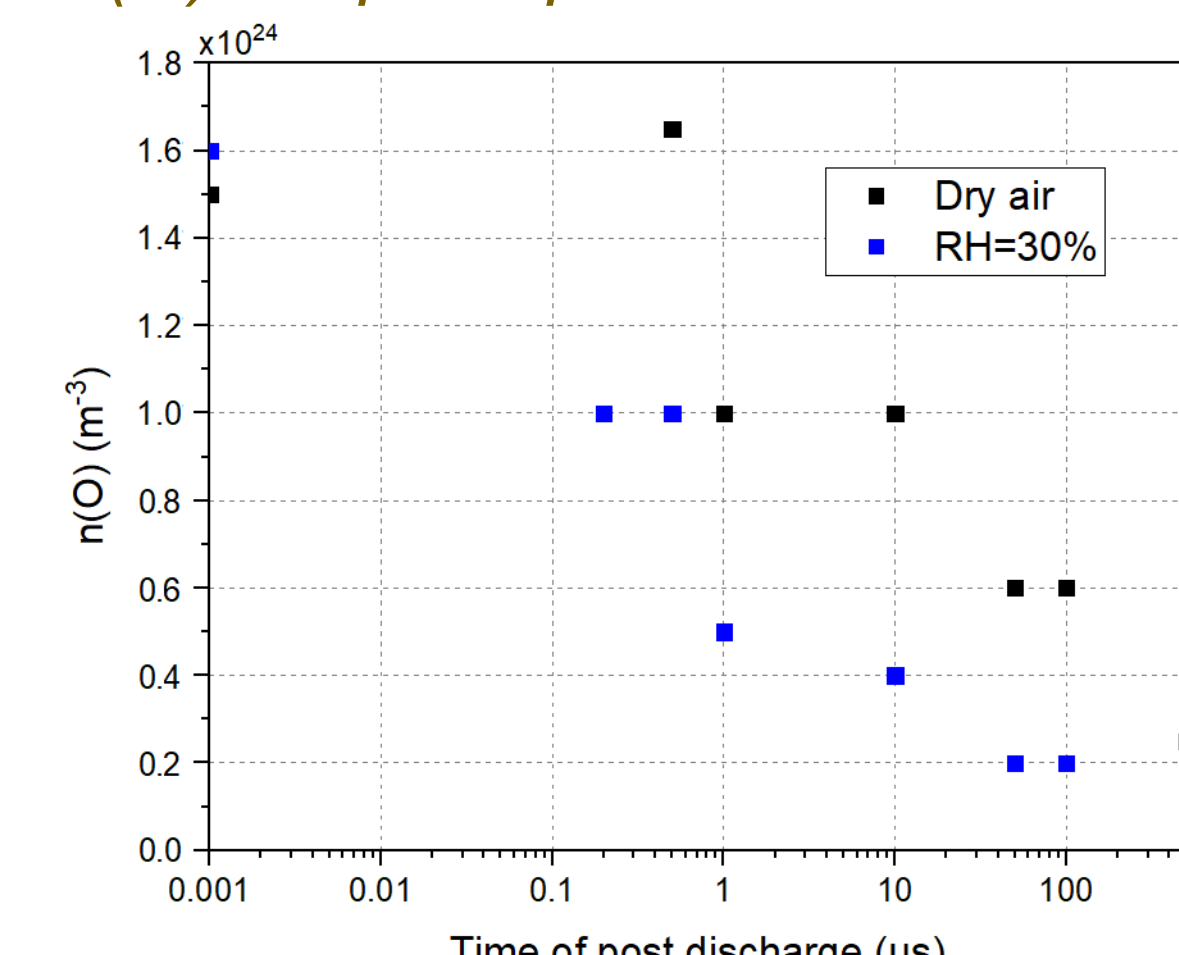
## Pressure temporal profiles:



