

# Kinetic modelling of $O_2$ discharges

Vasco Guerra

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico,  
Universidade de Lisboa, Portugal

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# Self-consistent kinetic model

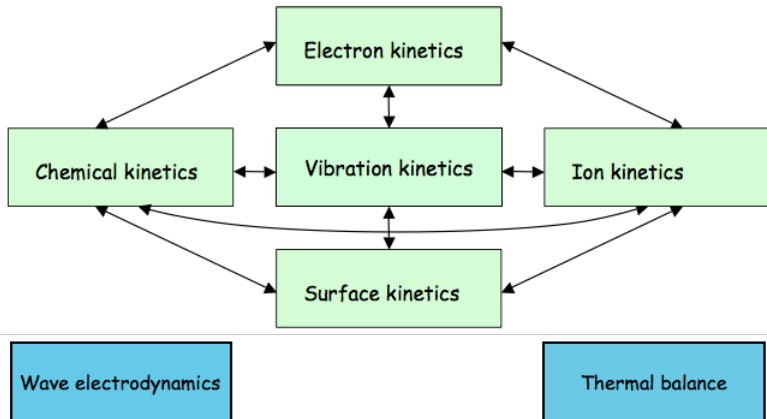
## Input

- Discharge operating parameters ( $p$ ,  $R$ ,  $P$  or  $n_e$ ,  $\omega$ )
- Wall temperature
- Gas temperature
- Collisional data (see IST-Lisbon database @ LXCat)

## Output

- Sustaining electric field
- Electron energy distribution function (EEDF)
- Vibration distribution functions (VDF)
- Concentration of electronically excited states and ions
- Gas temperature
- Wave number and attenuation coefficient

# Self-consistent model



## LoKI (LisbOn KInetics)

- Electron kinetics (electron Boltzmann equation in the mixture O<sub>2</sub>-O)

[L.L. Alves *et al*, *Eur. Phys. J. D.* **70** (2016) 1]

- Vibrational kinetics of O<sub>2</sub>( $X^3\Sigma_g^-, v'$ ) molecules
- Chemical kinetics of O<sub>2</sub>( $a, b$ ), O( $^3P, ^1D$ ), O<sub>3</sub> and O<sub>3</sub>\*
- Ion kinetics of Ion kinetics of O<sub>2</sub><sup>+</sup>, O<sup>+</sup> and O<sup>-</sup>
- Electrons and ion transport + quasi-neutrality (self-consistent  $E/N$ )

[V. Guerra and J. Loureiro, *Plasma Sources Sci. Technol.* **8** (1999) 110]

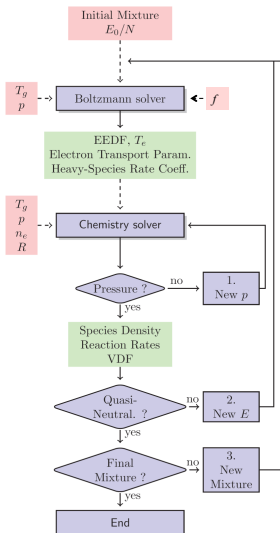
# A word on surface kinetics

- Usually treated as a separate module
- No conceptual problem in coupling gas phase and surface kinetics

[V. Guerra *et al*, *J. Phys D: Appl. Phys.* **47** (2014) 224012]

[V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 045001]

# The LoKI workflow (stationary case)



# In this lecture

## Illustrations

- Vibrationally excited  $O_2$  (*cf.* previous lecture by J.P. Booth!)
- $O_3$  kinetics in low-pressure discharges
- A glimpse at surface kinetics

# #1 Vibrationally excited $O_2(X^3\Sigma_g^-, v')$

In collaboration with

- J.P. Booth, M. Foucher, D. Marinov, A. Gibson, O. Guaitella (LPP)
- A. Annušová (Comenius University at Bratislava)
- M.Lino da Silva (IPFN, IST)
- B. Lopez (Univ. Illinois at Urbana)



# Vibrationally excited $O_2$

- Recent experiments have revealed highly excited  $O_2(X, v)$  in pure  $O_2$  ICP and DC discharges

[M. Foucher *et al*, *Plasma Sources Sci. Technol.* **24** (2015) 042001]

