



Zero-dimensional simulations of He, He/O₂, He/N₂ and He/N₂/O₂ microscale atmospheric pressure plasma jet

Y He, E Kemaneci, R P Brinkmann

Motivation

Model

Characterization

Results

Summary

Motivation

- **Applications** of atmospheric pressure plasma jet (APPJ):
 - Surface modification:
higher adhesion, effective cleaning ...
 - Deposition of coating:
high mechanical & electrical properties, corrosion resistance, high-purity coating ...
 - Biomedical application:
sterilization, bacterial inactivation, dentistry, wound healing ...

Penkov OV et al, J Coat Technol Res 12, 225-235 (2015)

Motivation

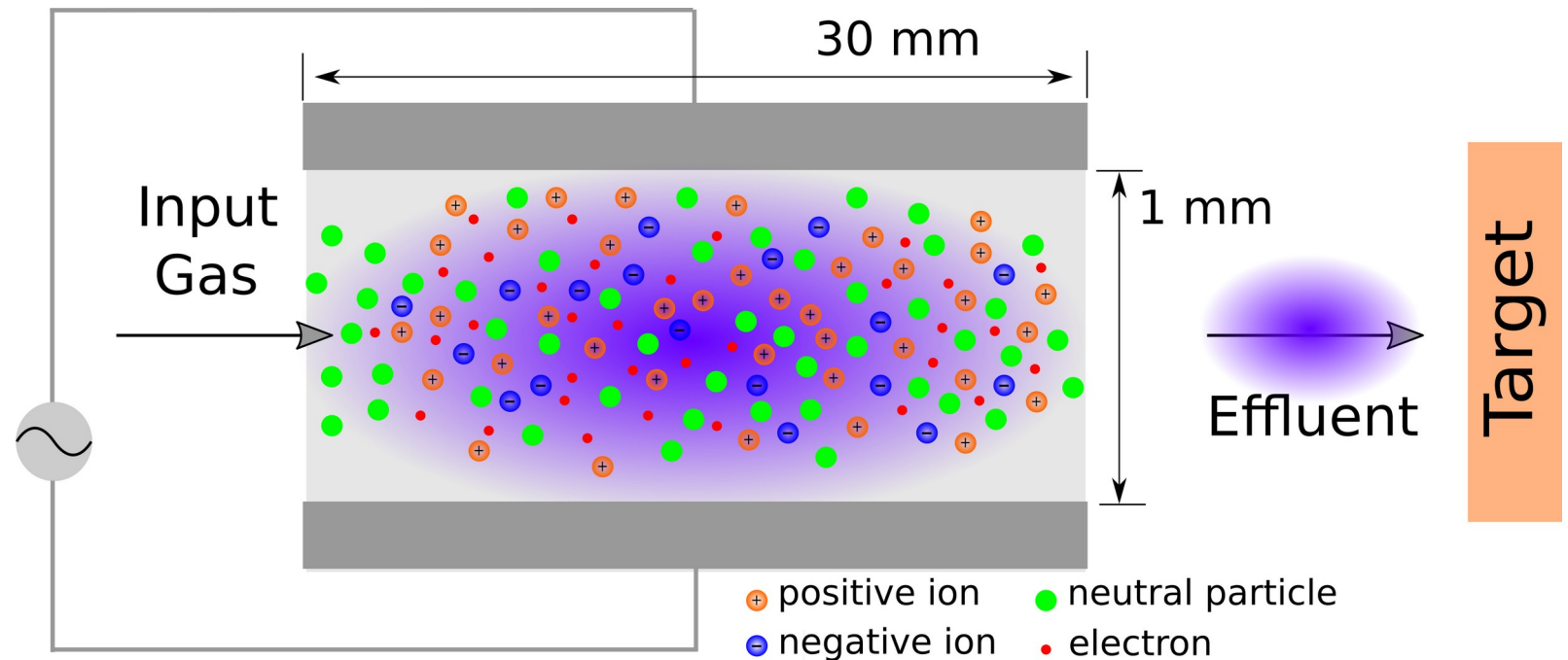
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Diverse applications → **Various designs**

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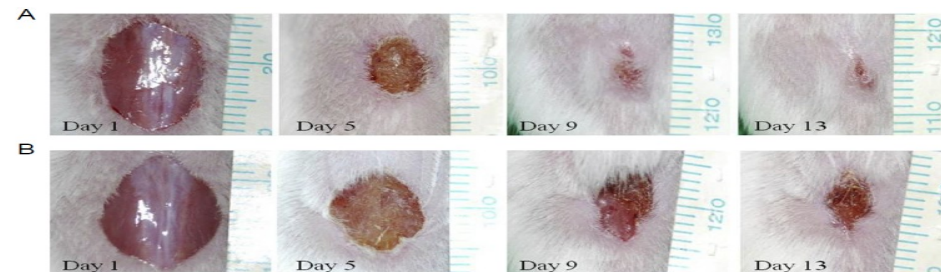
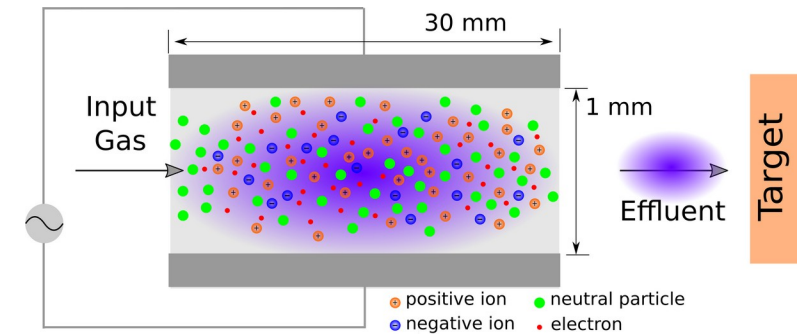
Motivation

- **In this work:** micro-scaled atmospheric pressure plasma jet (μ APPJ)



Motivation

- In this work: micro-scaled atmospheric pressure plasma jet (μ APPJ)
- **Why μ APPJ?**
 - Reduced cost & Enhanced flexibility
 - Highly produced reactive species & Room temperature
 - Sensitive surface → Bio-medicine

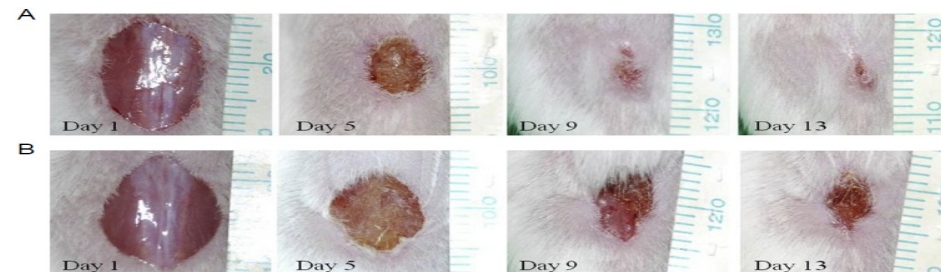
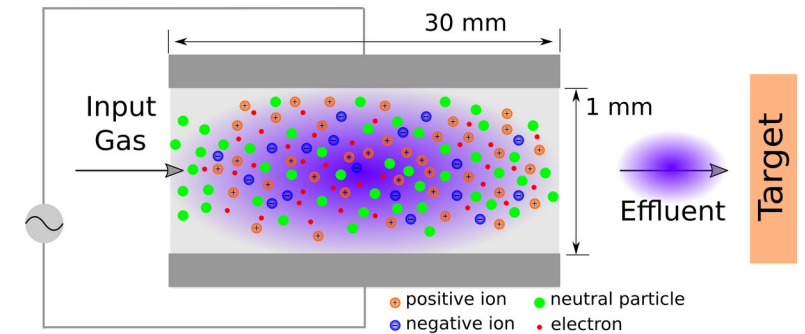


K-D Weltmann et al 2008 J. Phys. D: Appl. Phys. 41 194008

Y.-W. Hung et al. / Journal of the Chinese Medical Association 79 (2016) 320e328

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Reactive species
NO

↓
Dosis ?

Challenge: (N_2/O_2)

Complex chemical
kinetics

K-D Weltmann et al 2008 J. Phys. D: Appl. Phys. 41 194008

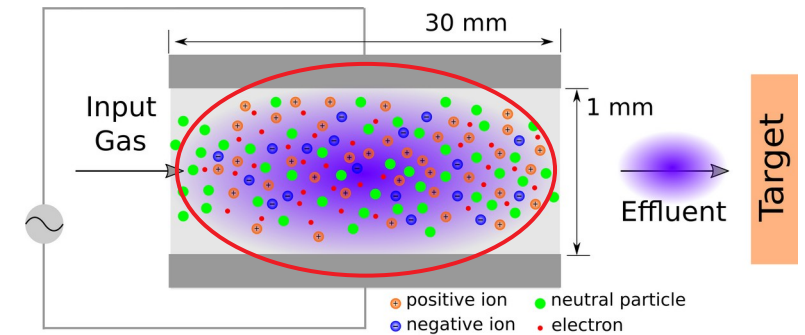
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Model(Physically)

- 0-D model (volume-averaged)
 - Particle & Electron energy balance equation (Z)

$$\frac{dN_i}{dt} = S_i^V + S_i^W \quad \frac{d}{dt} \left(\frac{3}{2} N_e T_e \right) = P^V + P^W$$

- Boltzmann solver (LoKI)
Electron kinetics in complex gas mixture
(Vibrational kinetics)



Model(Physically)

- 0-D model (volume-averaged) 

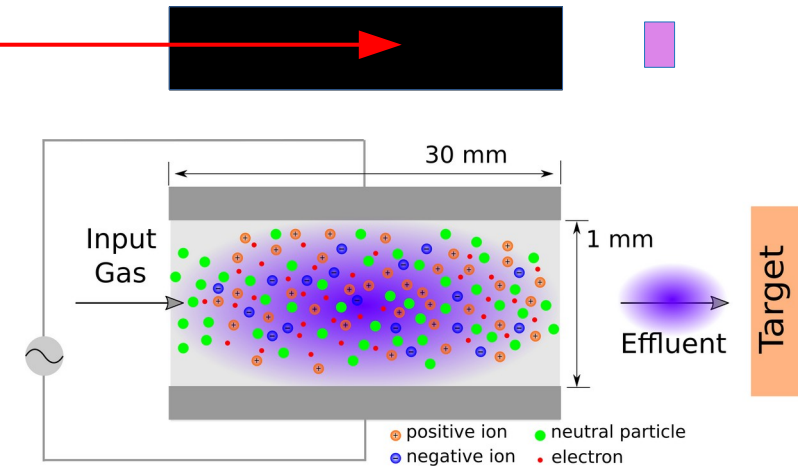
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- 0-D model + plug flow → pseudo 1-D model 