### 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:

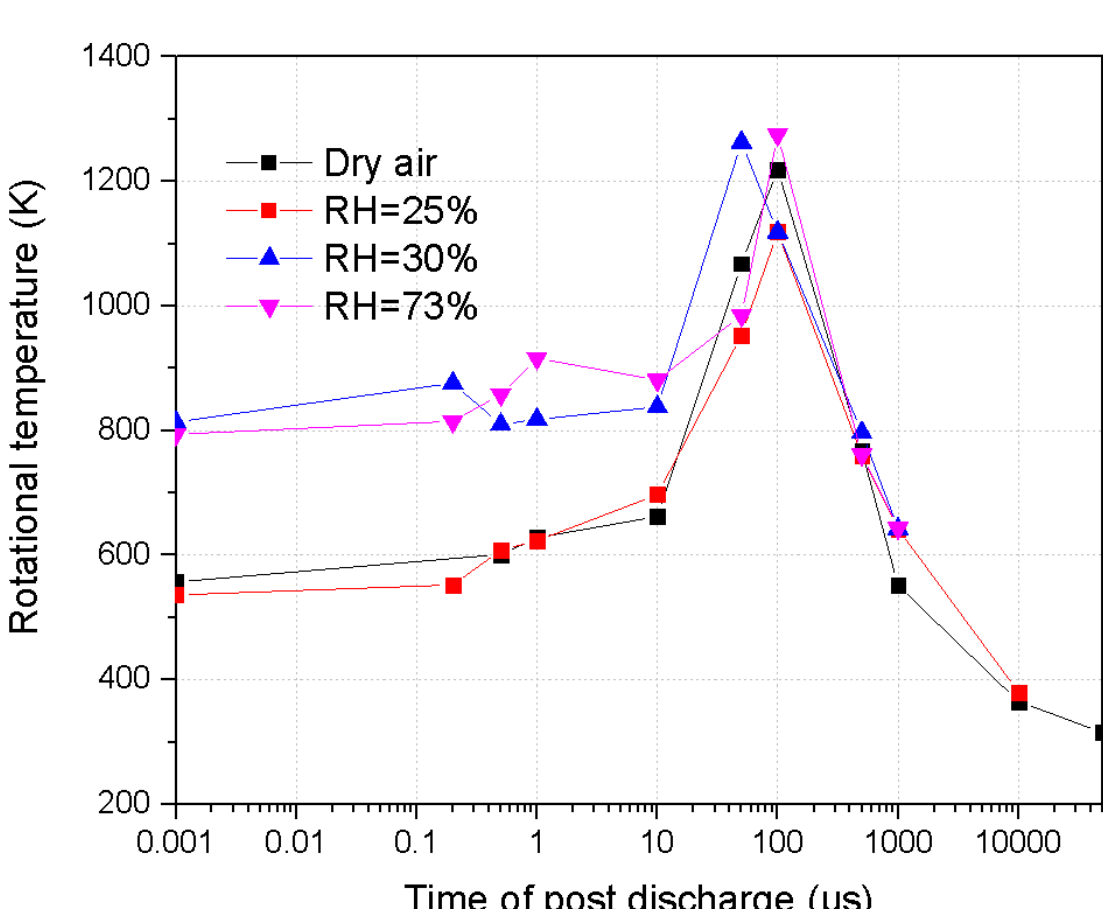


The evolution of the ratio of O<sub>2</sub> and N<sub>2</sub> atoms compared with the equilibrium gives n(O):

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

Just after the discharge, τ<sub>dissociation</sub>(O<sub>2</sub>) ~ 15%  
**O atoms loss is in humid air** is dominantly due to reaction **c**.