- The challenge: develop a detailed  $O_2(X, v)$  kinetics
  - Updated rates for V-V and V-T transfers in collisions with  $O_2$
  - Updated rates for V-T transfers in  $O_2$ -O collisions
  - Updated rates for e-V processes
  - Description of e-dissociation from  $v$ -levels

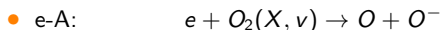
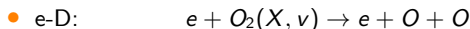
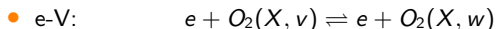
# Vibrational kinetics of $O_2(X)$

- VT  $O_2$ - $O_2$ :  $O_2(X, v) + O_2 \rightleftharpoons O_2(X, v - 1) + O_2$
- VV  $O_2$ - $O_2$ :  $O_2(X, v) + O_2(w) \rightleftharpoons O_2(X, v - 1) + O_2(w + 1)$

[C. Coletti and G.D: Billing, *Chem. Phys. Lett.* **356** (2002) 14]

[M. Lino da Silva *et al*, *Chem. Phys. Lett.* **531** (2012) 28]

- VT  $O_2$ -O:  $O_2(X, v) + O \rightleftharpoons O_2(X, v') + O$
- [F. Esposito *et al*, *Chem. Phys.* **351** (2008) 91]



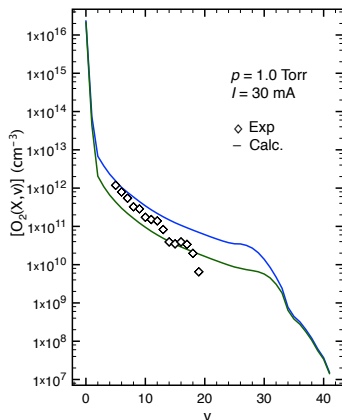
[V. Laporta *et al*, *Plasma Sources Sci. Technol.* **22** (2013) 025001]

[R. Celiberto *et al*, *Open Plasma Phys. J.* **7** (2014) 33]

- Wall:  $e + O_2(X, v) \rightarrow e + O_2(X, v - 1)$

# Results: O<sub>2</sub> DC discharge

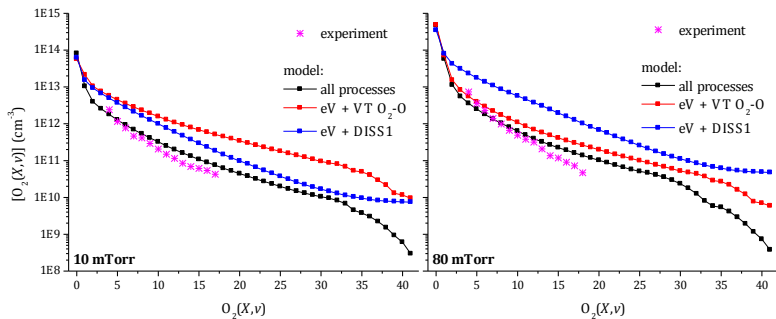
- Experiments by M. Foucher, D. Marinov, O. Guaitella and J.P. Booth
- e-V + V-T O<sub>2</sub>-O
- The good agreement is extended to other values of  $I$ ,  $p$  and to ICP
- For lower pressures  
 $e + O_2(X, v) \rightarrow e + O + O$   
becomes important



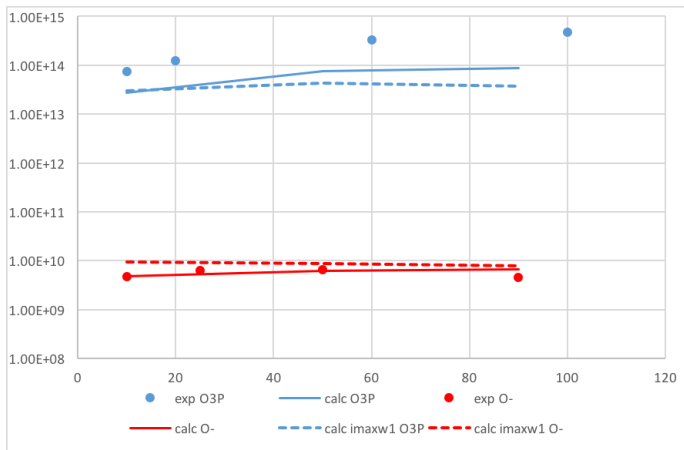
(—)  $\gamma_O = 2 \times 10^{-3}$ ;

