Controlling Vibrationally Excited Nitrogen and Overall Plasma Chemistry with Surface Micro-discharge in Ambient Air

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Outline

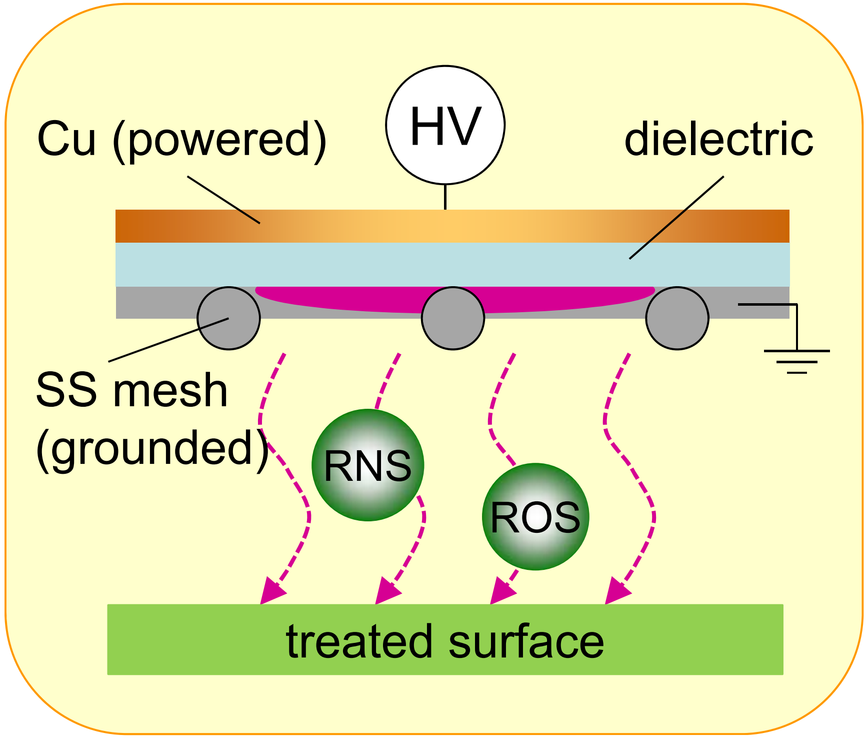
1. **Surface micro-discharge (SMD)**
2. **Distribution of RONS at low-power**
   - RONS in discharge layer and afterglow
   - Comparison with FTIR
3. **Mode transition in afterglow**
   - UV O_3 measurement
   - Fitting model with N_2 vibrational mode
   - Correlation with bactericidal effect
4. **Concluding remarks**

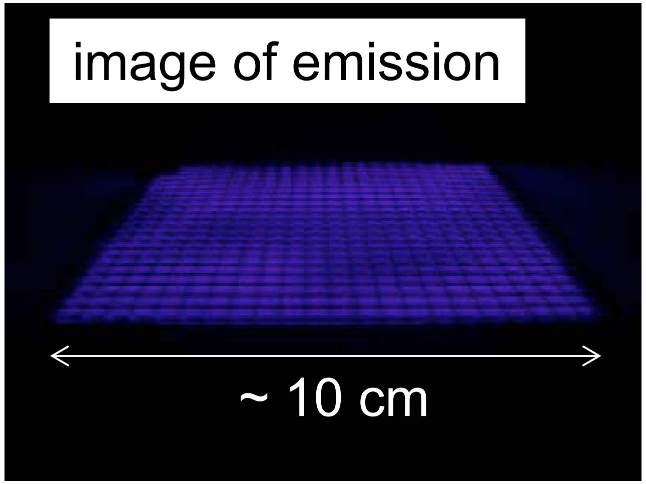
SMD: discharge characteristics

G. Morfill et al., New J. Phys. **11** (2009) 115019, T. Shimizu et al., New J. Phys. **13** (2011) 023026

SMD = surface micro-discharge

(surface dielectric barrier discharge in ambient air at room temperature)



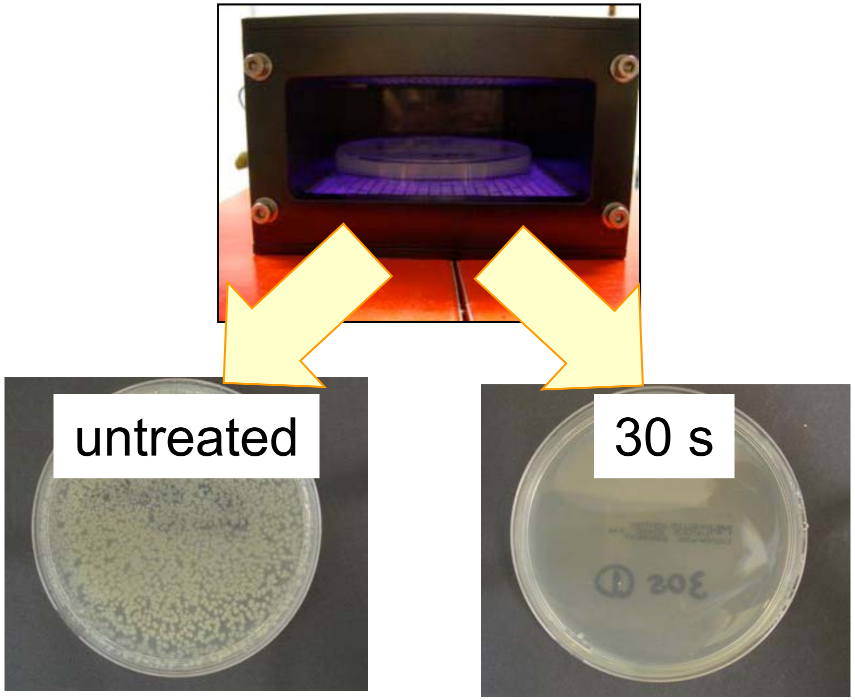


Frequency:	1-10 kHz
Voltage:	1-10 kV_{pp}
Power:	0.01-1 W/cm^2
Distance to sample:	1-10 mm
Exposure time:	1-1000 s

SMD: anti-microbial effect

Various microbes on agar plate

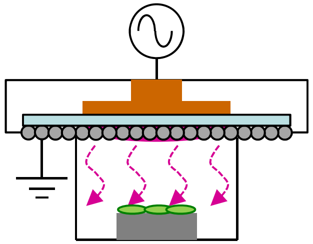
G. Morfill ., *New J. Phys.* **11** (2009) 115019