## Temperature profiles of N<sub>2</sub> for different relative humidities (85kV - r=0mm - z=1.5mm):



### In dry air:

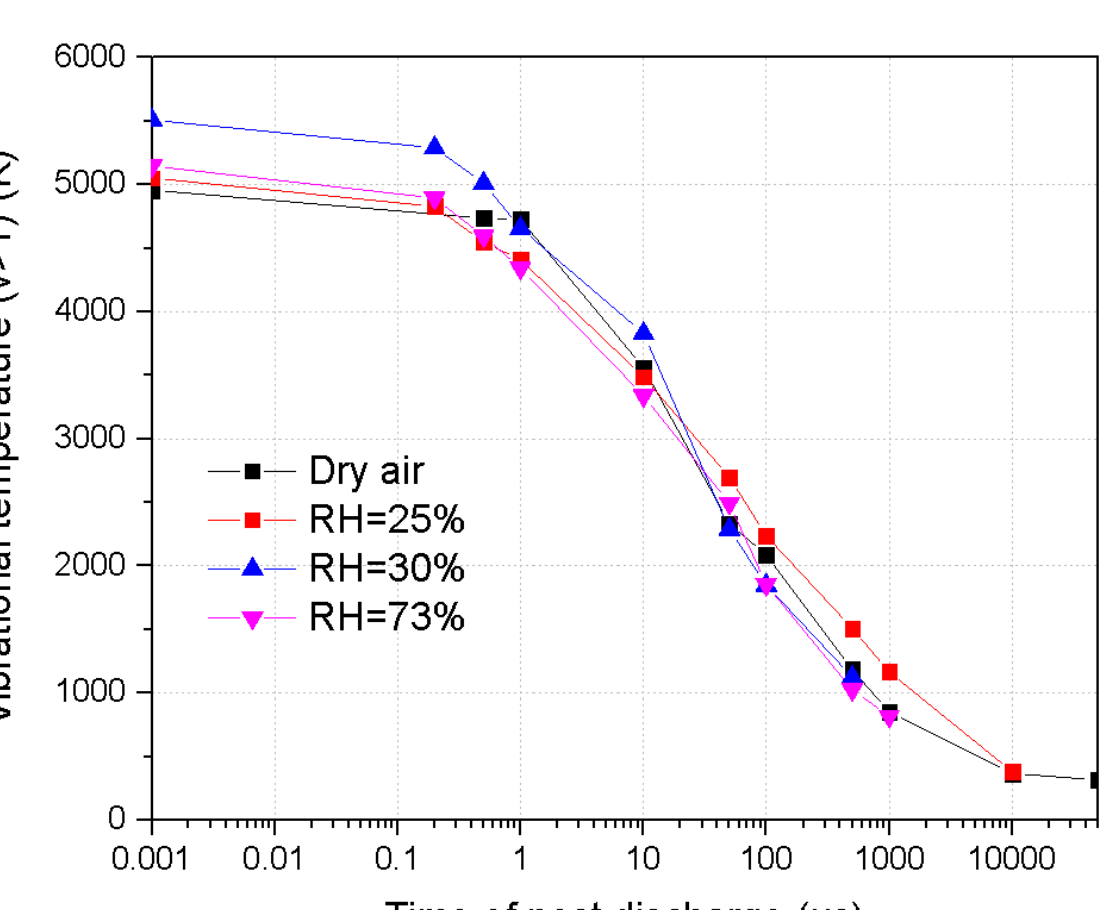
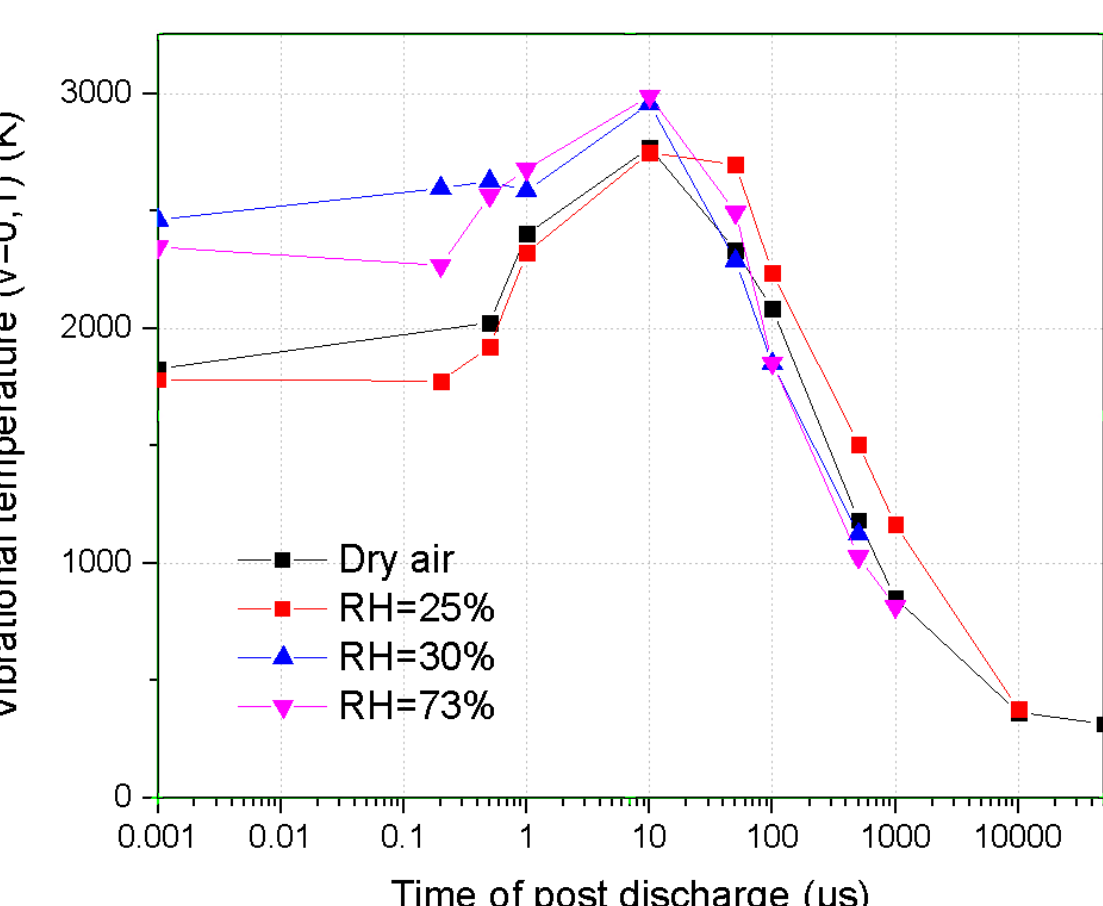
- **Fast heating (+250K)** dominantly due to [2]:
- Quenching of N<sub>2</sub>(C,B) states by O<sub>2</sub>
- Dissociation of O<sub>2</sub> and N<sub>2</sub> by electronic impact
- Quenching of O(<sup>1</sup>D) with N<sub>2</sub> and O<sub>2</sub>
- Reactions involving charged particles