 : Simulation region  : Chamber region  : Effluent region

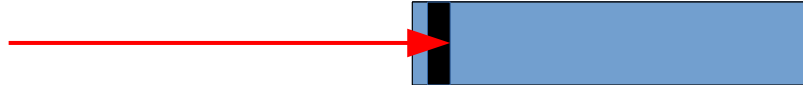
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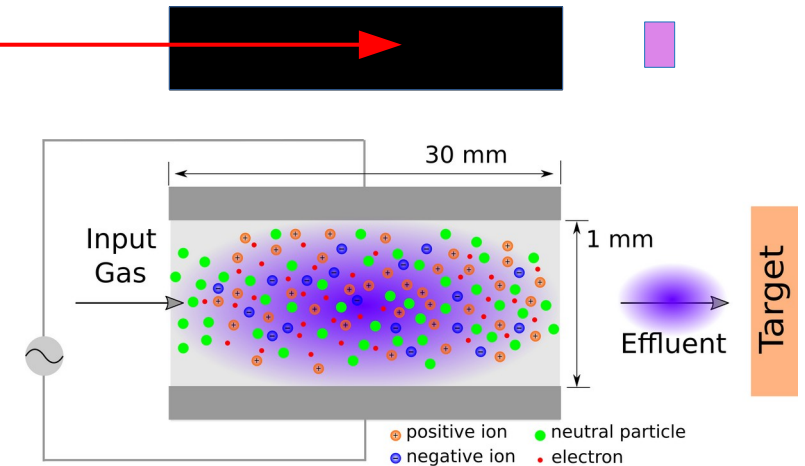
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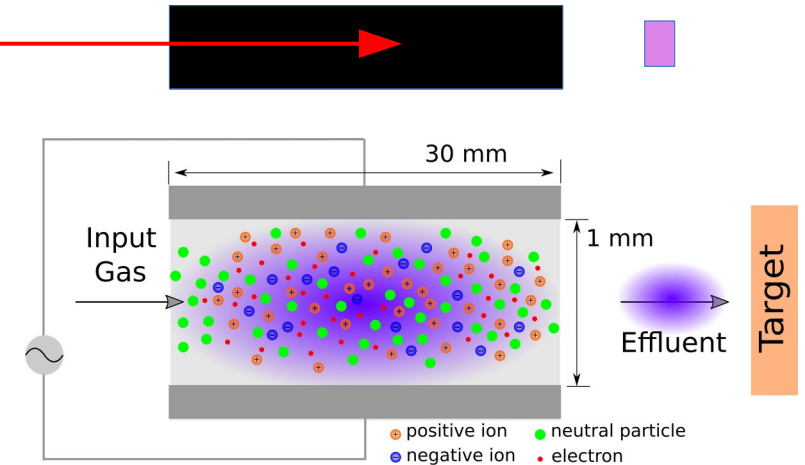
- 0-D model (volume-averaged) —————→

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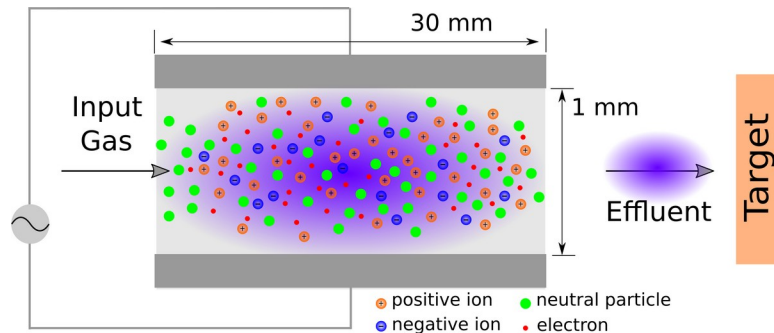
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: Simulation region
 : Chamber region
 : Effluent region

Model(Chemically)

- Input gas: He/N₂/O₂ (for RNOS)
 - He → He/N₂ , He/O₂ → He/N₂/O₂



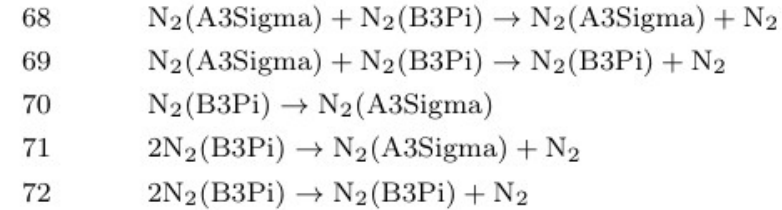
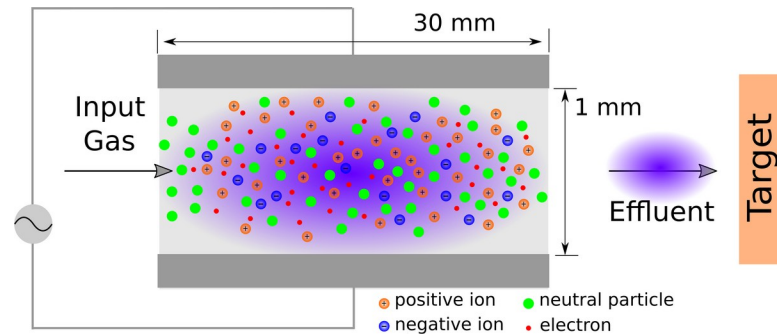
#	Reaction
#	Electron - Neutral Particle Collision
1	$e + \text{He} \rightarrow 2e + \text{He}^+$
2	$e + \text{He} \rightarrow e + \text{He}(2^3\text{S})$
3	$e + \text{He}(2^3\text{S}) \rightarrow 2e + \text{He}^+$
4	$e + \text{He}_2^* \rightarrow e + 2\text{He}$
5	$e + \text{He}_2^* \rightarrow 2e + \text{He}_2^+$
#	Electron - Ion Particle Collision
6	$e + \text{He}^+ \rightarrow \text{He}(2^3\text{S})$
7	$2e + \text{He}^+ \rightarrow e + \text{He}(2^3\text{S})$
8	$e + \text{He}^+ + \text{He} \rightarrow \text{He}(2^3\text{S}) + \text{He}$
9	$e + \text{He}_2^+ \rightarrow \text{He} + \text{He}$
10	$e + \text{He}_2^+ \rightarrow \text{He}(2^3\text{S}) + \text{He}$
11	$e + \text{He}_2^+ + \text{He} \rightarrow 3\text{He}$
12	$e + \text{He}_2^+ + \text{He} \rightarrow \text{He}(2^3\text{S}) + 2\text{He}$
13	$e + \text{He}_2^+ + \text{He} \rightarrow \text{He}_2^* + \text{He}$
14	$2e + \text{He}_2^+ \rightarrow e + \text{He}_2^*$
15	$2e + \text{He}_2^+ \rightarrow e + \text{He} + \text{He}(2^3\text{S})$
#	Ion - Neutral Particle Collision
16	$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$
#	Ion - Ion Particle Collision
#	Neutral - Neutral Particle Collision
17	$\text{He}(2^3\text{S}) + 2\text{He} \rightarrow \text{He}_2^* + \text{He}$
18	$\text{He}(2^3\text{S}) + 2\text{He} \rightarrow 3\text{He}$
19	$\text{He}(2^3\text{S}) + \text{He}(2^3\text{S}) \rightarrow e + \text{He}_2^+$
20	$\text{He}(2^3\text{S}) + \text{He}(2^3\text{S}) \rightarrow e + \text{He}^+ + \text{He}$
21	$\text{He}(2^3\text{S}) + \text{He}_2^* \rightarrow e + \text{He}_2^+ + \text{He}$
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23	$\text{He}_2^* \rightarrow 2\text{He}$
24	$\text{He}_2^* + \text{He} \rightarrow 3\text{He}$
25	$\text{He}_2^* + \text{He}_2^* \rightarrow e + \text{He}_2^+ + 2\text{He}$
26	$\text{He}_2^* + \text{He}_2^* \rightarrow e + \text{He}^+ + 3\text{He}$

He

- 6 species
- 26 reactions

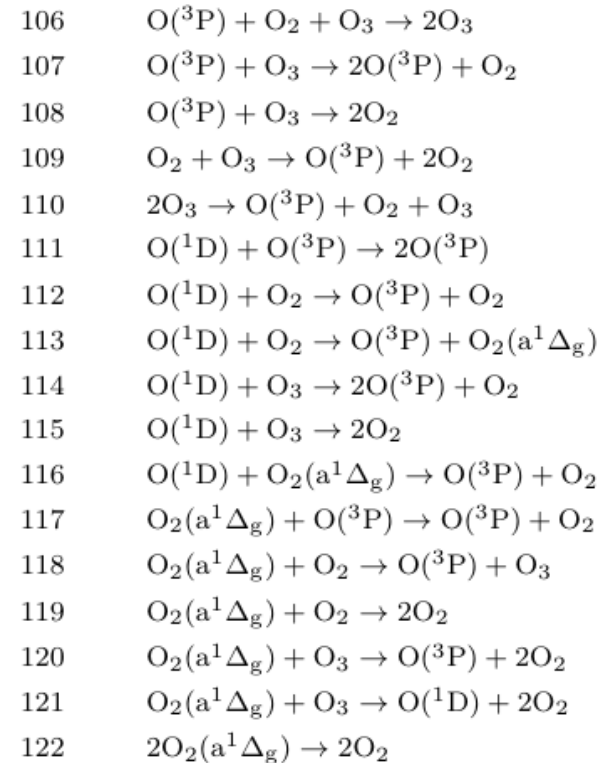
Model(Chemically)

- Input gas: $\text{He}/\text{N}_2/\text{O}_2$ (for RNOS)
 - $\text{He} \rightarrow \text{He}/\text{N}_2$, $\text{He}/\text{O}_2 \rightarrow \text{He}/\text{N}_2/\text{O}_2$



He/N_2

- 17 species
- 98 reactions

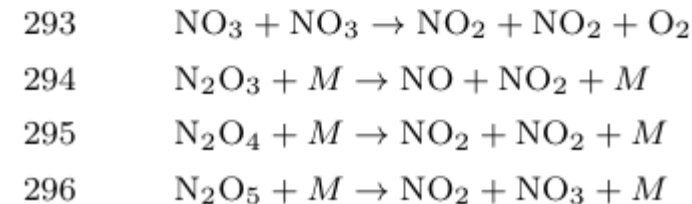
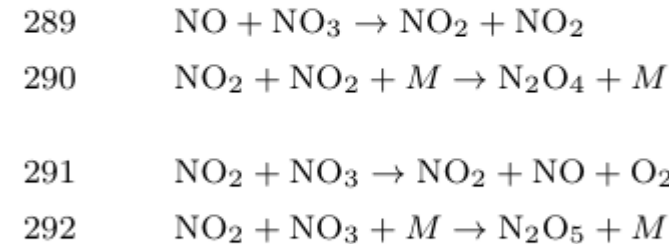
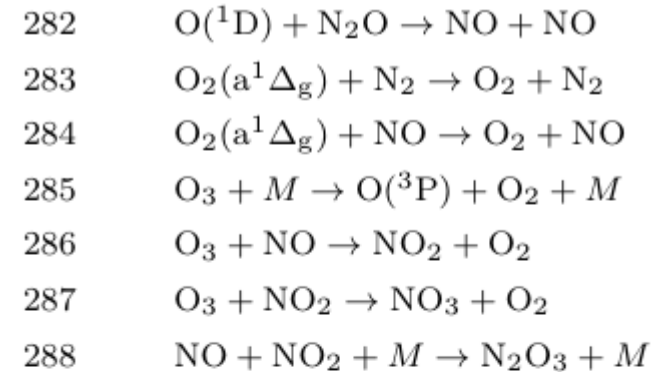
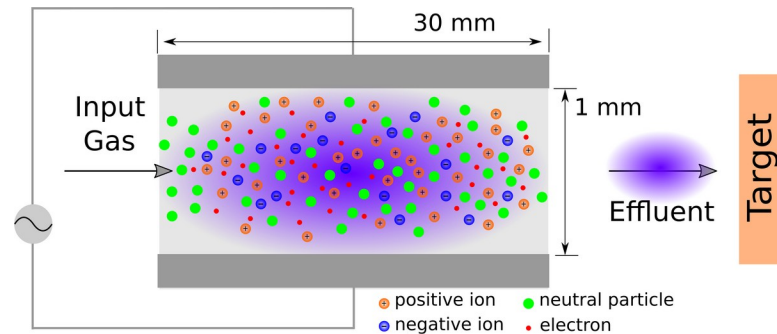


He/O_2

- 18 species
- 148 reactions

Model(Chemically)