(—)  $\gamma_O = 8 \times 10^{-3}$

# Results: O<sub>2</sub> ICP discharge



# Results: Influence of the EEDF



## #2 Vibrationally excited ozone

In collaboration with

- D. Marinov, O. Guaitella, J.P. Booth A. Rousseau (LPP)  
[D. Marinov *et al*, *Plasma Sources Sci. Technol.* **22** (2013) 055018]

# Motivation

- Ozone kinetics seems quite well established at atmospheric pressure
- What can we learn at lower pressures?
  - Surface processes ( $O_3$  formation at the wall)
  - Role of vibrationally excited ozone ( $O_3^*$ )
- Ozone formation at the wall
  - Jansen and Tuzson: “Isotope Evidence for Ozone Formation on Surfaces”  
[*J. Phys. Chem. A* **114** (2010) 9709]
  - Lopaev *et al*  $\gamma(O_3)$  increases with pressure:  $\sim 10^{-3}$  at 10 Torr;  $\sim 5 \times 10^{-4}$  at 5 Torr  
[*J. Phys. D: Appl. Phys* (2011) **44**]

# Motivation (continued)

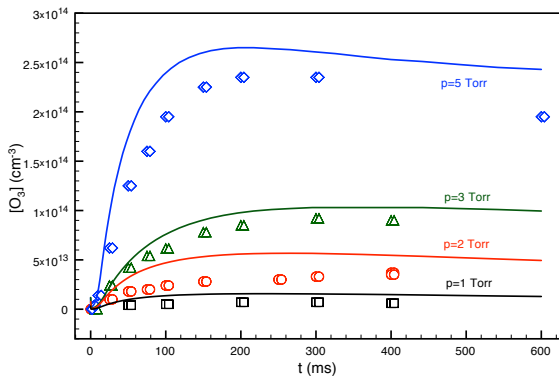
- Vibrationally excited ozone
  - Rawlings *et al*:  $O_3^*$  is mainly formed on the asymmetric stretching mode  $\nu_3$  ( $00\nu$ )  
[*J. Geophys. Res.* **90** (1985) 283]
  - Eliasson *et al* 1987, Eliasson and Kogelschatz 1990
    - $O_2 + O_2 + O \rightarrow O_3 + O_2$  produces  $O_3$  mainly in an excited state
    - $O_3^*$  decreases the absolute value of  $[O_3]$
    - $O_3^*$  increases the characteristic time for ozone formation  
[*J. Phys. D: Appl. Phys.* **20** (1987) 1421]
  - Lopaev *et al* 2011: Model with 5 vibration levels of  $O_3$



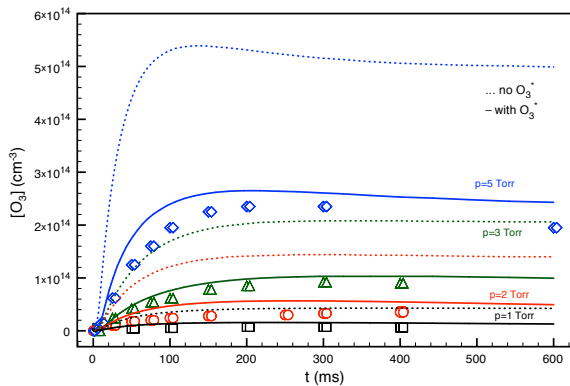
# The system under study

- Experiment
  - DC discharge with short pulses ( $\sim 1$  ms)
  - Silica tube,  $R=1\text{cm}$ ,  $p=1\text{-}5$  Torr
  - Time-resolved measurements of  $[O]$  (TALIF)
  - Time-resolved measurements of  $[O_3]$  (UV absorption)
- Modelling
  - Input:  $p, l, R, \Delta t, T_g = 300$  K
  - One effective vibrationally excited level  $O_3^*$
  - Collision rates taken essentially for the (001) level
  - $2/3$  of  $O_2 + O_2 + O \rightarrow O_3 + O_2$  produce  $O_3^*$