### In humid air:

- **Increased fast heating (+500K)** in less than 300ns [3,4]:
- **Exothermic OH formation**, during the discharge

- By electronic impact from H<sub>2</sub>O:
  - H<sub>2</sub>O + e<sup>-</sup> → H + OH + e<sup>-</sup>
  - H<sub>2</sub>O + e<sup>-</sup> → OH + H
  - H<sub>2</sub>O + e<sup>-</sup> → H + OH
- Other reactions:
  - H + O<sub>2</sub> + M → HO<sub>2</sub> + M, M ∈ [O<sub>2</sub>(v), N<sub>2</sub>(v)]
  - O(<sup>3</sup>P) + HO<sub>2</sub> → OH + O<sub>2</sub>(v)
  - O(<sup>3</sup>P) is decreased by OH + O(<sup>3</sup>P) → O<sub>2</sub>(v) + H and, by loss of O(<sup>1</sup>D) through **c** in quenching reactions with O<sub>2</sub> and N<sub>2</sub>
  - O(<sup>1</sup>D) + H<sub>2</sub>O → 2 OH
  - N<sub>2</sub>(a) + H<sub>2</sub>O → N<sub>2</sub>(v) + OH + H
- **Fast V-T transfers with H<sub>2</sub>O(v):**
  - H<sub>2</sub>O(v<sub>2</sub>) → H<sub>2</sub>O(T) τ = 40ns (independent of temperature)
  - H<sub>2</sub>O(v<sub>1,3</sub>) → H<sub>2</sub>O(T) τ = 100ns
- H<sub>2</sub>O(v) created by electronic impact:
  - H<sub>2</sub>O + e<sup>-</sup> → H<sub>2</sub>O(v<sub>2</sub>=1) + e<sup>-</sup>
  - H<sub>2</sub>O + e<sup>-</sup> → H<sub>2</sub>O(v<sub>1</sub>=1) + e<sup>-</sup>
  - H<sub>2</sub>O + e<sup>-</sup> → H<sub>2</sub>O(v<sub>3</sub>=1) + e<sup>-</sup>
- H<sub>2</sub>O(v) created by quenching with O<sub>2</sub> and N<sub>2</sub>:
  - O<sub>2</sub>(v) + H<sub>2</sub>O → O<sub>2</sub>(v-1) + H<sub>2</sub>O(v) τ ≈ 3μs
  - N<sub>2</sub>(v) + H<sub>2</sub>O → N<sub>2</sub>(v-1) + H<sub>2</sub>O(v) τ ≈ 100μs (300K)
  - τ ≈ 15μs (1000K)