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He/O_2

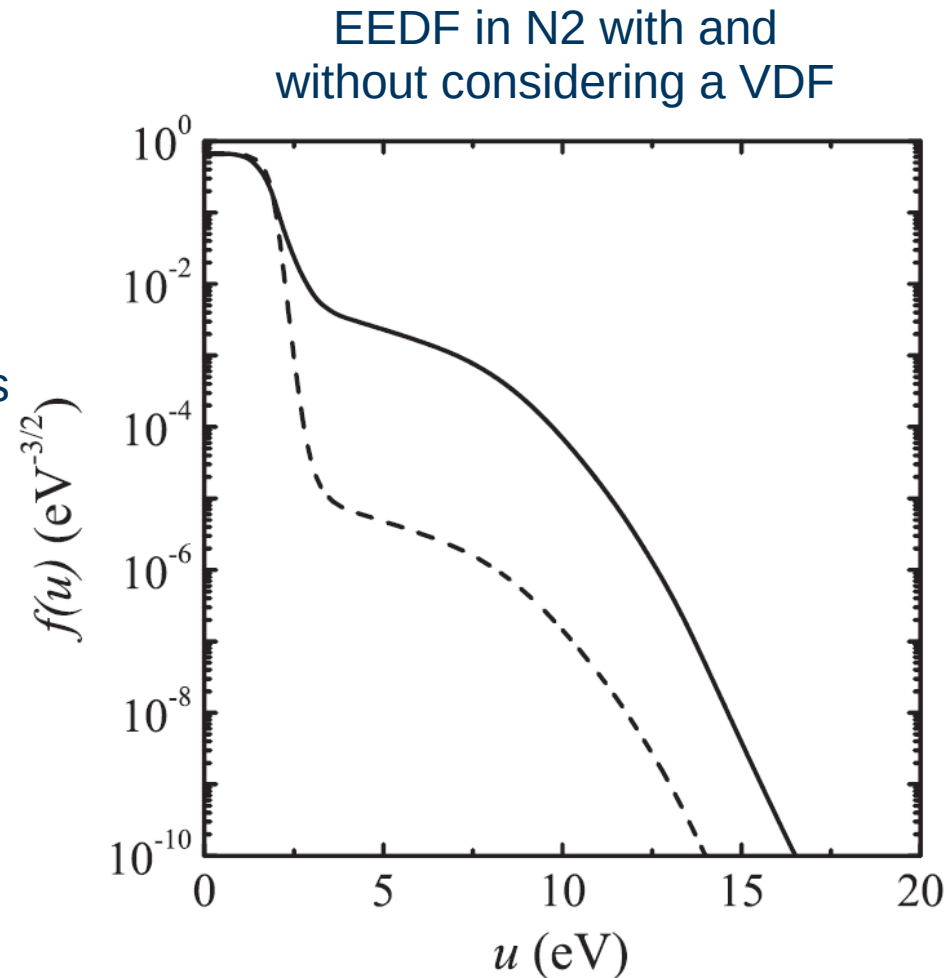
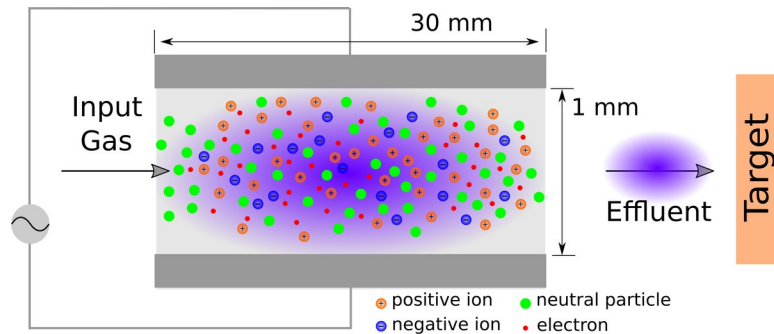
- 18 species
- 148 reactions

$\text{He}/\text{N}_2/\text{O}_2$

- 41 species
- 516 reactions

Model(Chemically)

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 - $\text{He} \rightarrow \text{He}/\text{N}_2$, $\text{He}/\text{O}_2 \rightarrow \text{He}/\text{N}_2/\text{O}_2$
 - Challenge: Complex chemical kinetics
 - Why vibrational level?



He/N_2

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He/O_2

- 18 species
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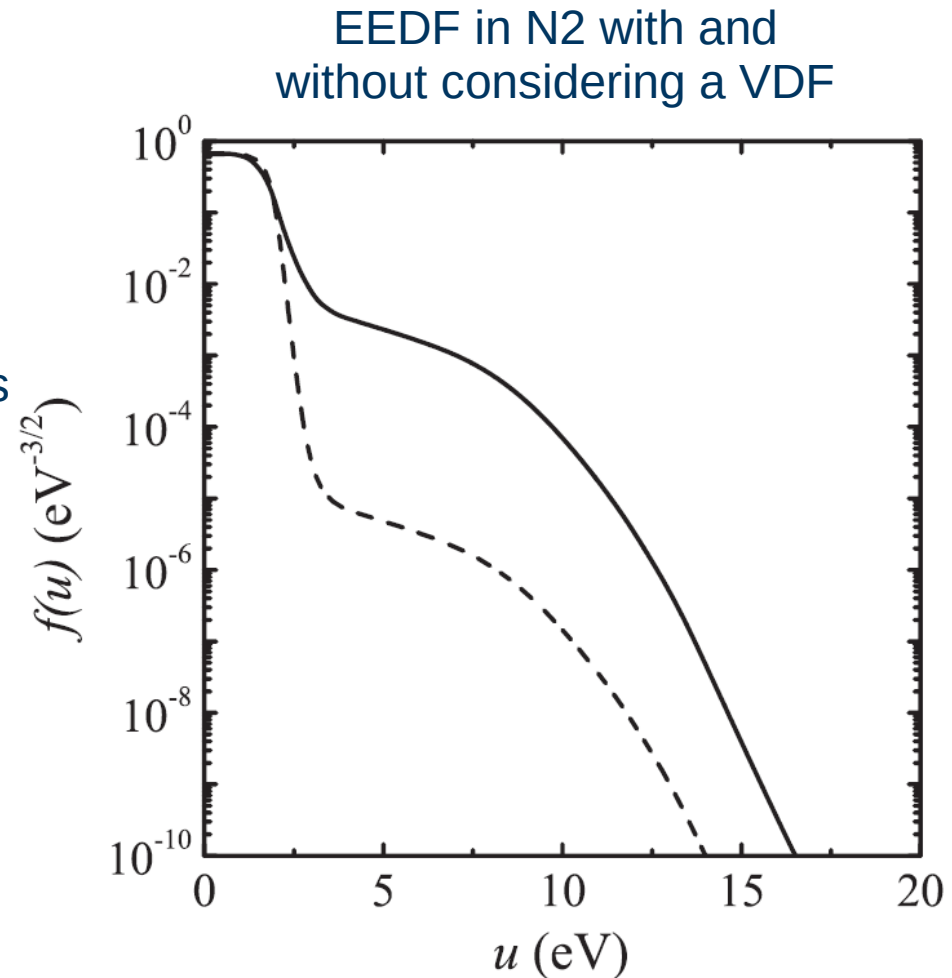
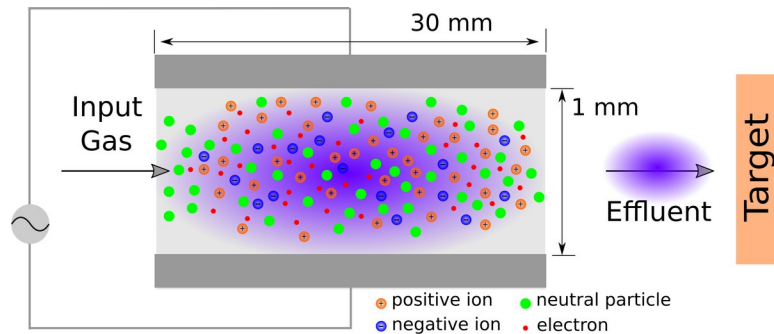
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Vasco Guerra et al 2019 Plasma Sources Sci. Technol. 28 073001

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$\text{He}/\text{N}_2 + \text{vib}$

- 72 species
- 5762 reactions

$\text{He}/\text{O}_2 + \text{vib}$

- 58 species
- 3164 reactions

$\text{He}/\text{N}_2/\text{O}_2 + \text{vib}$

- 138 species
- 11733 reactions

Vasco Guerra et al 2019 Plasma Sources Sci. Technol. 28 073001

Model(Chemically)

He-N₂(0<v<58) vibrational kinetics

#	Reaction
#	E-V Kinetics
1	$e + N_2(v \geq 0) \rightarrow e + N_2(v < w)$
2	$e + N_2(v > 0) \rightarrow e + N + N$
3	$e + N_2(v = 1 - 35) \rightarrow e + N + N(^2D)$
4	$e + N_2(v = 1 - 35) \rightarrow e + e + N_2^+$
#	V-T Kinetics
5*	$N + N_2(v \geq 1) \rightarrow N + N_2(v - 1)$
6*	$N_2 + N_2(v \geq 1) \rightarrow N_2 + N_2(v - 1)$
7*	$He + N_2(v \geq 1) \rightarrow He + N_2(v - 1)$
#	V-V Kinetics
8	$N_2(v \geq 0) + N_2(w > 0) \rightarrow N_2(v + 1) + N_2(w - 1)$
#	Other Kinetics
9	$He^+ + N_2(v \geq 1) \rightarrow He + N_2^+$
10	$He^+ + N_2(v \geq 1) \rightarrow He + N + N^+$
11	$He(2^3S) + N_2(v \geq 1) \rightarrow e + He + N_2^+$

He-O₂(0<v<41) vibrational kinetics

#	Reaction
#	E-V Kinetics
1	$e + O_2(v \geq 0) \rightarrow e + O_2(v < w)$
2	$e + O_2(v > 0) \rightarrow e + O + O$
3	$e + O_2(v > 0) \rightarrow O + O^-$
4	$e + O_2(v = 1 - 32) \rightarrow e + e + O_2^+$
#	V-T Kinetics
5*	$O + O_2(v \geq 1) \rightarrow O + O_2(v - 1)$
6*	$O_2 + O_2(v \geq 1) \rightarrow O_2 + O_2(v - 1)$
7*	$He + O_2(v \geq 1) \rightarrow He + O_2(v - 1)$
#	V-V Kinetics
8	$O_2(v \geq 0) + O_2(w > 0) \rightarrow O_2(v + 1) + O_2(w - 1)$
#	Other Kinetics
9	$He^+ + O_2(v \geq 1) \rightarrow He + O_2^+$
10	$He^+ + O_2(v \geq 1) \rightarrow He + O + O^+$
11	$He(2^3S) + O_2(v \geq 1) \rightarrow e + He + O_2^+$
12	$O + O_2(v > 0) \rightarrow 3O$

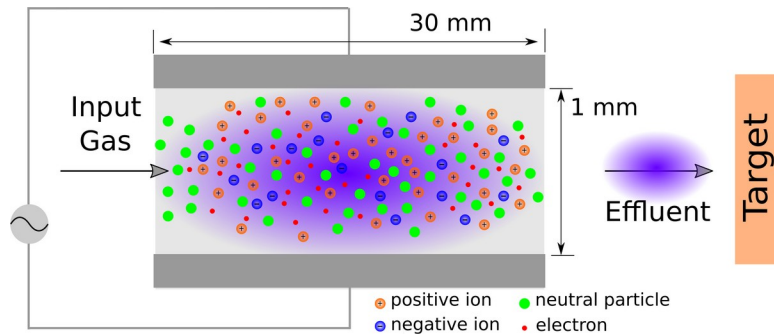
Model(Chemically)

$\text{N}_2\text{-O}_2$ vibrational kinetics

#	Reaction
1 V-T	$\text{O} + \text{N}_2(v \geq 1) \rightarrow \text{O} + \text{N}_2(v - 1)$
2 V-T	$\text{O}_2 + \text{N}_2(v \geq 1) \rightarrow \text{O}_2 + \text{N}_2(v - 1)$
3 V-T	$\text{N}_2 + \text{O}_2(v \geq 1) \rightarrow \text{N}_2 + \text{O}_2(v - 1)$
4 V-V	$\text{O}_2(v \geq 0) + \text{N}_2(w > 1) \rightarrow \text{O}_2(v + 1) + \text{N}_2(w - 1)$
5	$\text{N}_2(v \geq 13) + \text{O}({}^3\text{P}) \rightarrow \text{NO} + \text{N}({}^4\text{S})$
6	$\text{N}({}^4\text{S}) + \text{NO} \rightarrow \text{N}_2(v = 3) + \text{O}({}^3\text{P})$

Model

- Input gas: $\text{He}/\text{N}_2/\text{O}_2$ (138/11733)
 - $\text{He} \rightarrow \text{He}/\text{N}_2 \rightarrow \text{He}/\text{O}_2 \rightarrow \text{He}/\text{N}_2/\text{O}_2$
 - Why vibrational level?
 - **Validity?**
 - Yes, **bechmarked.**