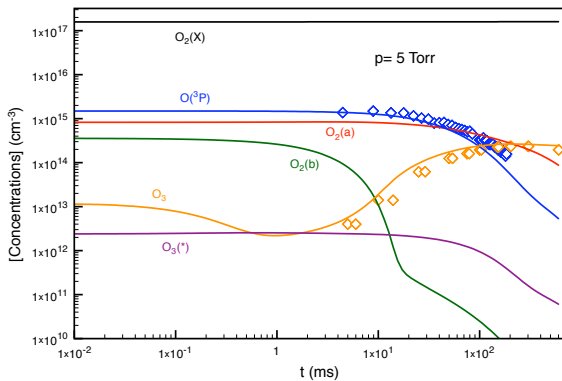
# Results: O<sub>3</sub> molecules



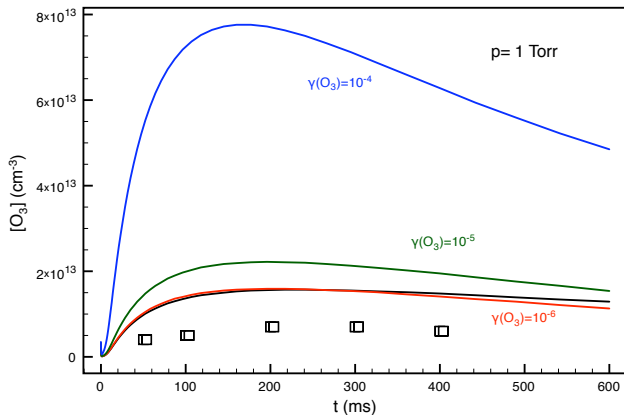
# Results: role of $O_3^*$ molecules



# Results: species concentrations

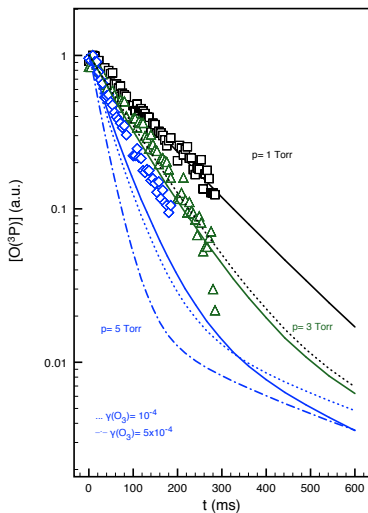


# Results: $\gamma(O_3)$



$p = 1$  Torr:  $\gamma(O_3) < 10^{-5}$

# Results: $\gamma(O_3)$



$p = 5$  Torr:  
 $\gamma(O_3) < 10^{-4}$

## #3 A glimpse at surface

In collaboration with

- D. Marinov (LPP)
- C. Teixeira (IPFN, IST)

[V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 045001]

# Modelling surface kinetics

- Macroscopic description
- Atomic scale simulations

[M. Rutigliano *et al*, *PSST* **23** (2014) 045016]

[A. Bogaerts *et al*, *J. Phys. D: Appl. Phys.* **44** (2011) 174030]

[E.C. Neyts and A. Bogaerts, *J. Phys. D: Appl. Phys.* **47** (2014) 224010]

- Application to realistic molecule formation on silica (under plasma conditions) is still difficult
- Coupling with complex gas-phase chemistry unpractical
- Mesoscopic description
  - “coarse-grained” description of the surface
  - lacks predictive power
  - ⇒ the best approach for our purpose!



# Mesososcopic descriptions

- *Deterministic* approach

- reaction-rate differential equations

[Y.C. Kim and S. Boudart, *Langmuir* **7** (1991) 2999]

[V. Guerra 2007, *IEEE Trans. Plasma Sci.* **35** (2007) 1397]

[D.V. Lopaev *et al*, *J. Phys. D: Appl. Phys.* **44** (2011) 015201]

- *Stochastic* kinetic (dynamical) Monte Carlo

- exact and simple to implement
- describe fluctuations
- probabilities may depend on local configurations
- good treatment of physisorbed species
- bridge the gap between MD and simpler models
- *n*-fold way (BKL) algorithm

[V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 054001]