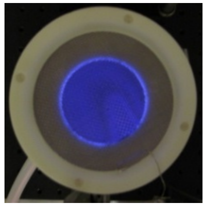


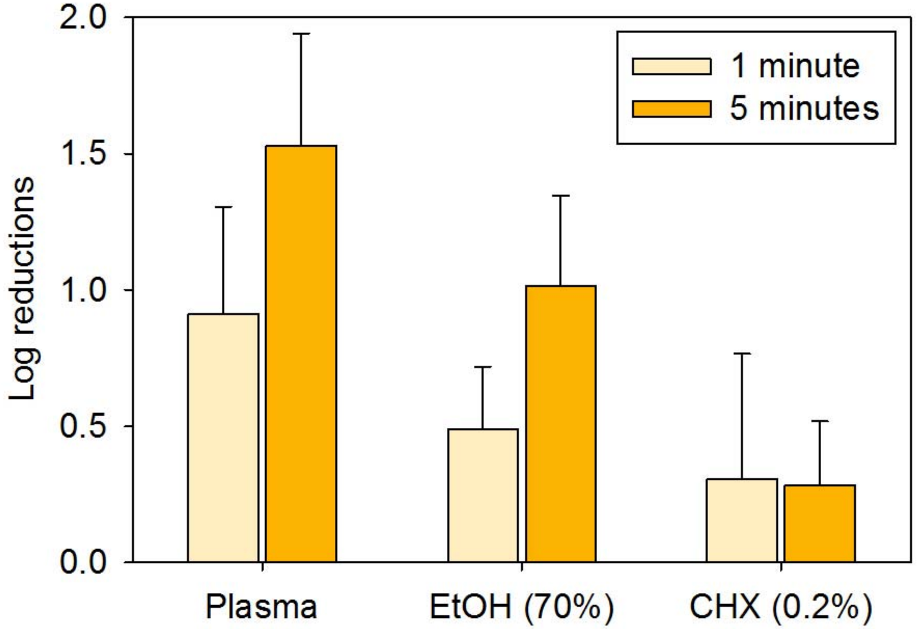
gram positive/negative bacteria, spores, viruses, etc…

E. coli on pig skin

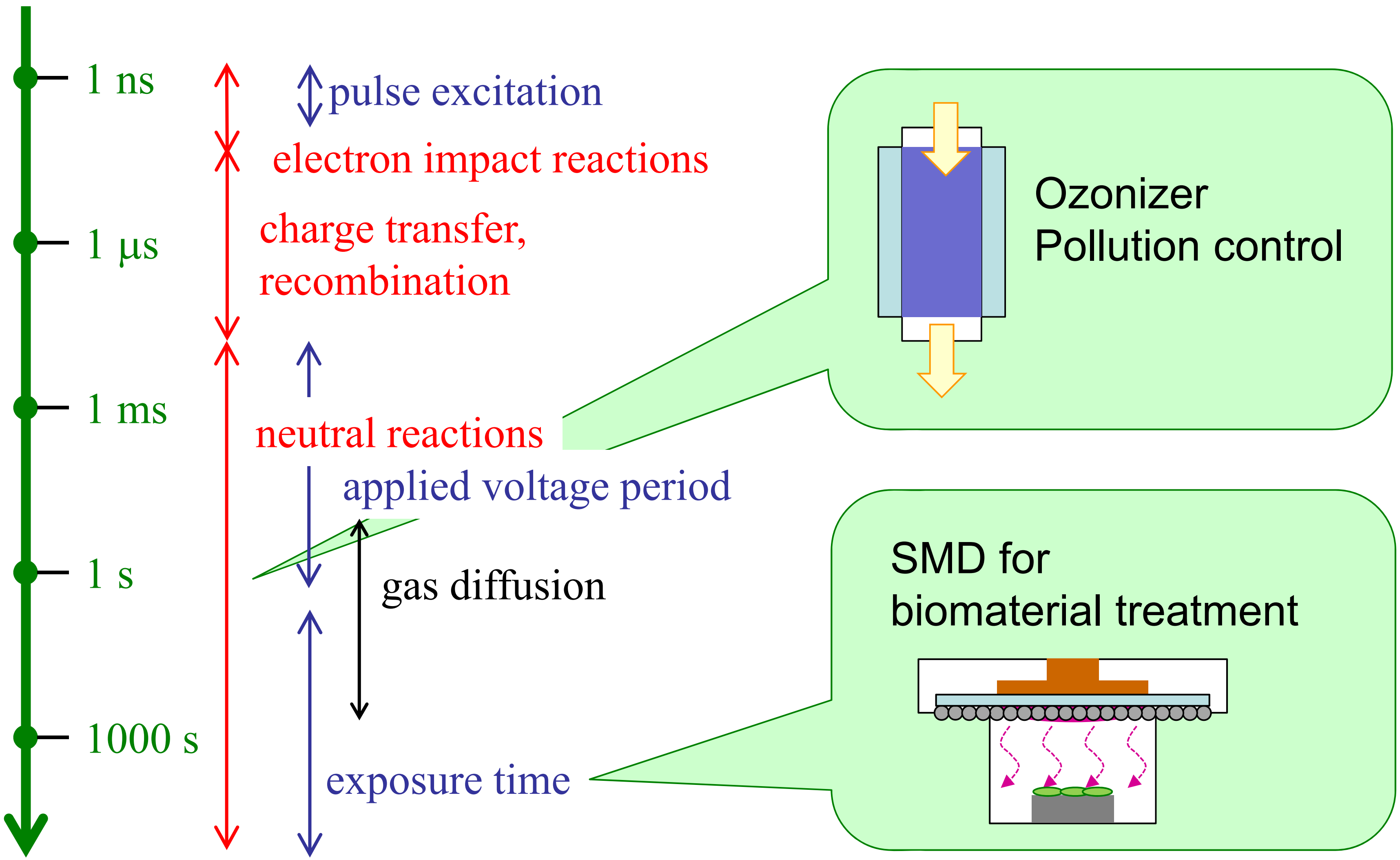
M. Pavlovich,, *Plasma. Process. Polm.* (submitted)