Model

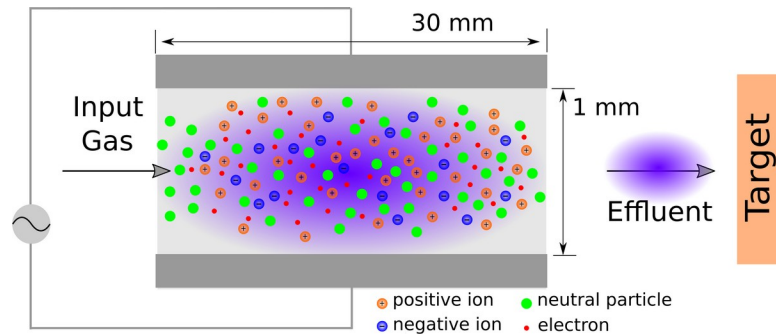
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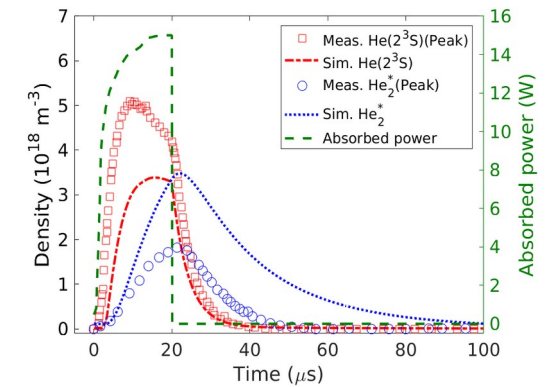
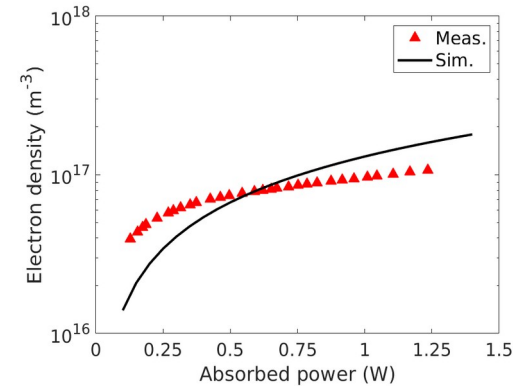
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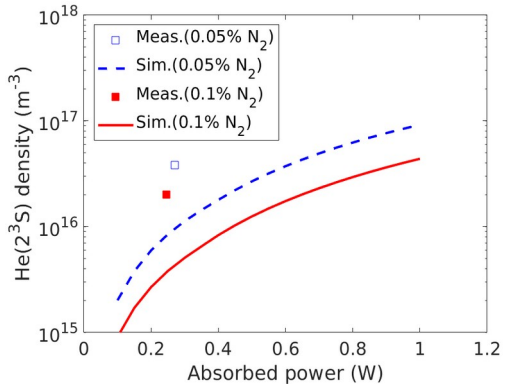
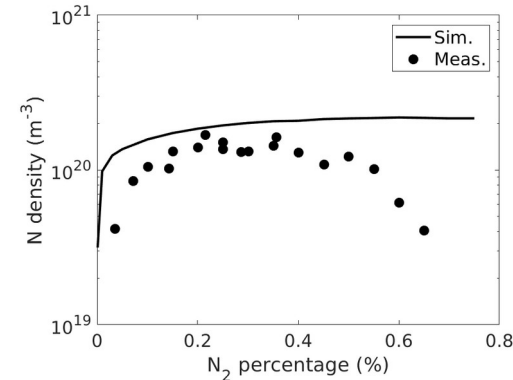
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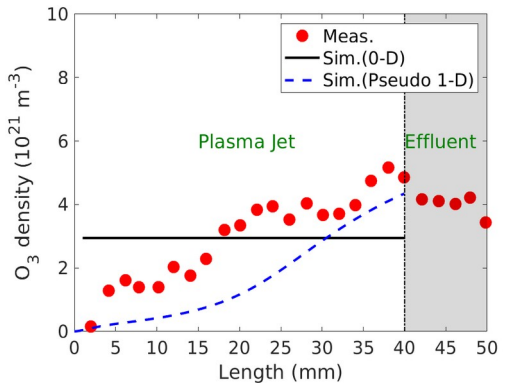
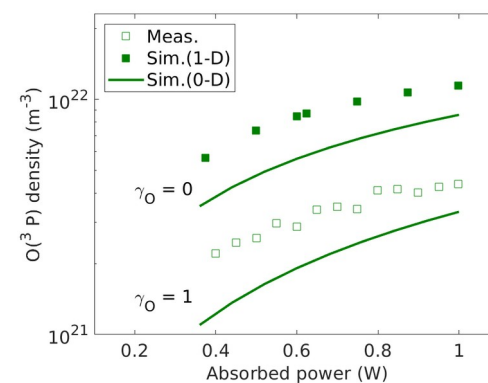
He



He/N_2



He/O_2



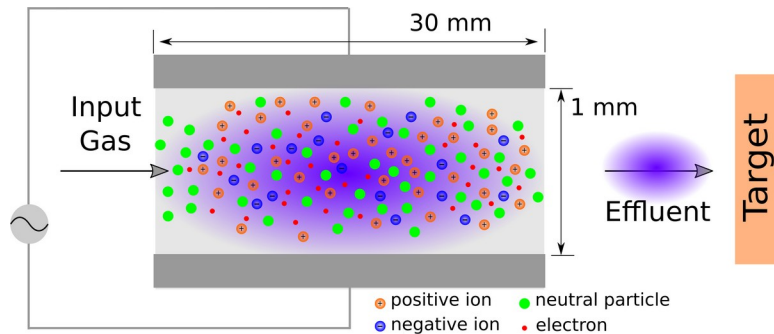
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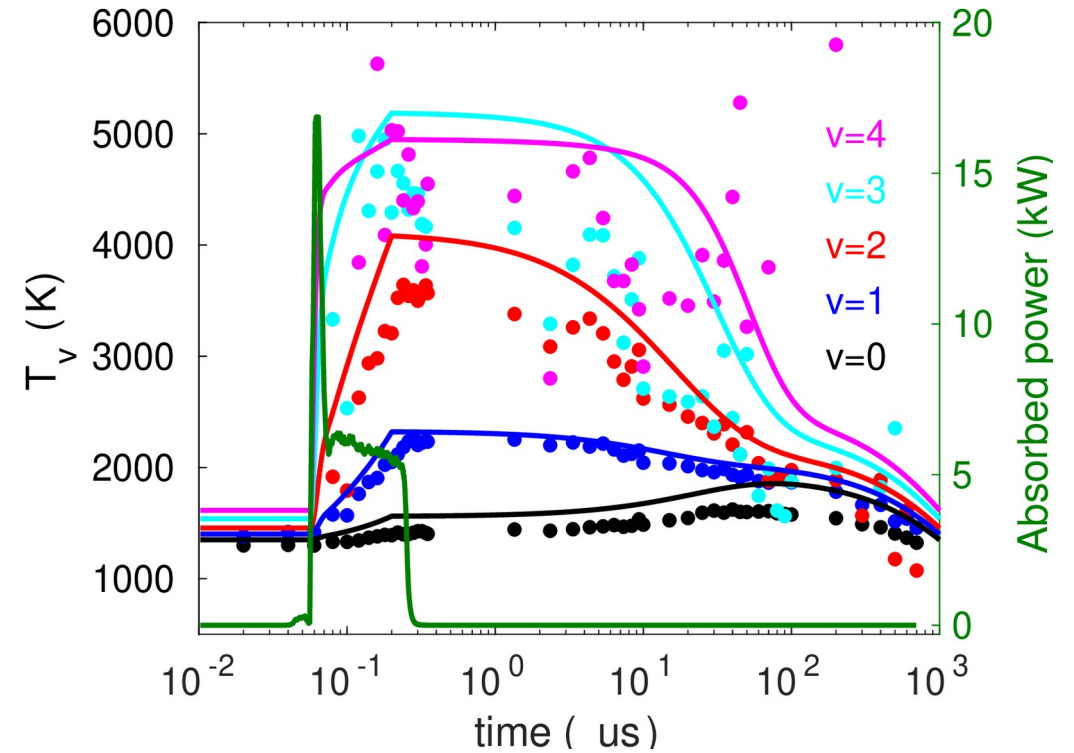
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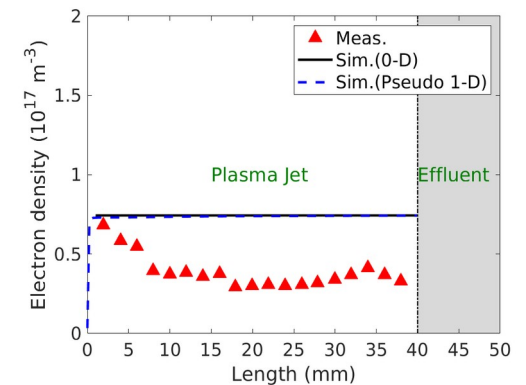
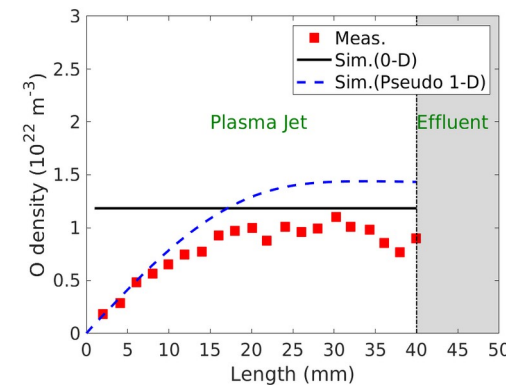
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N_2

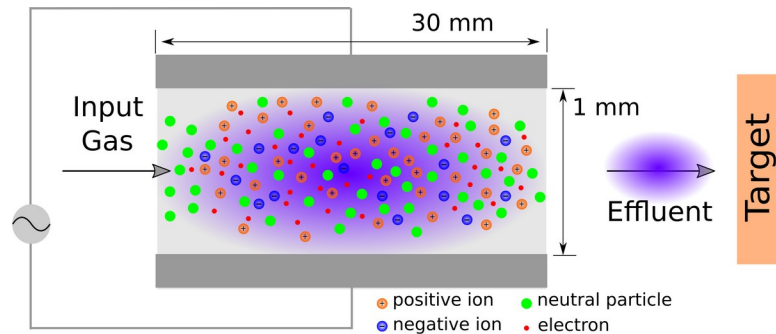


He/O_2



Characterization

- Input gas: He/N₂/O₂
 - Dosis of NO? How to control?
 - Admixture?
 - He gas flow?
 - Absorbed power?