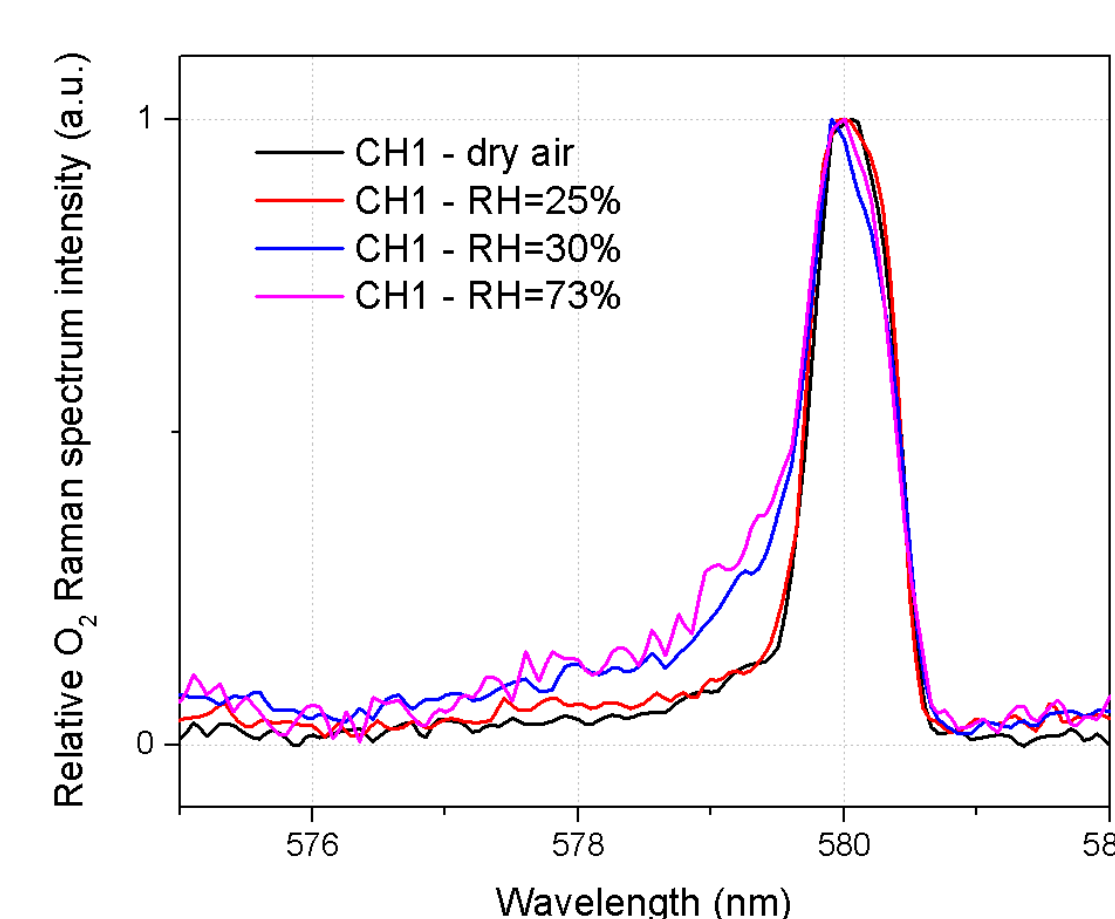
**Increased heating of low vibrational levels of N<sub>2</sub> not yet described.**



## Discussion:

- The large majority of the additional heating due to water vapour probably comes from **fast discharge processes** involving OH or H<sub>2</sub>O(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<sub>2</sub>O(v) quenching with O<sub>2</sub> probably comes from:

- **low vibrational excitation of O<sub>2</sub> in dry air**



Vibrational excitation of O<sub>2</sub> by electron impact is weak due to **low cross sections** contrary to N<sub>2</sub>.