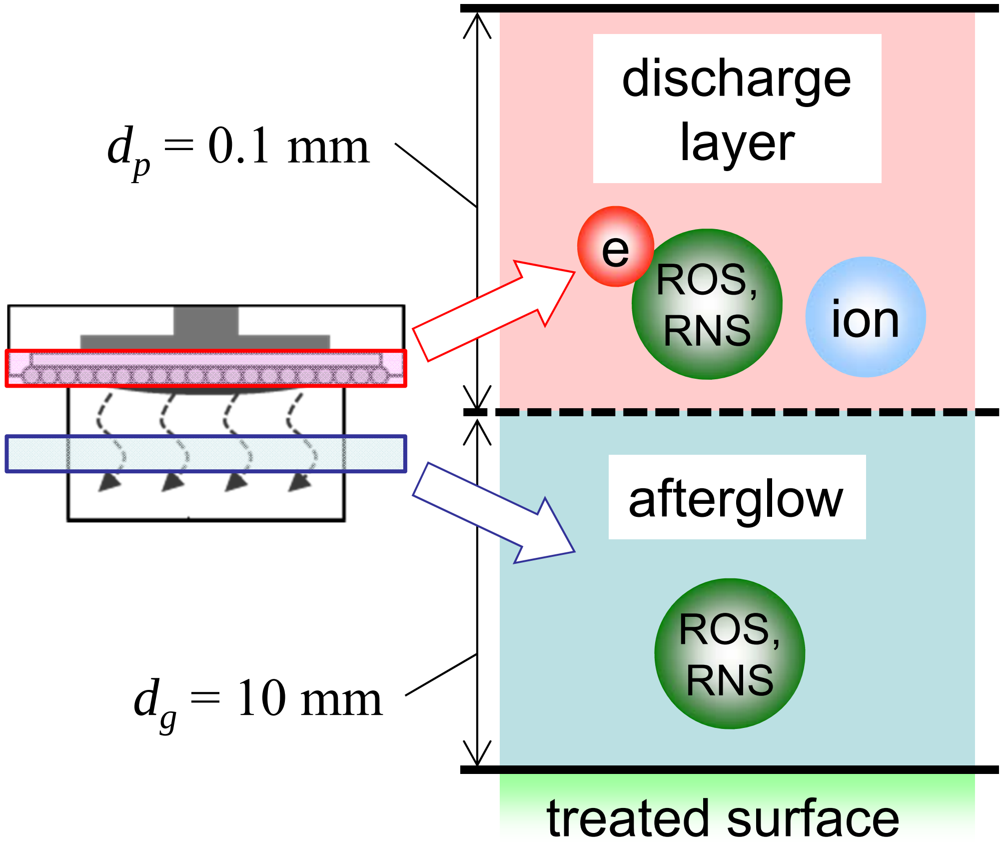


SMD: multi-scale phenomena



Modeling: domain and equations

- Humid air at 1 atm: 79% N_2, 20% O_2, 1% H_2O (30% relative humidity)
- Gas temperature: 300 K

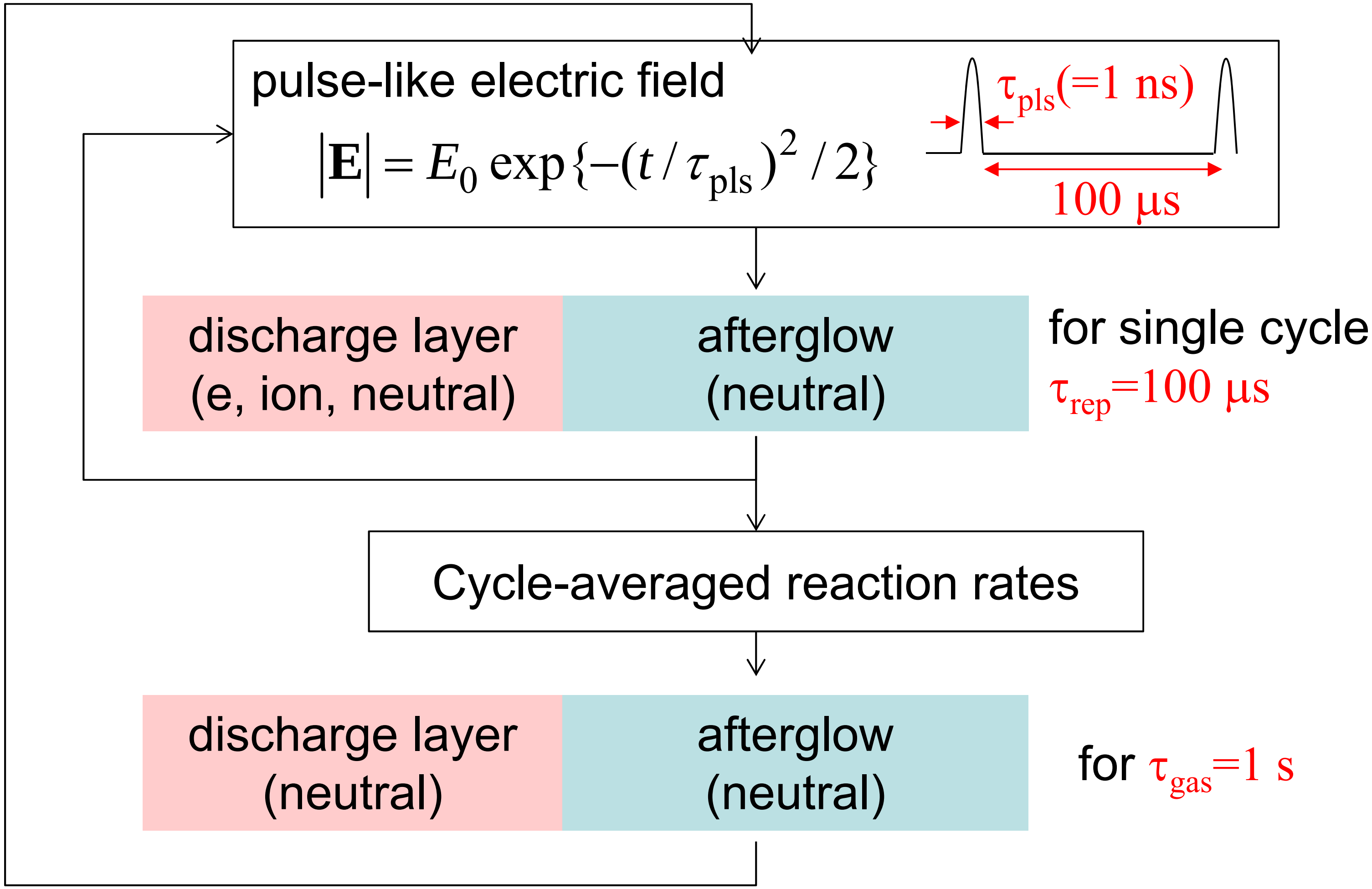


$$\frac{\partial n_p}{\partial t} = \sum_j k_j \prod n_{r,j} - \frac{\Gamma_{pg}}{d_p}$$

$$\Gamma_{pg} = \frac{D(n_p - n_g)}{(d_p + d_g)/2}$$

$$\frac{\partial n_g}{\partial t} = \sum_j k_j \prod n_{r,j} + \frac{\Gamma_{pg}}{d_g}$$