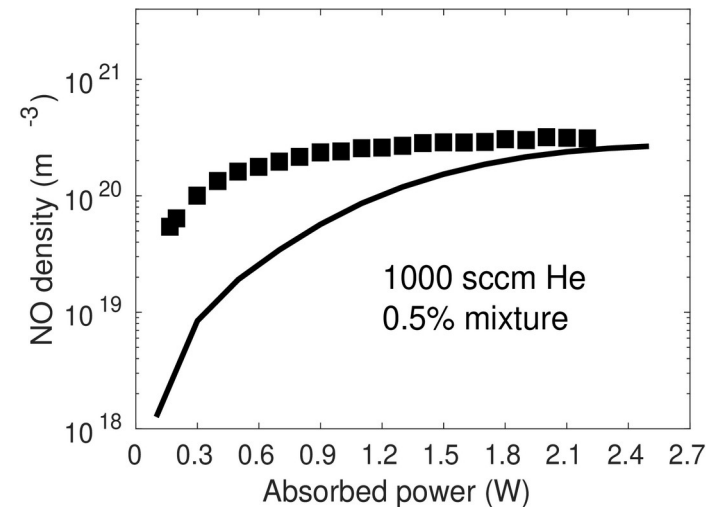
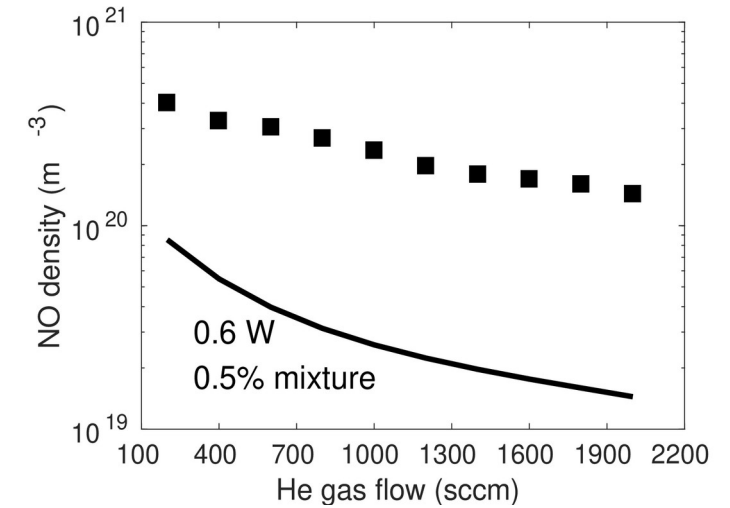
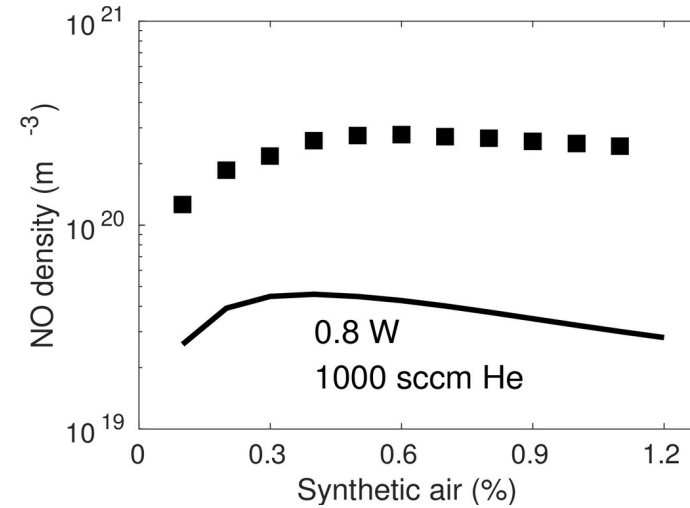
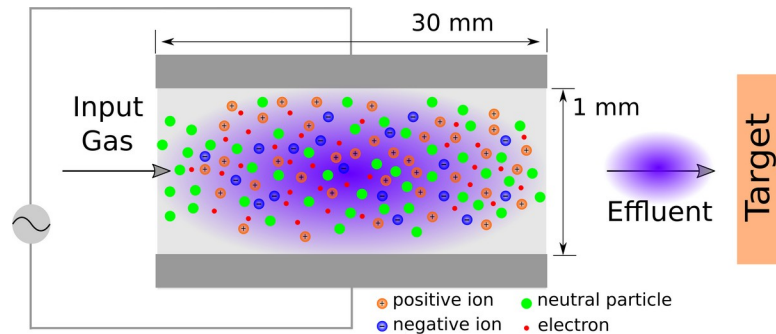


Characterization

- Input gas: He/N₂/O₂

Dosis of NO? **Controlled by:**

- Admixture
- He gas flow
- Absorbed power



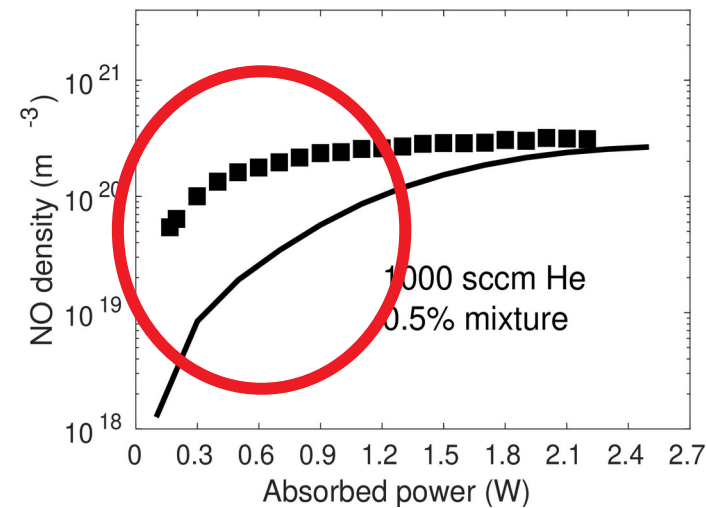
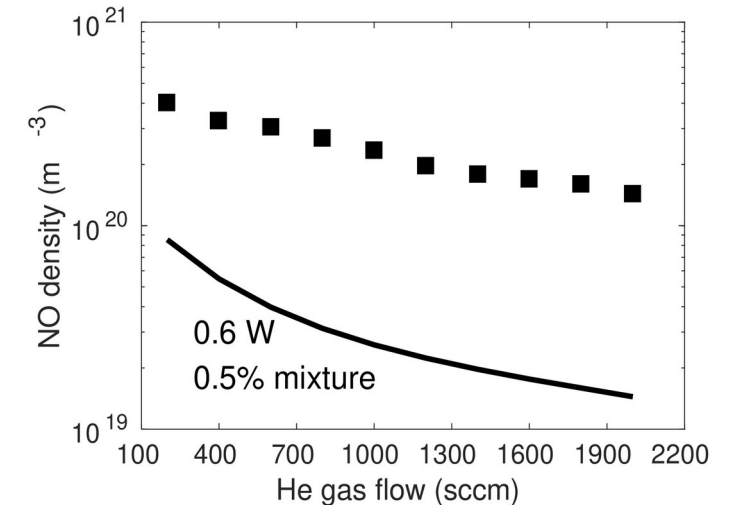
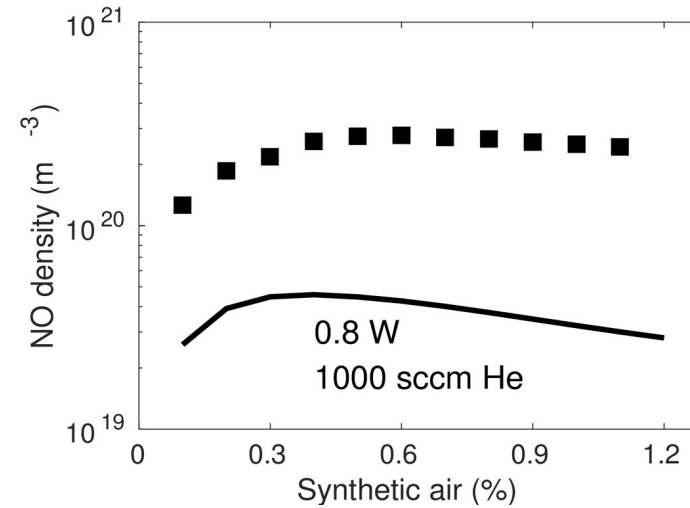
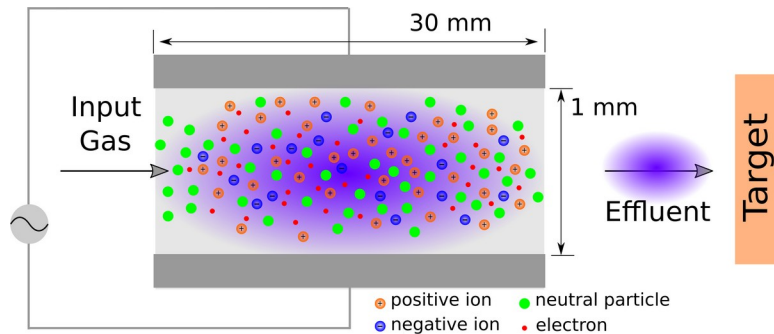
Deviation !

Characterization

- Input gas: He/N₂/O₂

Dosis of NO? **Controlled by:**

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- He gas flow
- Absorbed power



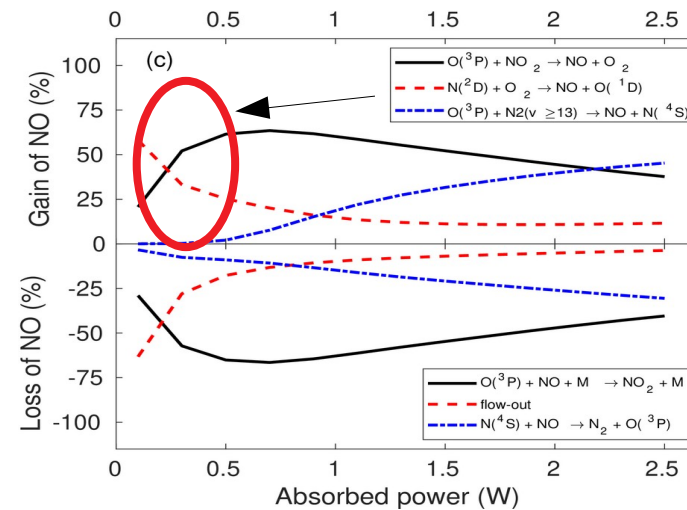
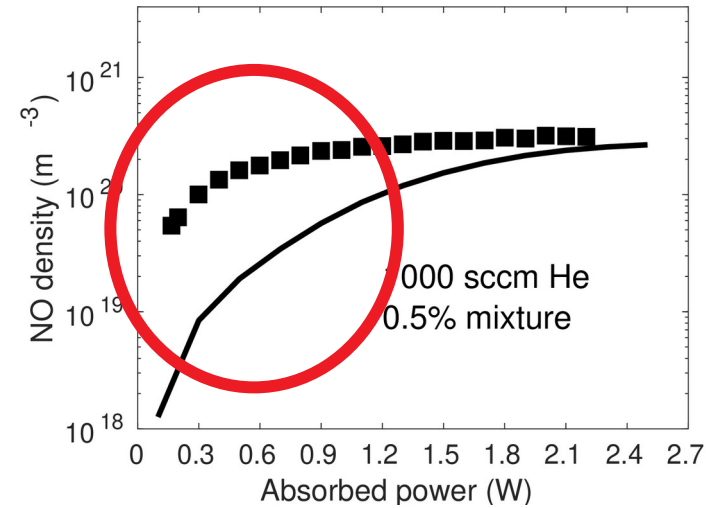
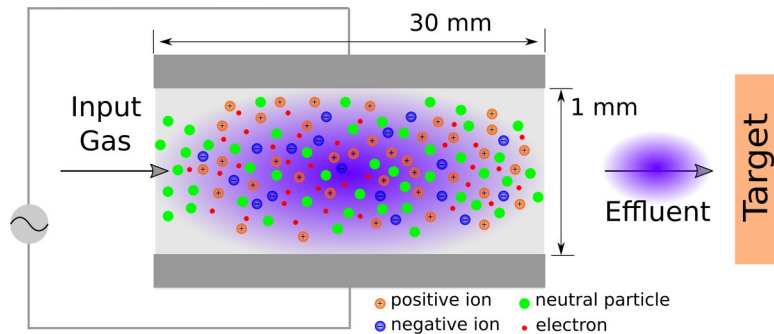
Main problem !