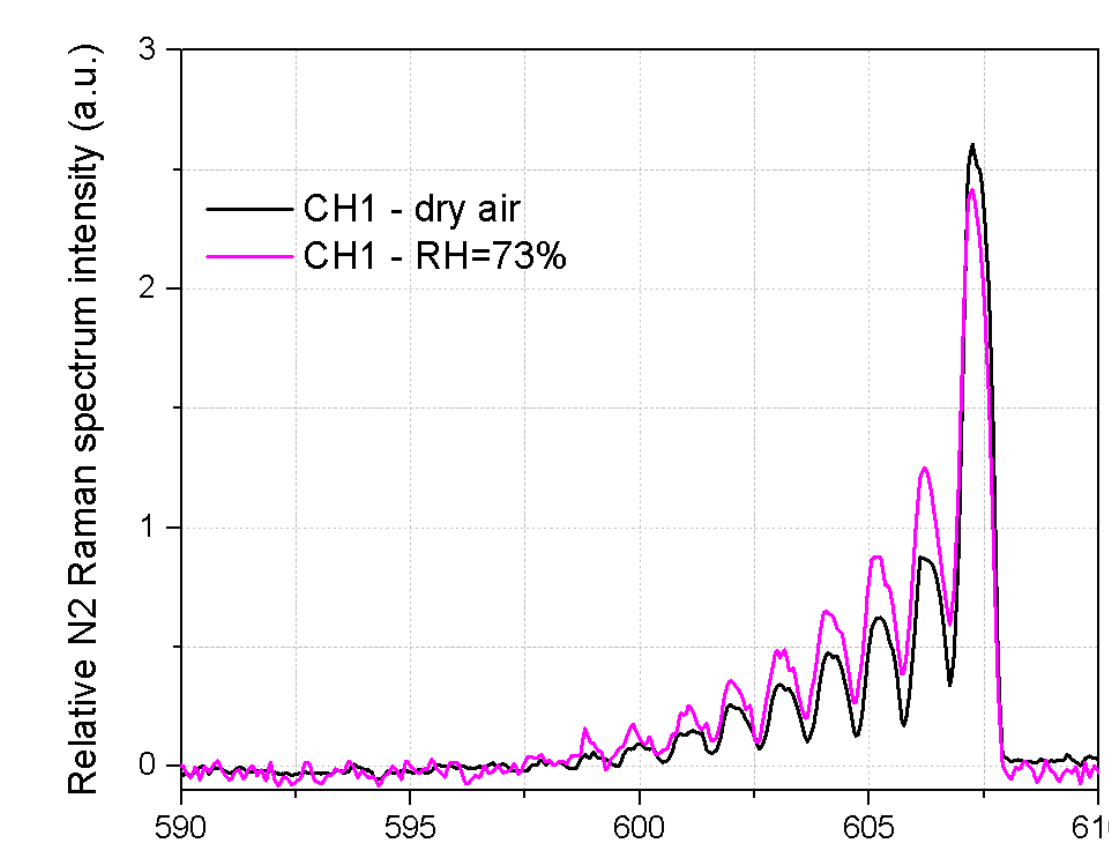
Also O<sub>2</sub>(v) experiences vibrational relaxation by **quenching with O**.

**In humid air**, vibrational excitation of O<sub>2</sub> is enhanced by reactions involving OH and O (reactions **b**, OH + O(<sup>3</sup>P) → O<sub>2</sub>(v) + H) and the quenching with O is much less efficient due to reaction **c**.

- **high O<sub>2</sub> dissociation**

## Vibrational excitation of N<sub>2</sub>:

- 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<sub>2</sub> molecules is stored in vibrational excitation at the end of the discharge and up to ~15% of O<sub>2</sub> 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<sub>2</sub>O. 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:

- [1] P. Tardiveau, L. Magne, E. Marode, K. Ouaras, P. Jeanney and B. Bournonville, Plasma Sources Sci. Technol. 00 (2016) 000000 (16pp)
- [2] N. A. Popov, J. Phys. D: Appl. Phys. 44 285201 (2011)
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