Modeling: simulation procedure (solver: MATLAB)



Modeling: humid air plasma chemistry

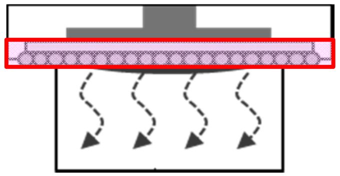
- **53 species:**
  electrons, 16 positive ions, 10 negative ions, and 26 neutrals
- **624 reactions**
  23 electron impact excitation/ionization
  84 electron recombination/attachment/detachment
  169 charge transfer and ion conversion
  231 ion-ion recombination
  116 neutral-neutral reactions

References

- H.Matzing, *Adv. Chem. Phys.* **80** (1991) 315
- I. A. Kossyi, *Plasma Sources Sci. Technol.* **1** (1992) 207
- R. Atkinson, *Atmos. Chem. Phys.*, **4** (2004) 1461
- M.Capitelli, "*Plasma kinetics in atmospheric gases*" (Springer, Berlin 2000)

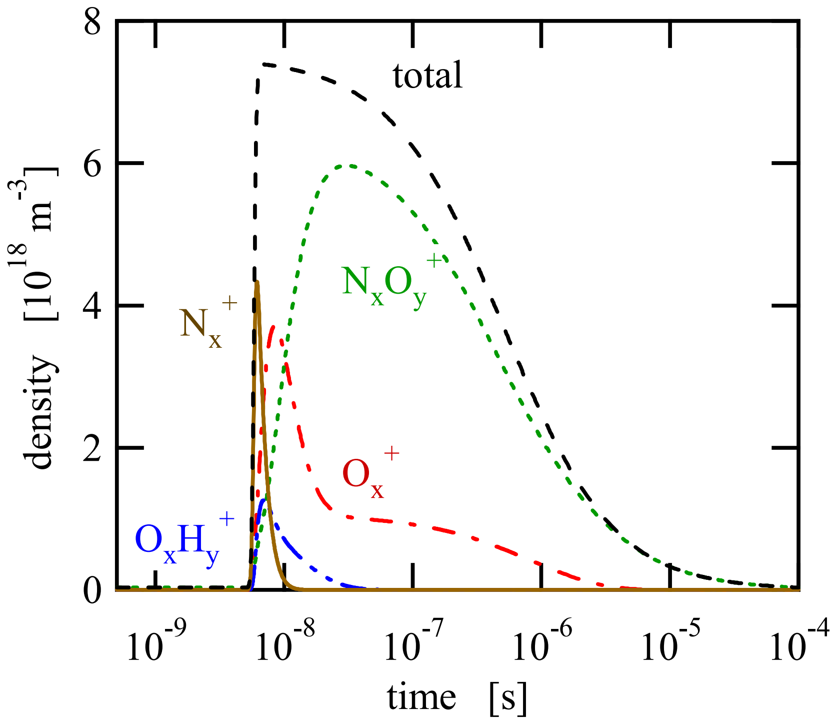
etc., etc., etc….