Characterization

- Input gas: $\text{He}/\text{N}_2/\text{O}_2$

Dosis of NO? Controlled by:

- Admixture
- He gas flow
- Absorbed power



Dominant channels

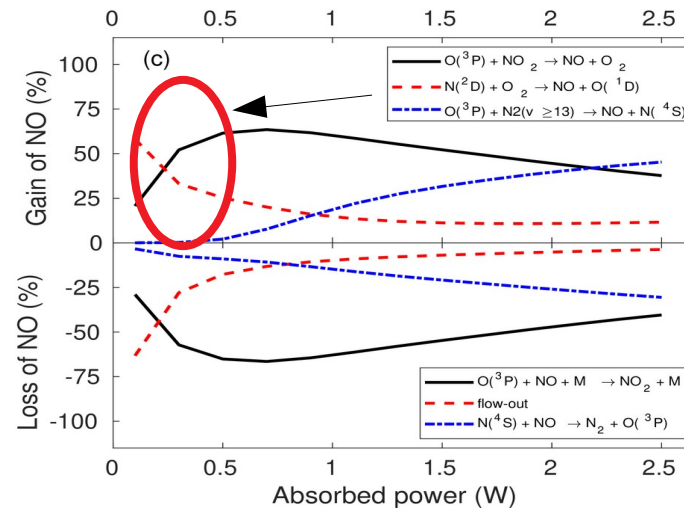
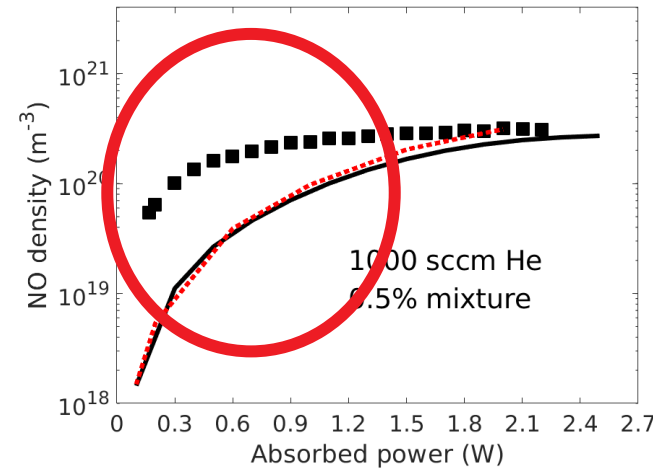
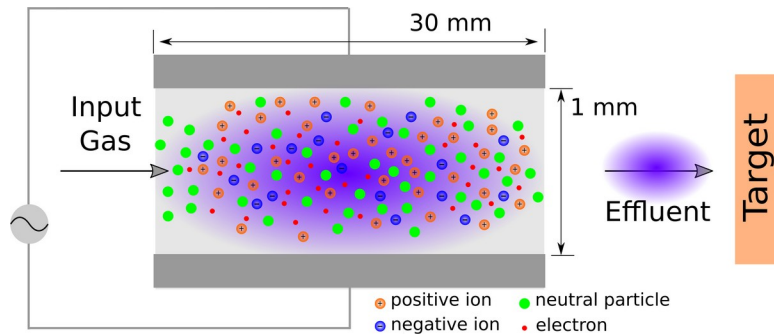


Characterization

- Input gas: $\text{He}/\text{N}_2/\text{O}_2$

Dosis of NO? Controlled by:

- Admixture
- He gas flow
- Absorbed power



still
Deviation !

$$k \sim 10^{-18} \text{ m}^3/\text{s} \rightarrow \sim 10^{-15} \text{ m}^3/\text{s}$$

Dominant channels

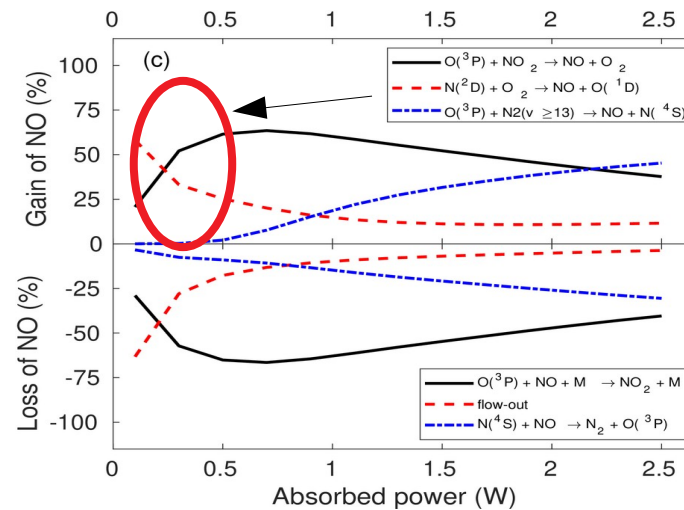
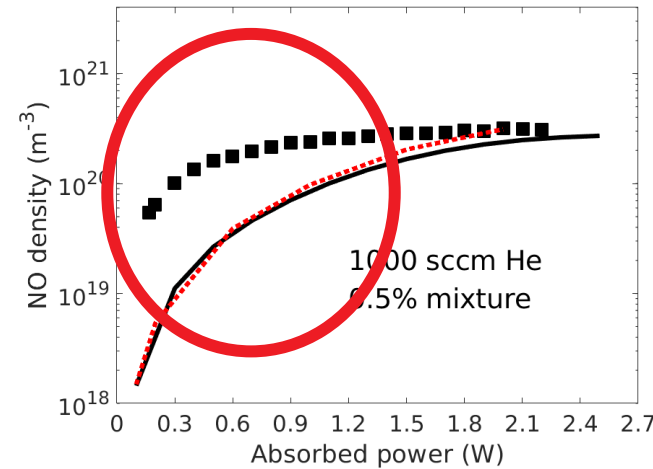
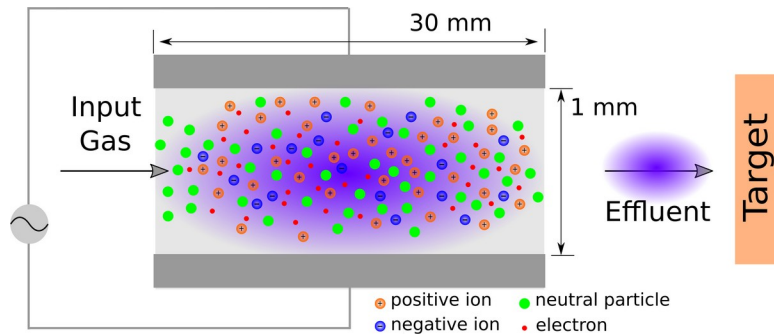


Characterization

- Input gas: He/N₂/O₂

Dosis of NO? Controlled by:

- Admixture
- He gas flow
- Absorbed power



still
Deviation !

$$k \sim 10^{-18} \text{ m}^3/\text{s} \rightarrow \sim 10^{-15} \text{ m}^3/\text{s}$$

Dominant channels



$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

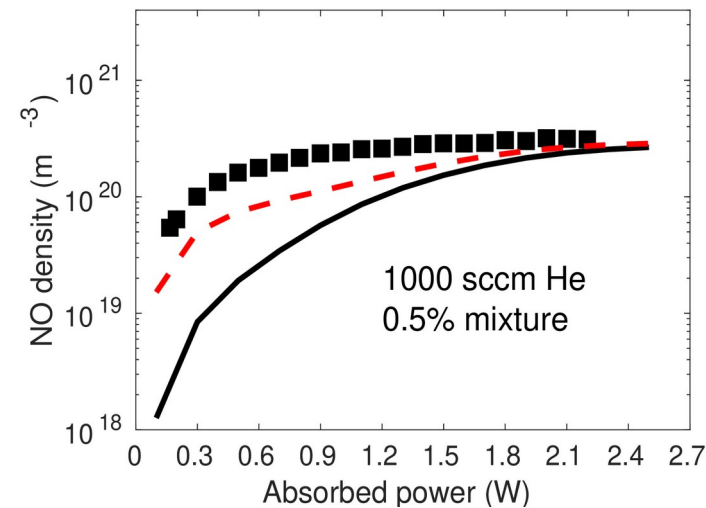
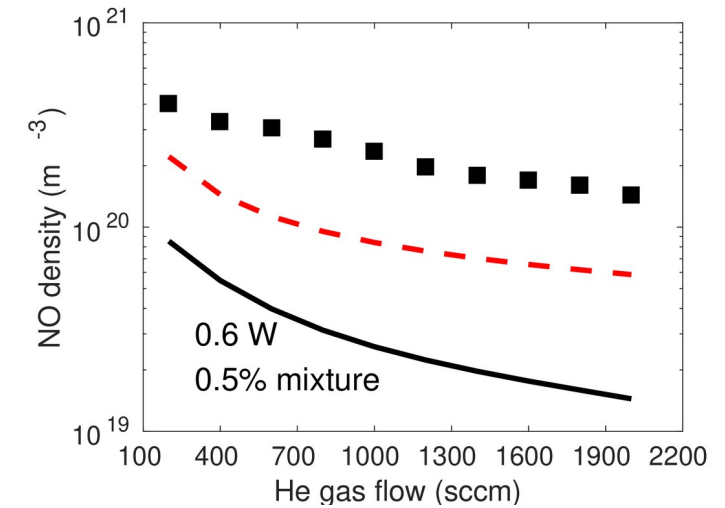
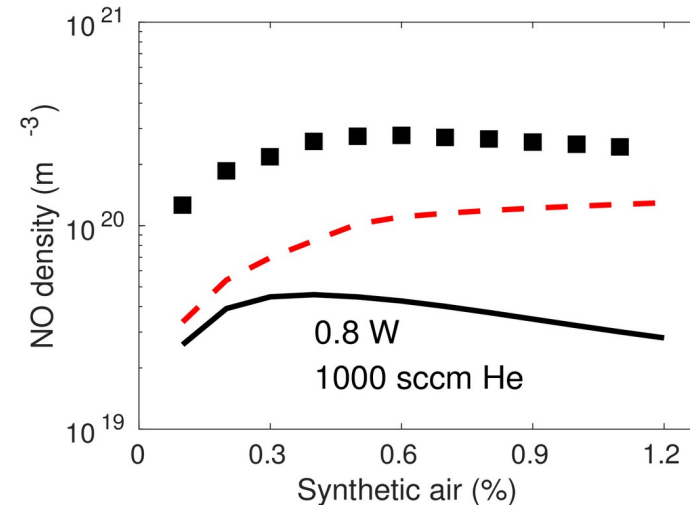
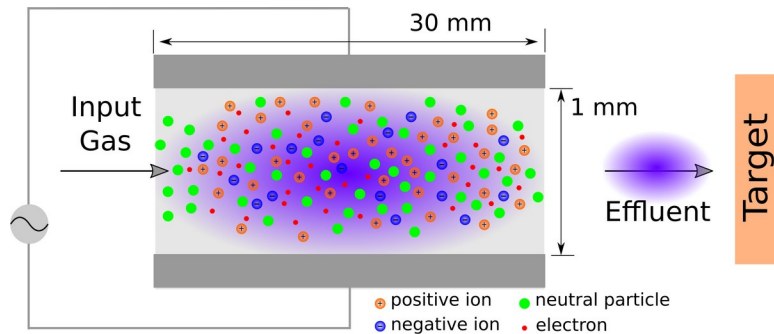
Y Ionikh et al 2006 Chemical Physics, 322(3):411–422

Characterization

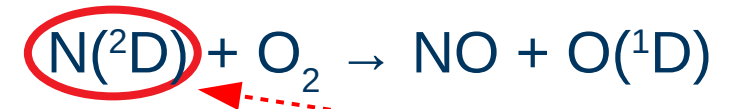
- Input gas: He/N₂/O₂

Dosis of NO? Controlled by:

- Admixture
- He gas flow
- Absorbed power



Dominant channels



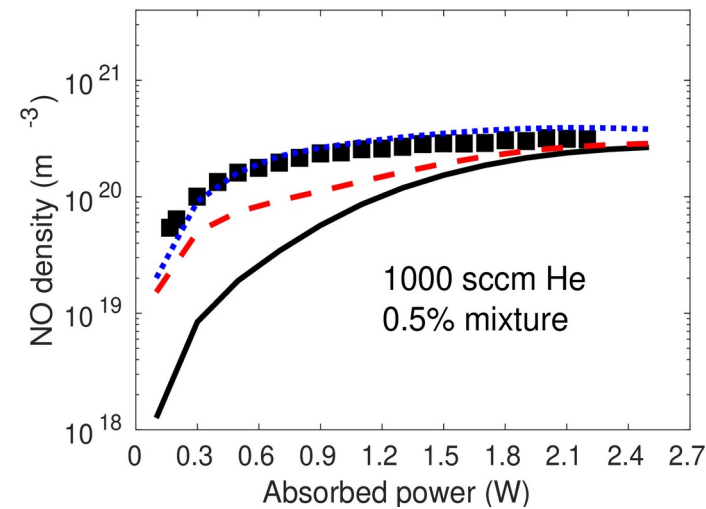
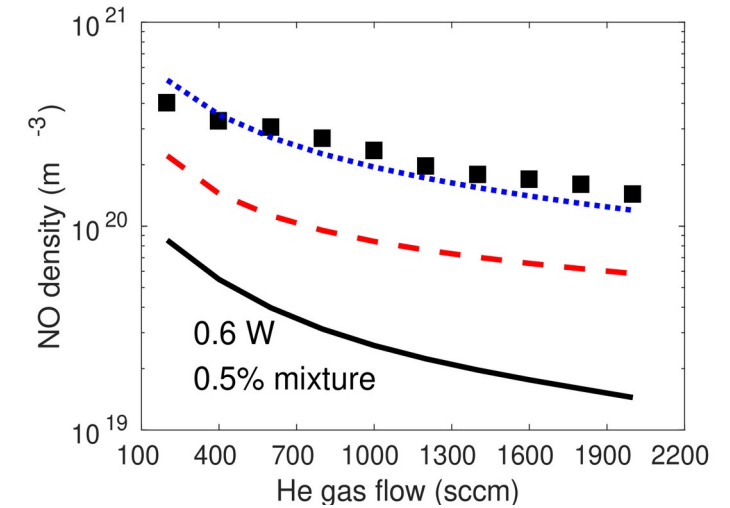
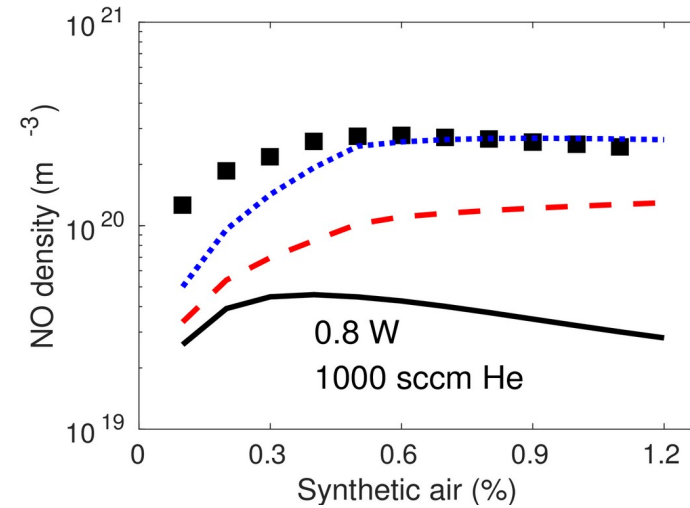
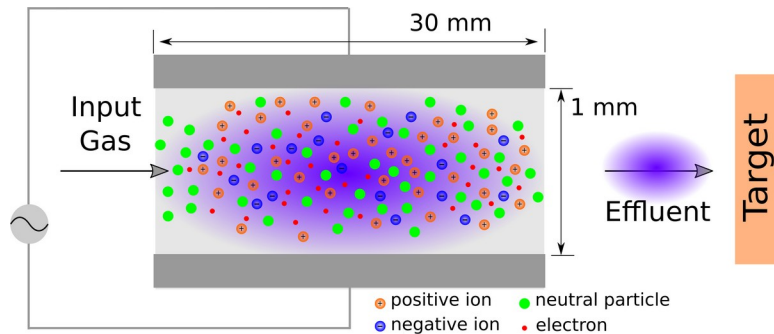
$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

Characterization

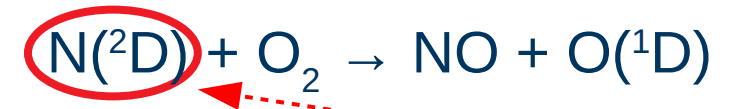
- Input gas: $\text{He}/\text{N}_2/\text{O}_2$

Dosis of NO? Controlled by:

- Admixture
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- Absorbed power



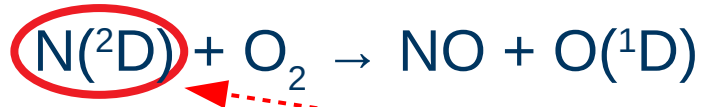
Dominant channels



$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

Characterization

- Dominant channels



$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \quad \rightarrow \quad 7 \times 10^{-15} \text{ m}^3/\text{s}$$

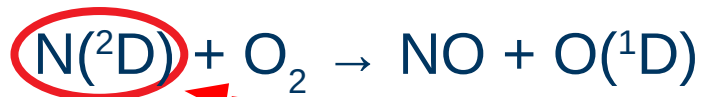
$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \quad \diamond (\text{---}) \diamond \text{ for } \text{N}_2(\text{A}) + \text{O} \rightarrow \text{NO} + \text{N}(\text{}^2\text{D})$$

- *V Guerra et al 2019 Plasma Sources Science and Technology, 28(7):073001*
- *M Capitelli et al 2001 Book review: Plasma kinetics in atmospheric gases*
- *I A Kossyi et al 1992 Plasma Sources Sci. Technol., 1:207*

$$k = 7 \times 10^{-15} \text{ m}^3/\text{s} \quad (\text{---}) \text{ for } \text{N}_2(\text{A}, \text{B}) + \text{O} \rightarrow \text{NO} + \text{N}(\text{}^2\text{D}) \quad ?$$

Characterization

• Dominant channels



$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

$\text{N}_2(\text{A}, v > 0) + \text{O} \rightarrow \text{NO} + \text{N}(^2\text{D})$ Importance & Possibility

- L G Piper et al 1981 *The Journal of Chemical Physics*, 75(6):2847–2852
- L G Piper et al 1982 *The Journal of Chemical Physics*, 77(5):2373–2377
- J M Thomas et al 1996 *The Journal of Physical Chemistry*, 100(21):8901–8906
- J D Yonker et al 2019 *Journal of Geophysical Research: Space Physics*, 125(1)
- S D Benedictis et al 1997 *The Journal of chemical physics*, 107(16):6219–6229
- G Dilecce et al 1999 *Plasma Sources Science and Technology*, 8(2):266

$\text{N}_2(\text{A}, v > 0) \rightarrow$ Another 10000 reactions ($\frac{1}{2} - \frac{1}{2}$)

$k = 7 \times 10^{-15} \text{ m}^3/\text{s} \diamond (\approx \text{ — } \approx) \diamond$ estimates the role of $\text{N}_2(\text{A}, v > 0)$!

Energy of $\text{N}_2(\text{B}) >$ Energy of $\text{N}_2(\text{A})$

$k = 7 \times 10^{-15} \text{ m}^3/\text{s} \diamond (\approx \text{ — } \approx) \diamond$ estimates the role of $\text{N}_2(\text{B}, v > 0)$?

Characterization

- Dominant channels



$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

Strong reduction of
O density

?

Characterization

- Dominant channels

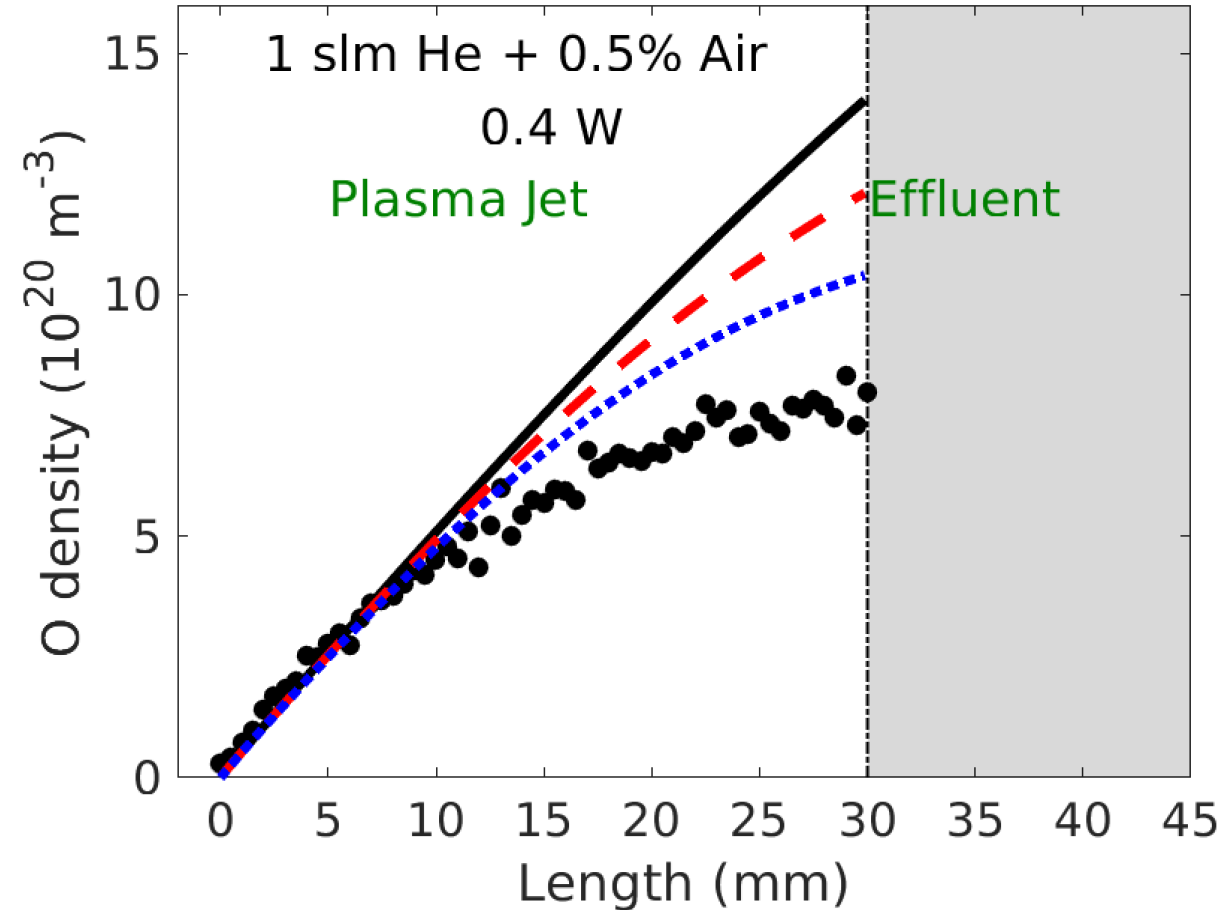


$$k = 7 \times 10^{-18} \text{ m}^3/\text{s} \rightarrow 7 \times 10^{-15} \text{ m}^3/\text{s}$$

Strong reduction of
O density

?

Cross Validation !