# Kinetic Monte Carlo in a nutshell

- Simulate the *time-evolution of the system* without dealing with the *master equation* directly

$$\frac{\partial P(\sigma, t)}{\partial t} = \sum_{\sigma'} [W(\sigma' \rightarrow \sigma)P(\sigma', t) - W(\sigma \rightarrow \sigma')P(\sigma, t)]$$

- Generate “what, where, when”
- $n$ -fold way (BKL algorithm)  
[A.B. Bortz, M.H. Kalos and J.L. Lebowitz, *J. Comput. Phys.* **17** (1975) 10]  
[D.T. Gillespie, *J. Phys. Chem.* **81** (1977) 2340]
- Time increment selected randomly from an exponential distribution with parameter  $\lambda = \sum_i n_i r_i = \sum_i \lambda_i$

# The $n$ -fold way (BKL) algorithm

- chose the next event type,  $e_j$   
 $\left( \sum_{i=1}^{j-1} \lambda_i < \text{rand} \times \lambda \leq \sum_{i=1}^j \lambda_i \right)$
- chose the site, *from the list of possible sites for  $e_j$*
- calculate the time increment and update the system

[A.B. Bortz, M.H. Kalos and J.L. Lebowitz, *J. Comput. Phys.* **17** (1975) 10]

[D.T. Gillespie, *J. Phys. Chem.* **81** (1977) 2340]

[V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 054001]

- A new variant: the BKL\* algorithm
  - $\theta_f$  is quite small ( $10^{-7} - 10^{-4}$ )
  - huge grids may be necessary in the simulations
  - keeping track of  $[F_v]$  is computationally **very expensive**
  - modification of the BKL algorithm: find the site with a null-event scheme!
- ⇒ can be up to 20% faster!

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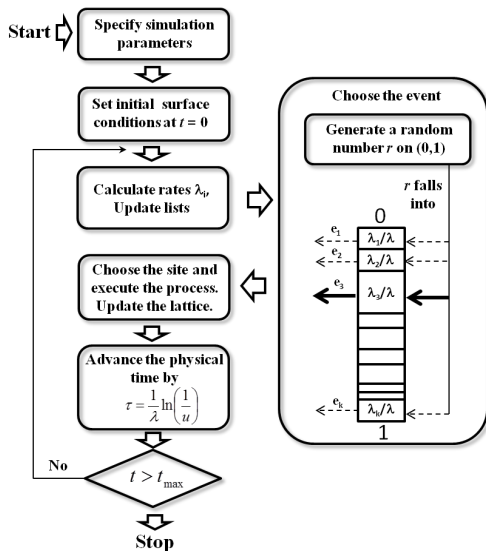
[A.B. Bortz, M.H. Kalos and J.L. Lebowitz, *J. Comput. Phys.* **17** (1975) 10]

[D.T. Gillespie, *J. Phys. Chem.* **81** (1977) 2340]

[V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 054001]

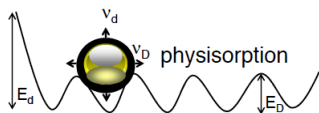
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# The $n$ -fold way (BKL) algorithm flowchart



# Transition rates

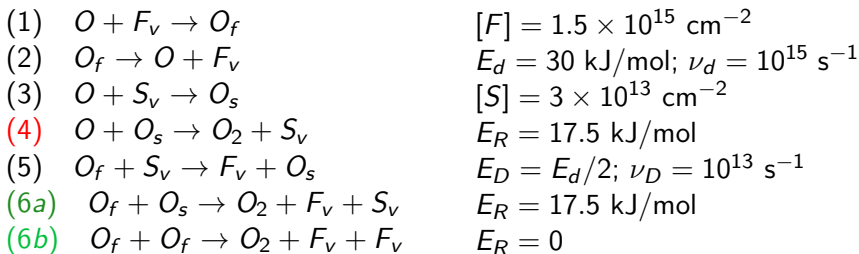
- Desorption:  $r_d = \nu_d \exp(-E_d/kT_w)$ 
  - $\nu_d \sim 10^{15} \text{ s}^{-1}$
  - $E_d \sim 0.5 \text{ eV}$  ( $\sim 50 \text{ kJ/mol}$ )
- Adsorption:  $r_f = k'_f \phi_A/[F]$ ,  $r_s = k'_s \phi_A/[S]$ 
  - $[F] \sim 10^{15} \text{ cm}^{-2}$ ;  $[S] \sim 10^{13} \text{ cm}^{-2}$
  - $k'_f \sim 1$ ;
- Recombination:  $P_R = \exp(-E_R/kT_w)$ 
  - $E_R \sim 0.2 \text{ eV}$  ( $\sim 20 \text{ kJ/mol}$ )
- Surface diffusion:  $r_D = \nu_D \exp(-E_D/kT_w)$ 
  - $\nu_d \sim 10^{13} \text{ s}^{-1}$
  - $E_D \sim E_d/2$