Modeling: discharge layer at low power

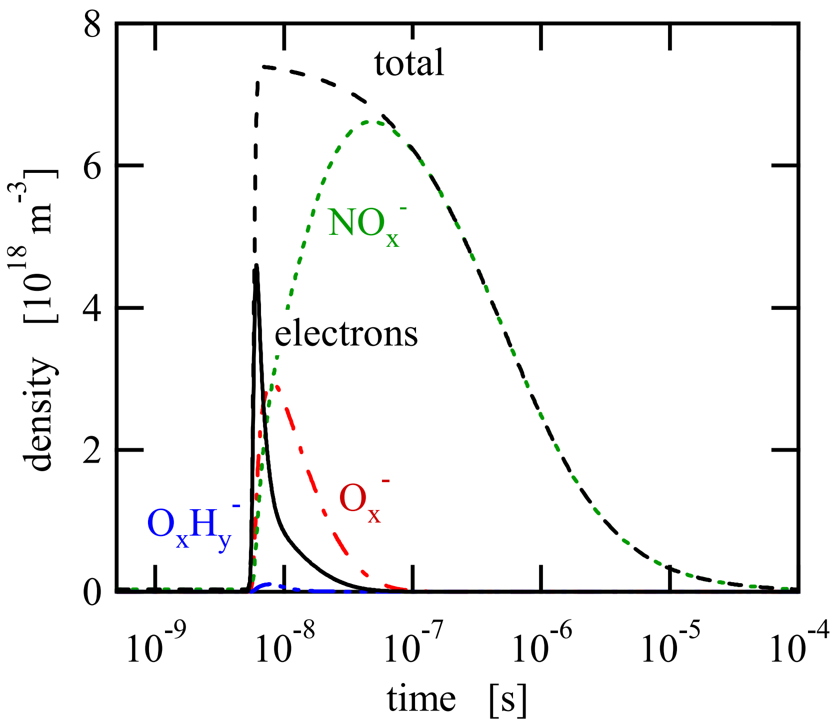


Power density: 0.05 W/cm^2
Peak density: ~10^{19} m^{-3}

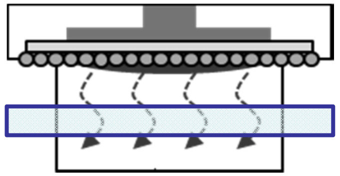
Positive ions at 1000 s



Negative ions at 1000 s

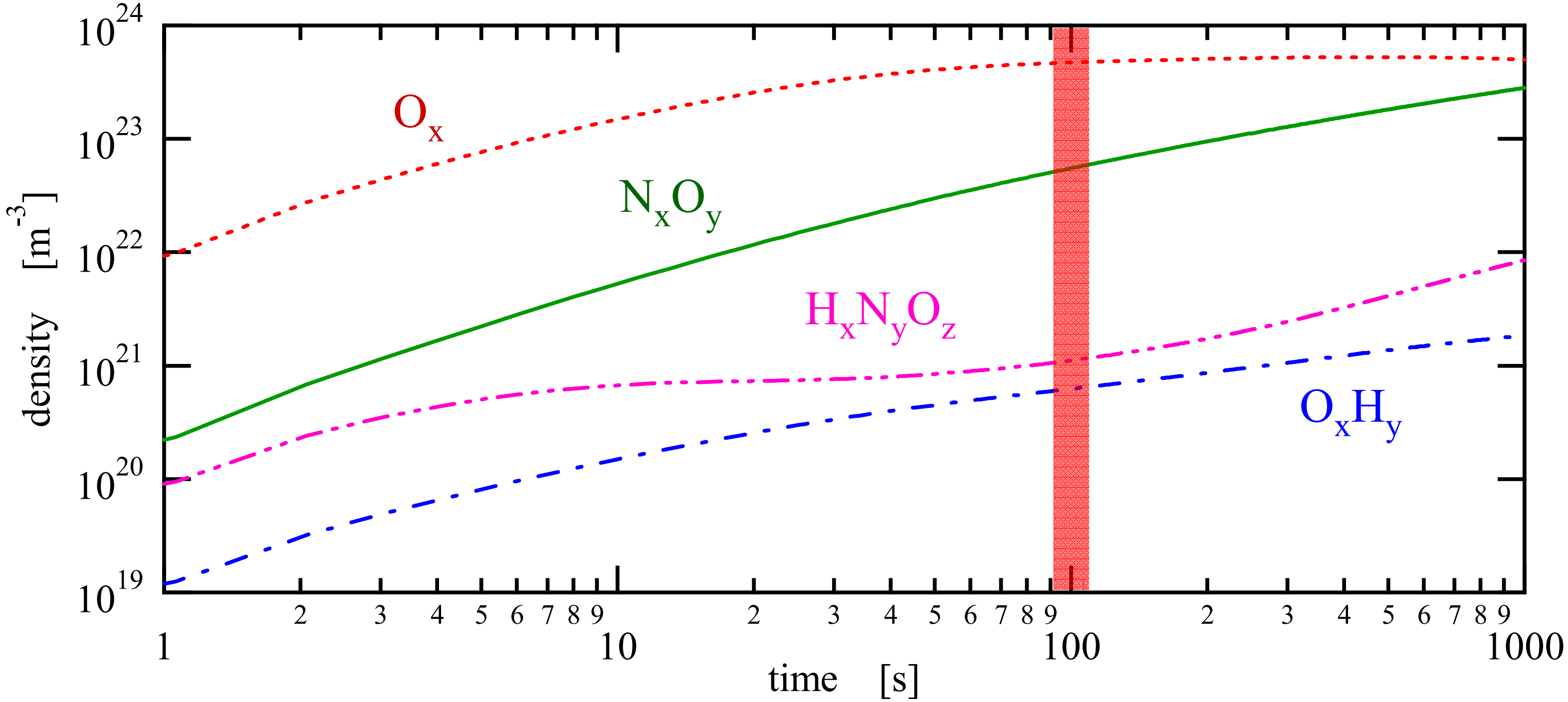


Modeling: neutrals still in transient after 1000 s

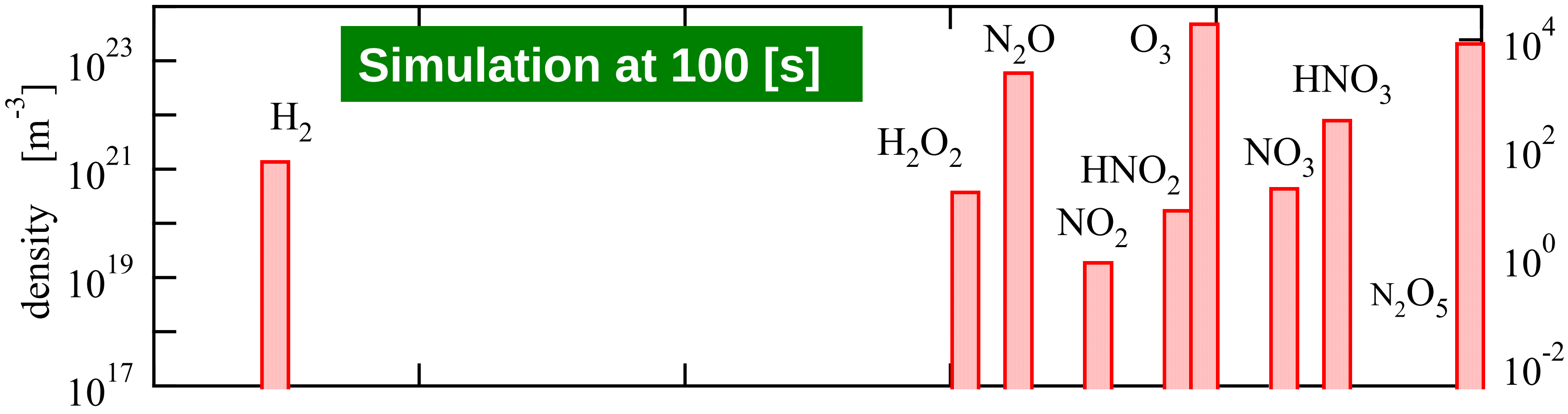


Power density: 0.05 W/cm^2
Peak density: > 10^{19} m^{-3}

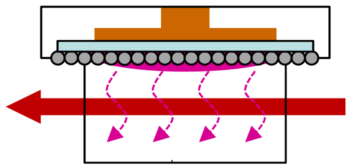
Cycle-averaged neutral density at 1000 s