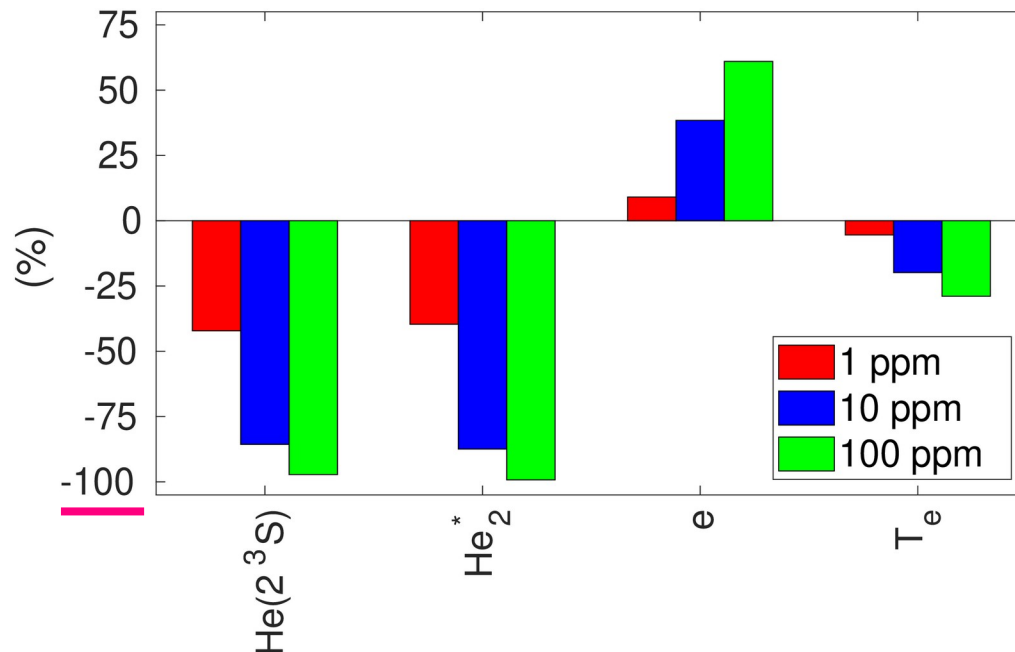


Results

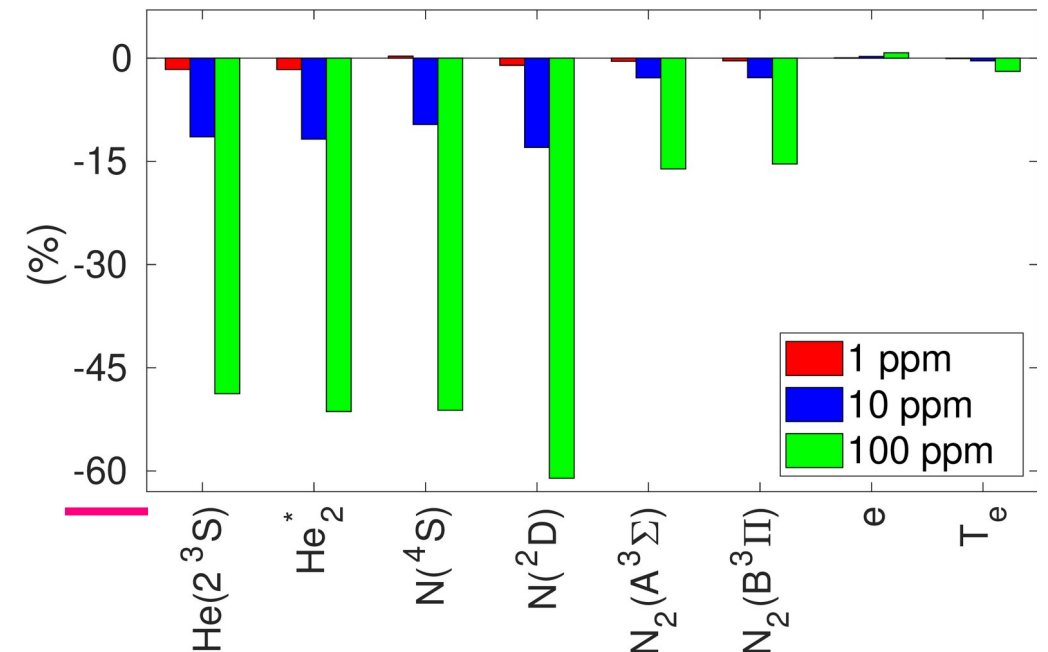
- Role of **impurity** (synthetic air)

1400 sccm He or + 0.5% mixture
0.6W, 101325Pa, 345K

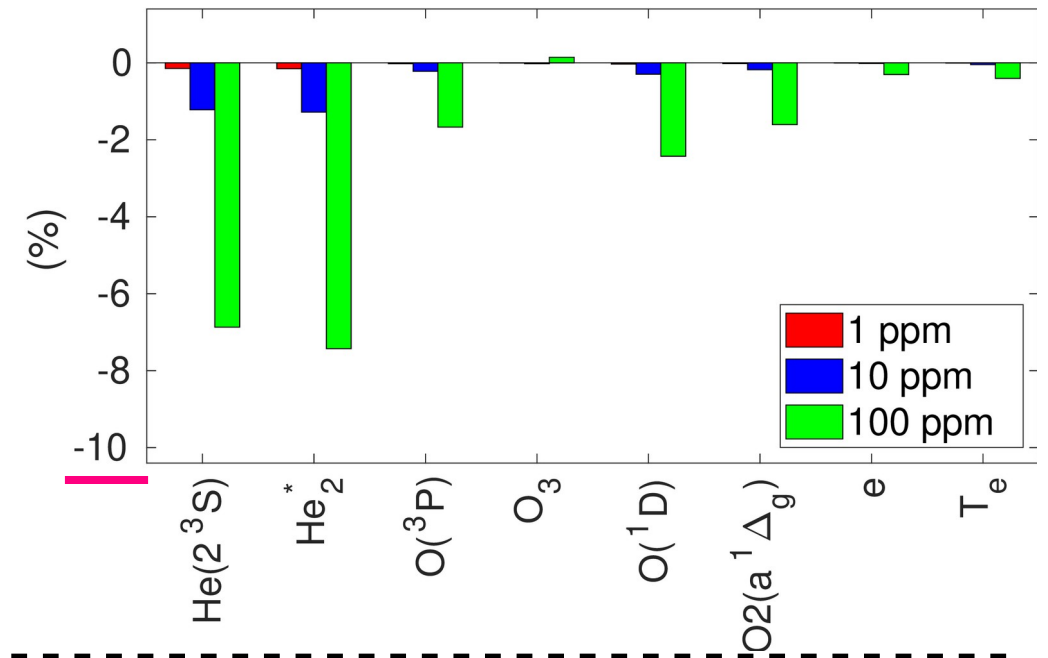
He



He/N₂



He/O₂

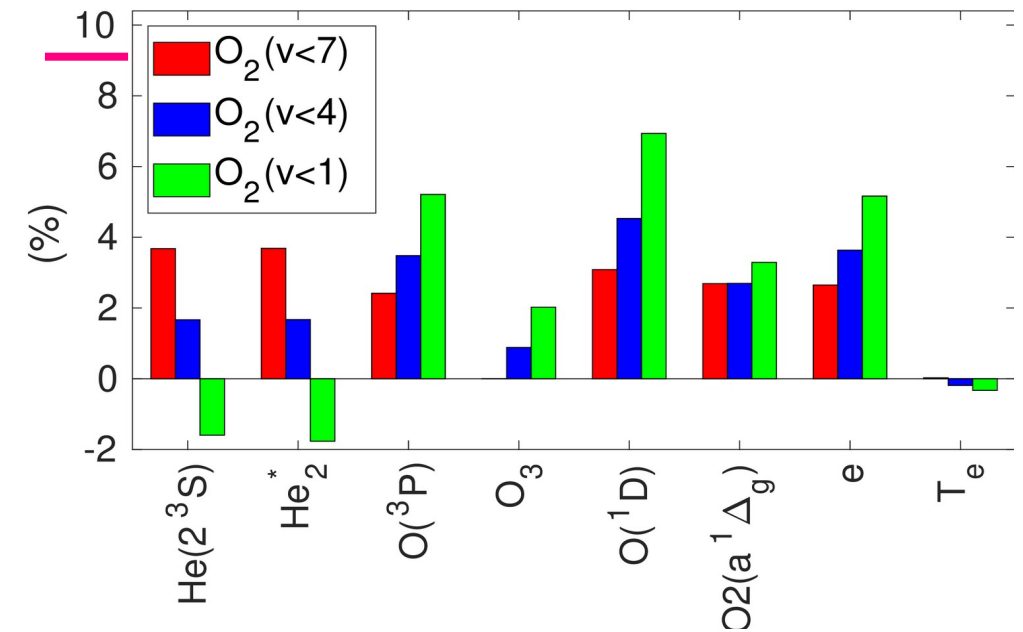


Results

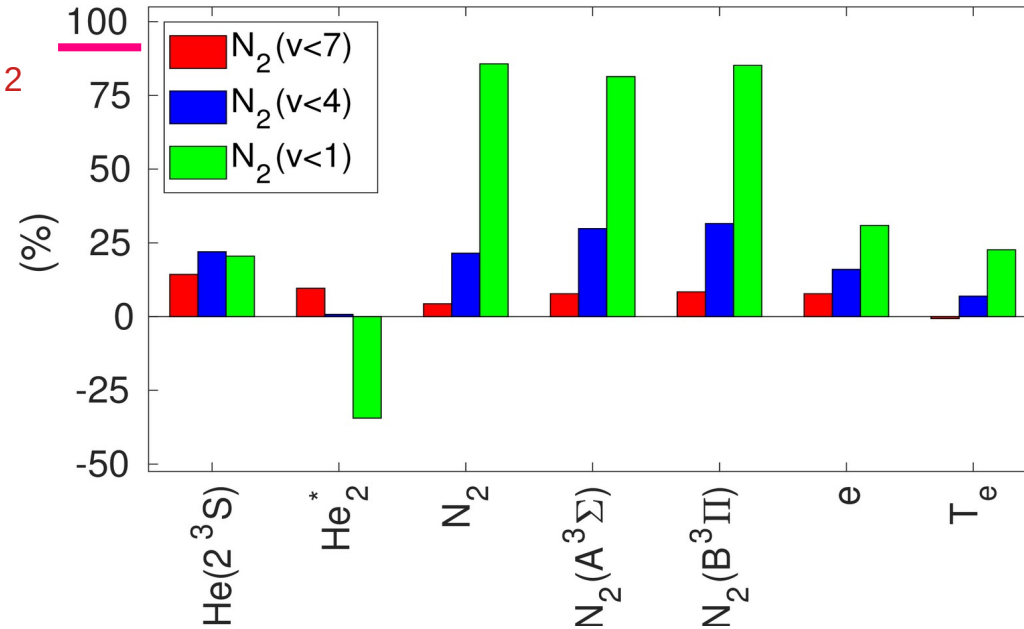
- Role of **VDF** $N_2(v=1-57)$ $O_2(v=1-40)$

1400 sccm He or + 0.5% mixture
0.6 W, 101325 Pa, 345 K

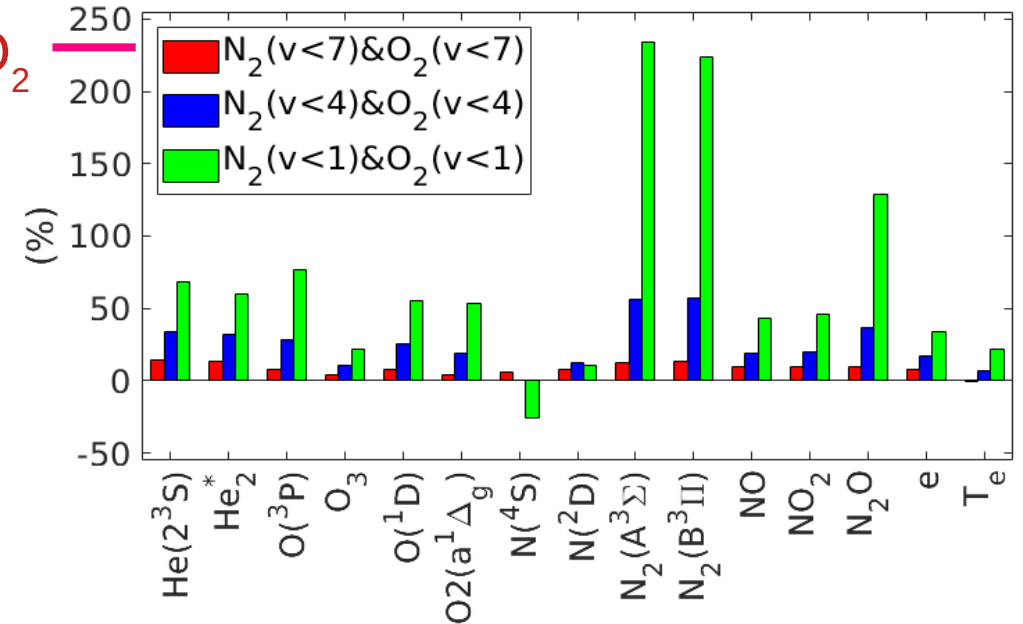
He/O_2



He/N_2



$He/N_2/O_2$



Summary

- A 0-D model for plasma jet was developed
- The detailed chemical kinetics for He/N₂/O₂ plasma (vibrational kinetics)
(validated through various device, gas flow, gas mixture, power)
- Well characterization of NO density
- Role of synthetic air impurity, vibrational kinetics
- Outlook: ns-pulsed μ APPJ $\rightarrow$ vibrational kinetics of N₂ and O₂

Acknowledgement



This work is supported by the German Research Foundation DFG in the frame of Collaborative Research Centre SFB 1316.

The authors thank: Vasco Guerra for the discussions on vibrational kinetics.
Colleagues from SFB 1316 and TET

**Thanks a lot for
your kind attention!**