Credits: D. Marinov

The transition rates can differ by 10 orders of magnitude!

## O recombination in O<sub>2</sub>

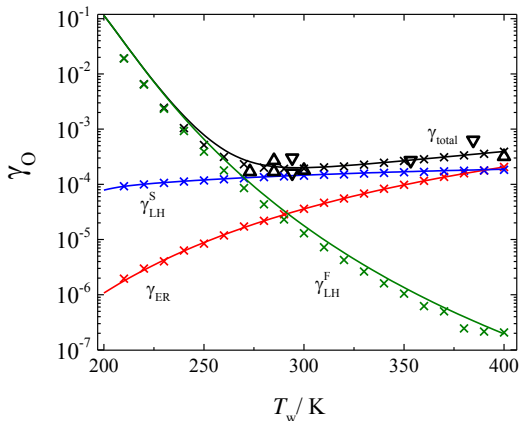


- At steady-state:

$$\gamma = 2 \left( \frac{\theta_s(r_4 + \theta_f r_{6a})[S] + \theta_f \theta_f r_{6b}[F]}{\phi_O} \right) = \gamma_{ER} + \gamma_{LH}^s + \gamma_{LH}^f$$

- $\gamma_{LH}^f$  may be dominant at intermediate pressures (10-50 Torr)  
[D. Lopaev et al, *J. Phys. D: Appl. Phys.* **44** (2011) 015201]

# $\gamma_0$ vs $T_w$



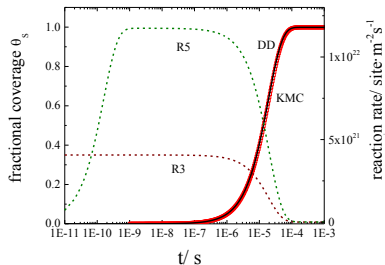
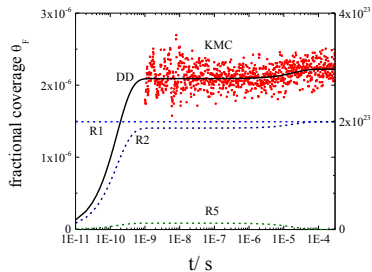
[O] =  $10^{15}$  cm $^{-3}$ ;  $\times$  KMC; (—) DD

$\triangle$  [Y.C. Kim and M. Boudart, *Langmuir* **7** (1991) 2999]

$\nabla$  [J.C. Greaves and J.W. Linnett, *Trans. Faraday Soc.* **55** (1959) 1355]



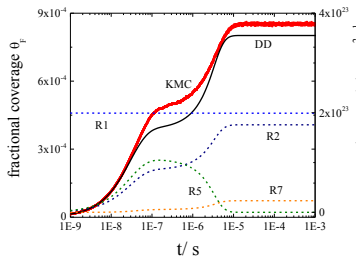
# Adsorption kinetics at $T_W = 300$ K



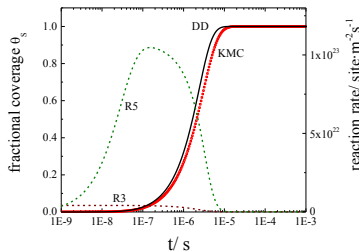
R<sub>1</sub>: physisorption  
R<sub>3</sub>: chemisorption