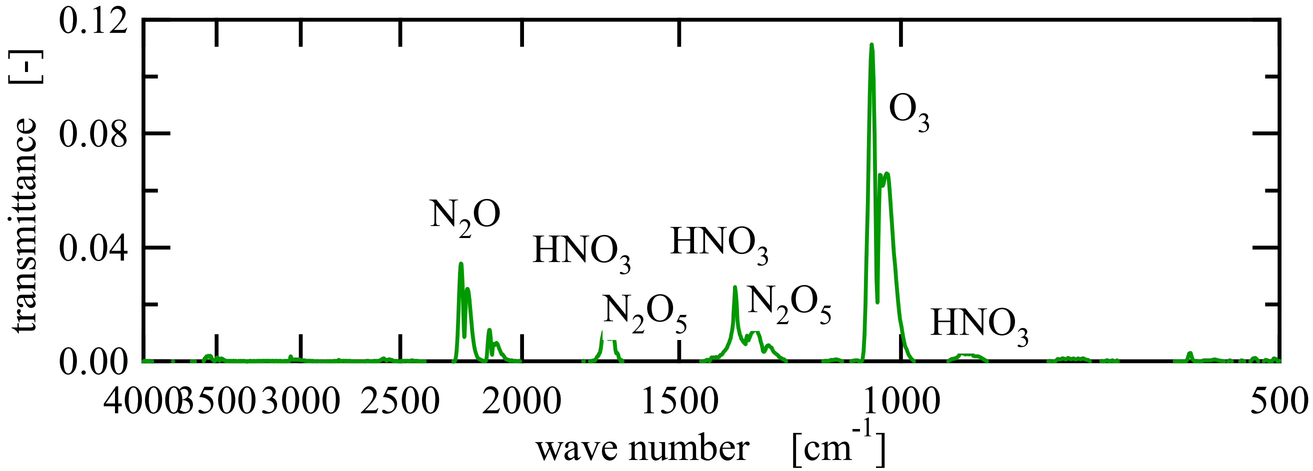
Modeling: distributions of neutrals



FTIR measurement (qualitative comparison)



200 scans for 60-120 [s]



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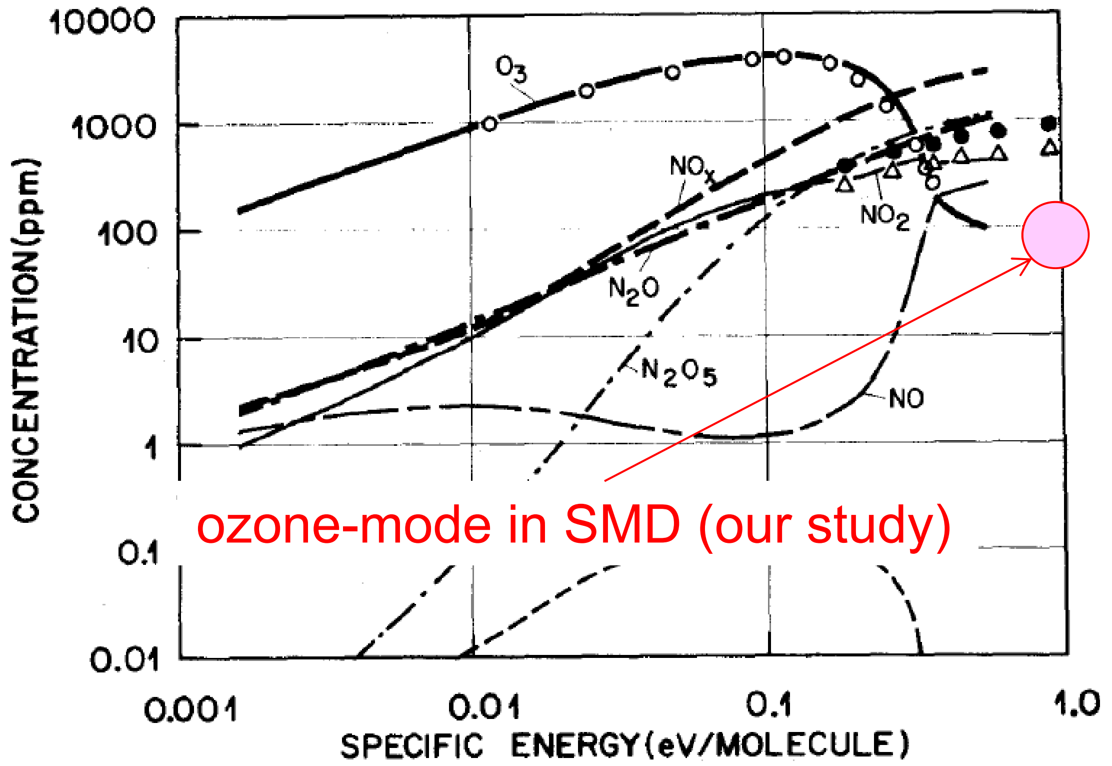
Gas-phase ozone: modulation by power density



U. Kogelschatz, et al., *Ozone Sci. Eng.* **10** (1988) 367

m[2]

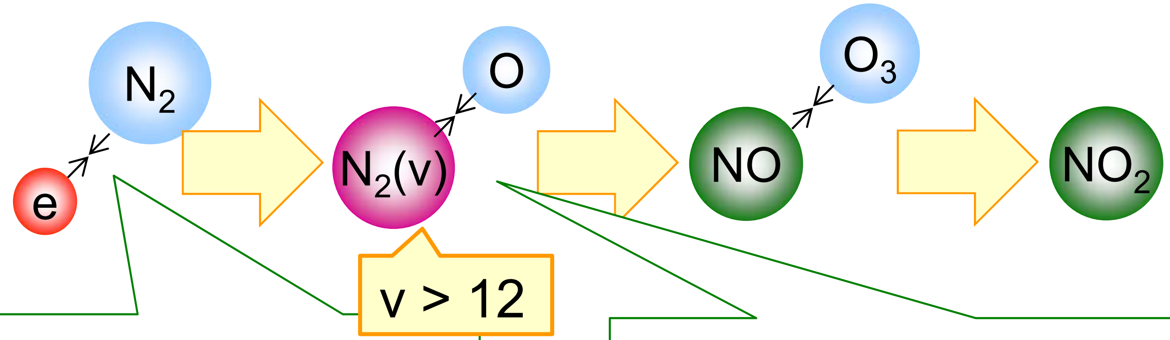
mode”

ide mode”

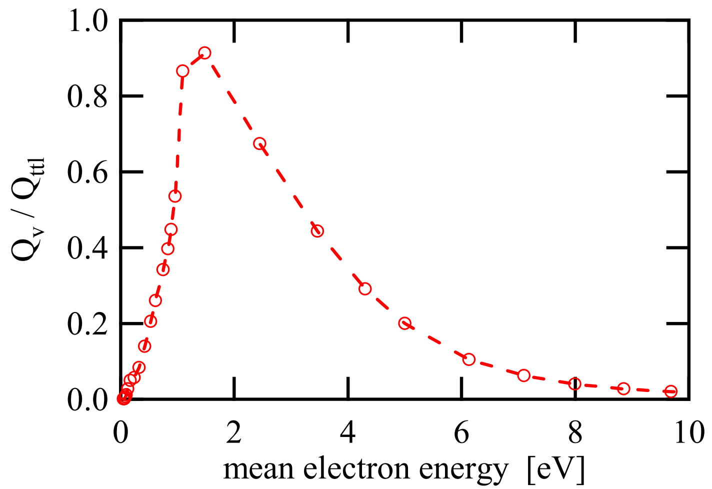
time [s]