R<sub>2</sub>: thermal desorption  
R<sub>5</sub>: surface diffusion

# Adsorption kinetics at $T_W = 200$ K

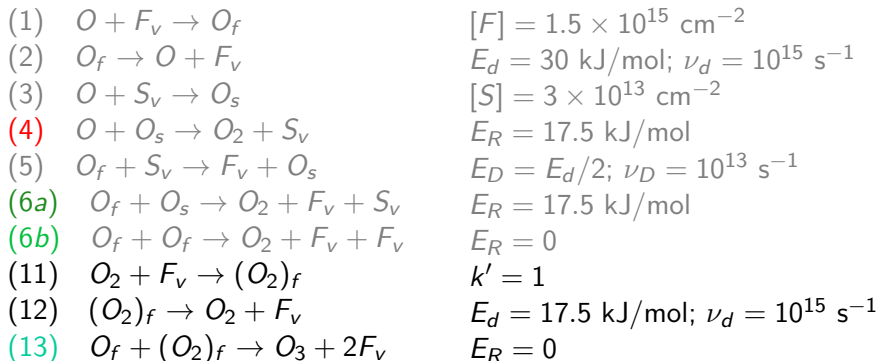


R<sub>1</sub>: physisorption  
R<sub>3</sub>: chemisorption



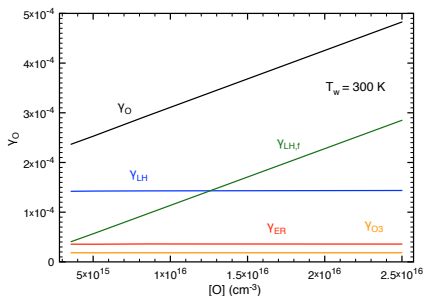
R<sub>2</sub>: thermal desorption  
R<sub>5</sub>: surface diffusion

# O recombination with formation of $O_2$ and $O_3$

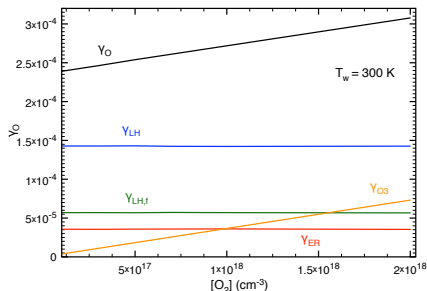


[Lopaev et al 2011]:  $E_d^{O_2} \simeq 18.3 \text{ kJ/mol}$ ;  $E_d^O \simeq 31.6 \text{ kJ/mol}$

# Recombination probability



$$[O_2] = 5 \times 10^{17} \text{ cm}^{-3}$$



$$[O] = 5 \times 10^{15} \text{ cm}^{-3}$$

$\gamma_{LH}^{O_2}$  ( $\sim 3 \times 10^{-5}$ ) is about one order of magnitude lower than in [Lopaev *et al* 2011]  
 [D. Marinov *et al*, *PSST* 22 (2013) 055018]:  $\gamma_{LH}^{O_2} < 10^{-4}$  at  $p = 5$  Torr

# Conclusions

- Modelling constitutes a powerful tool to understand, predict and optimize the plasma behaviour
- A comprehensive kinetic model has been developed to study oxygen discharges . . . associated with the LoKI simulation tool
- Oxygen exhibits a highly excited VDF, as a result of significant e-V rates

“But to what purpose / (...) / I do not know.”

- Vibrationally excited ozone plays an important role in  $O_3$  kinetics
- Formation of ozone at surfaces could not be established at the present conditions
- Upper limits for  $\gamma(O_3)$  were established at  $10^{-5}$  and  $10^{-4}$  for  $p = 1$  and 5 Torr, respectively, in good agreement with [Lopaev *et al* 2011]

## Conclusions (continued)

- Powerful Kinetic Monte Carlo algorithms are available to simulate surface kinetics and coupled gas phase and surface chemistries
  - A variant of the  $n$ -fold way algorithm was used to investigate systems with rates varying over 10 orders of magnitude (!)
  - O recombination on silica:
    - reactions involving physisorbed O and O<sub>2</sub> dominate the surface kinetics
    - the complex behaviour of  $\gamma_O$  with  $T_W$  was interpreted
    - O<sub>3</sub> formation on surfaces was described, in fair agreement with experimental data
- ⇒ Coupled with MD, *Dynamical Monte Carlo methods constitute a powerful tool to simulate surface processes* up to large space/time scales
- Near future: explore the impact of a distribution of reactivity

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