Mode transition: N_2 vibrational state

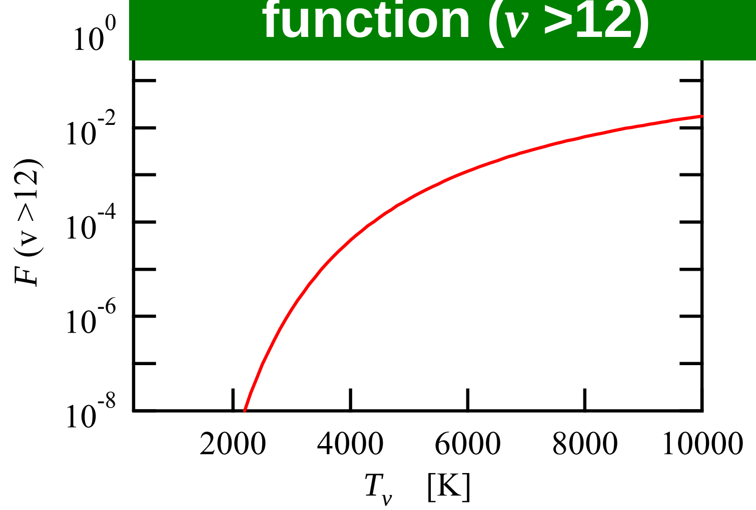
Ref: M. Capitelli, "*Plasma kinetics in atmospheric gases*" (Springer, Berlin 2000)



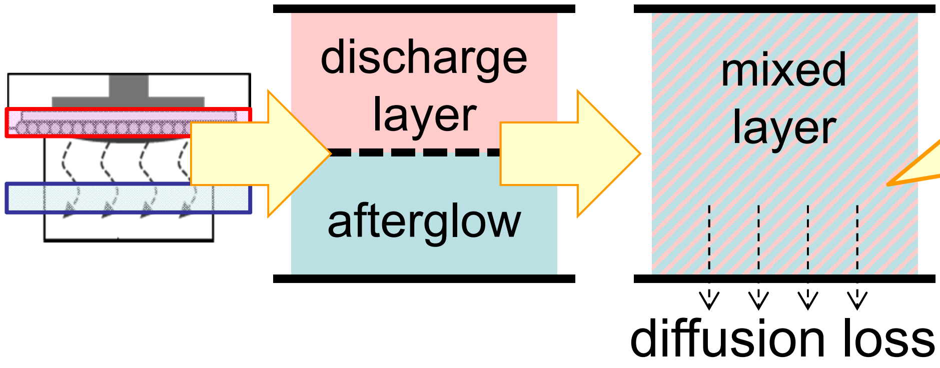
Energy transfer efficiency



Cumulative distribution function (*v* >12)



Mode transition: simplified fitted model



$$\text{R1: O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$
$$\text{R2: N}_2(v) + \text{O} \rightarrow \text{NO} + \text{N}$$
$$\text{R3: O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$$
$$\text{R4: O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$$

Governing equations

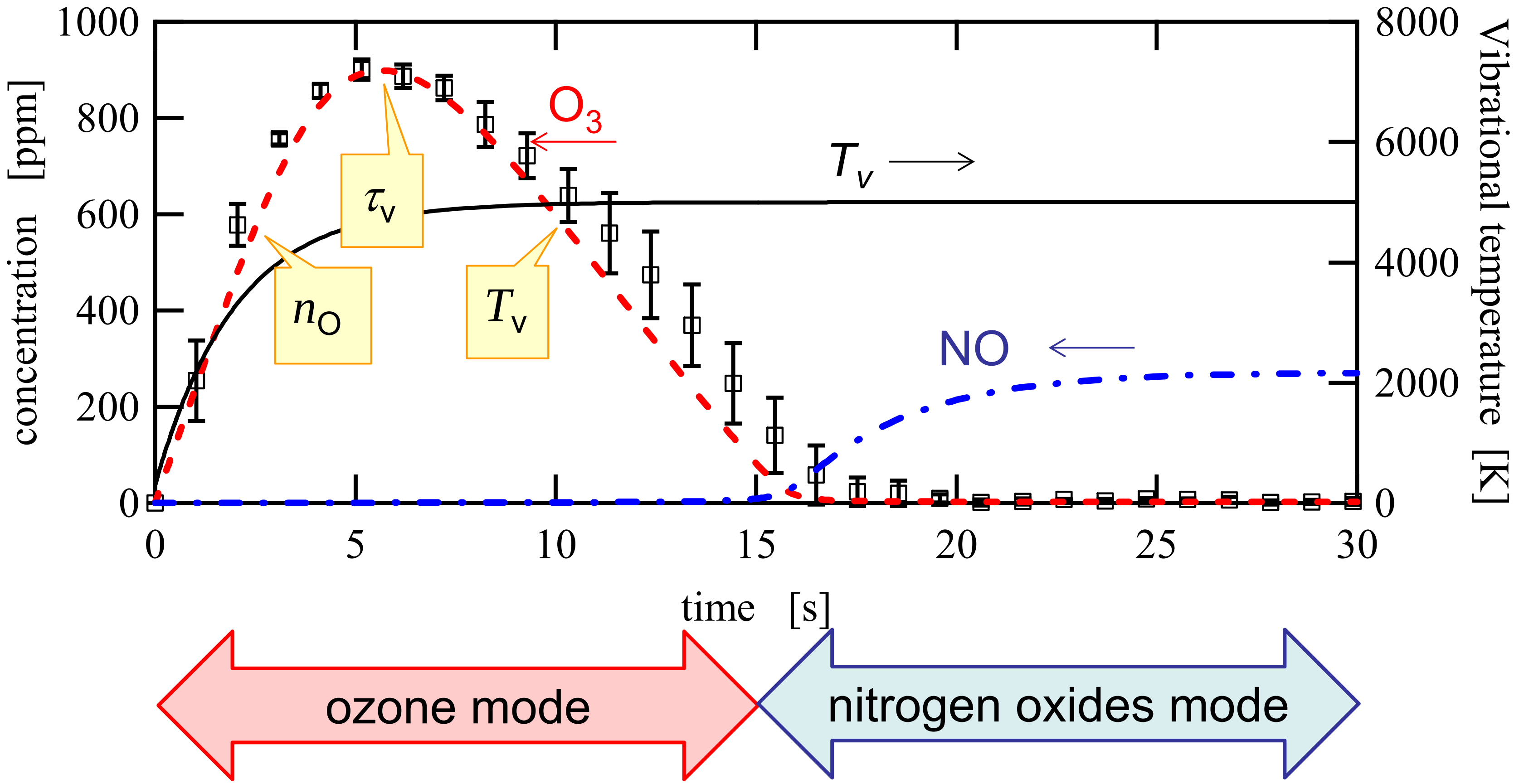
$$\begin{cases} \dfrac{dn_{O_3}}{dt} = k_1 n_M n_O n_{O_2} - k_3 n_{NO} n_{O_3} - \dfrac{n_{O_3}}{\tau_{dif}} \\ \dfrac{dn_{NO}}{dt} = k_2 n_{N_2(v)} n_O - k_3 n_{NO} n_{O_3} - k_4 n_O n_{NO} n_M - \dfrac{n_{NO}}{\tau_{dif}} \\ n_{N_2(v)} = n_{N_2} F_{v>12} = n_{N_2} \exp(-\dfrac{12\Delta\varepsilon_v}{kT_v}) \\ T_v = T_g + T_{vmax}\{1 - \exp(-t/\tau_v)\} \end{cases}$$

2 unknown variables
- n_{O3} and n_{NO}

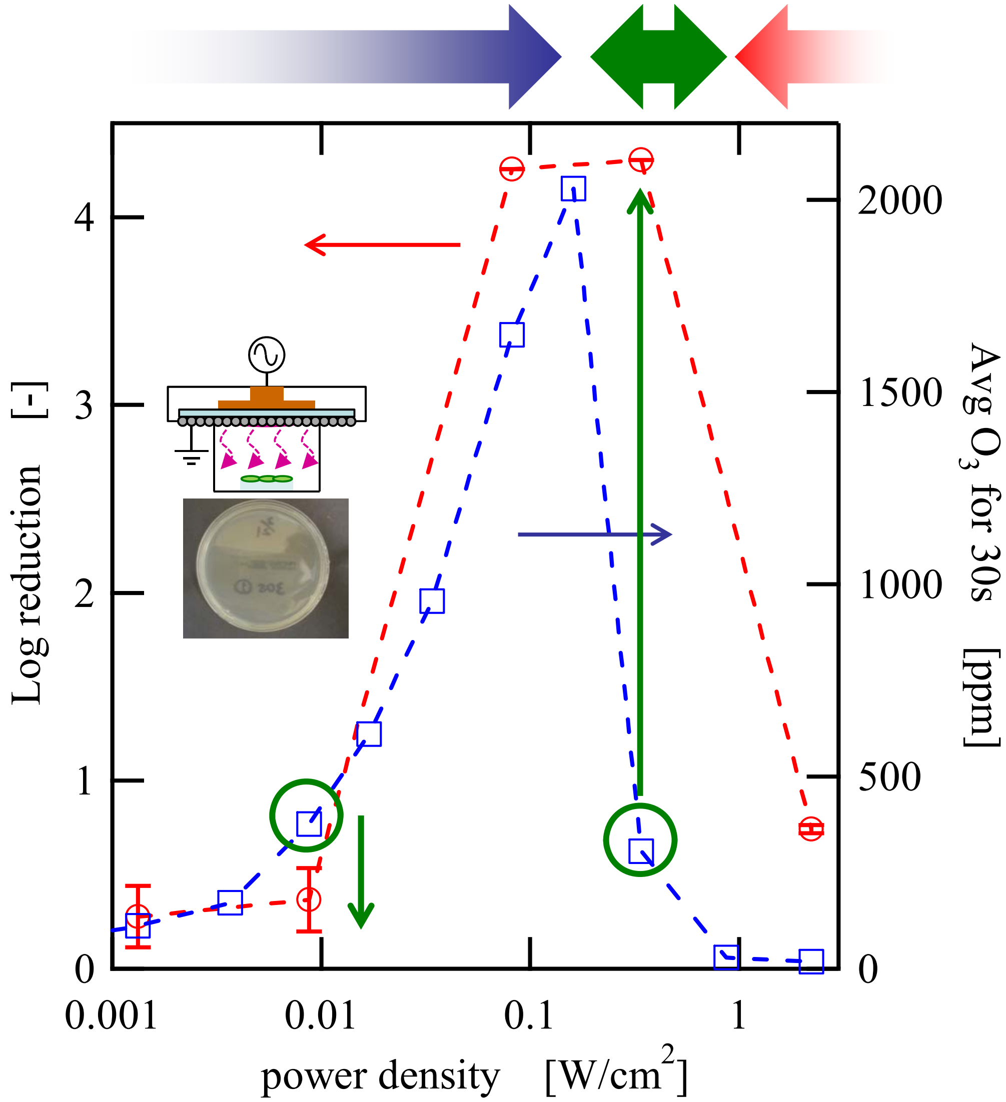
3 fitting parameters
- n_O, T_{vmax}, τ_v

Mode transition: O_3 model and N_xO_y mode

fitted parameters: $n_O = 8 \times 10^{17}\ m^{-3}$, $T_{vmax} = 5000$ K, $\tau_v = 2$ s

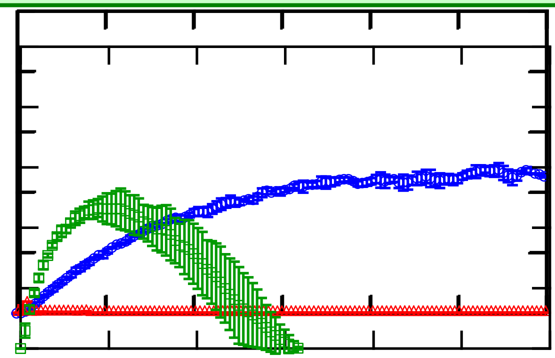


Gas-phase ozone: bactericidal activity on agar plate



Intermediate power (0.1-1.0 Wcm^2)

- O_3: quenched
- L-R: high



- ozone is not responsible for inactivation?
- Nonlinear reaction on lipid membrane?

Concluding Remarks

1. We developed multi-scale model of SMD. Our simulation results at low power (0.05 W/cm^2) shows good agreement with our FTIR measurement.

2. We presented one example of modulating plasma chemistry in SMD. The modulation is achieved by controlling distribution functions of electrons and neutrals through pulsing of electric field.

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