Kinetic modelling of air plasmas

self-consistency, bottlenecks, successes

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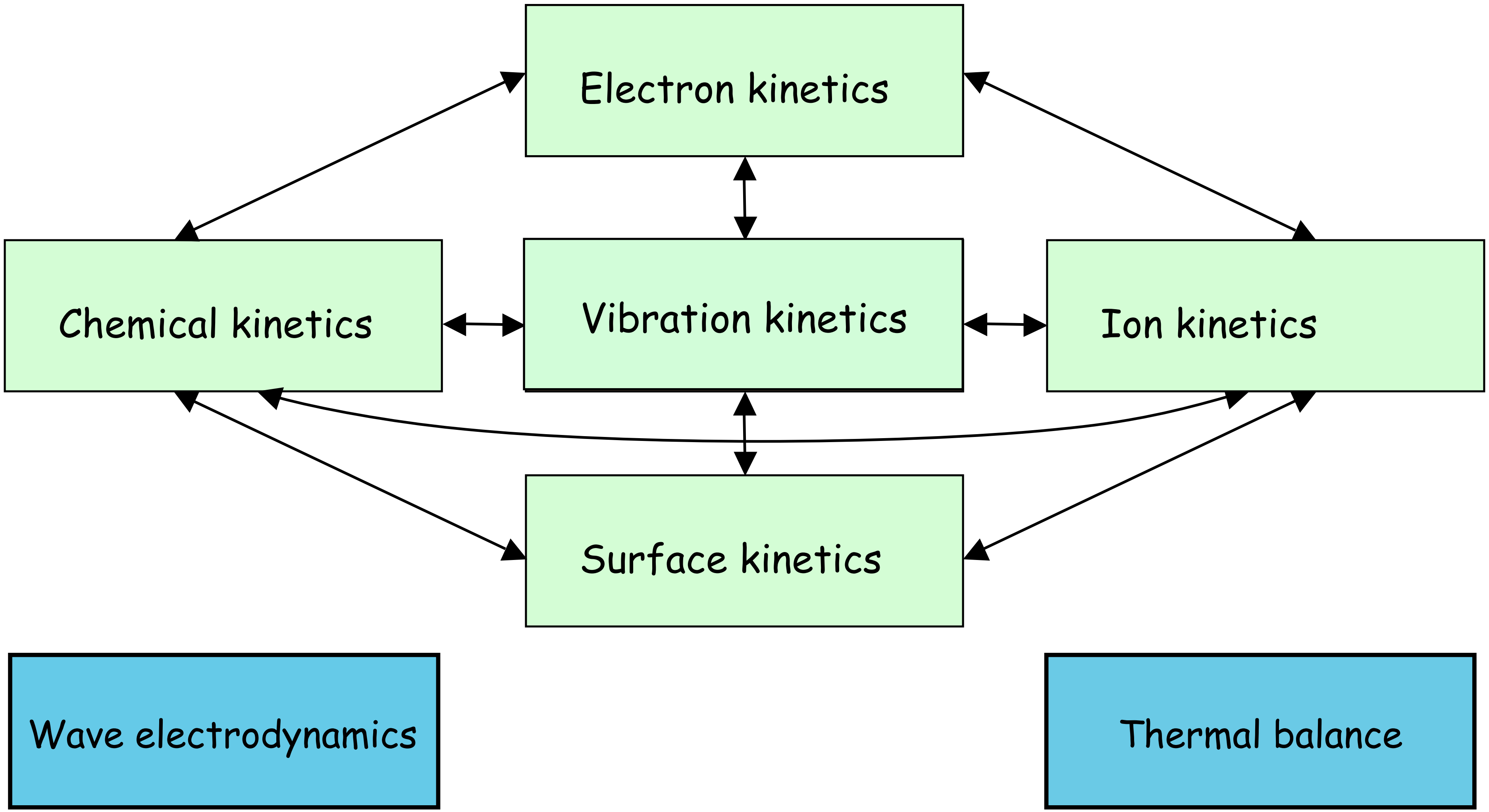
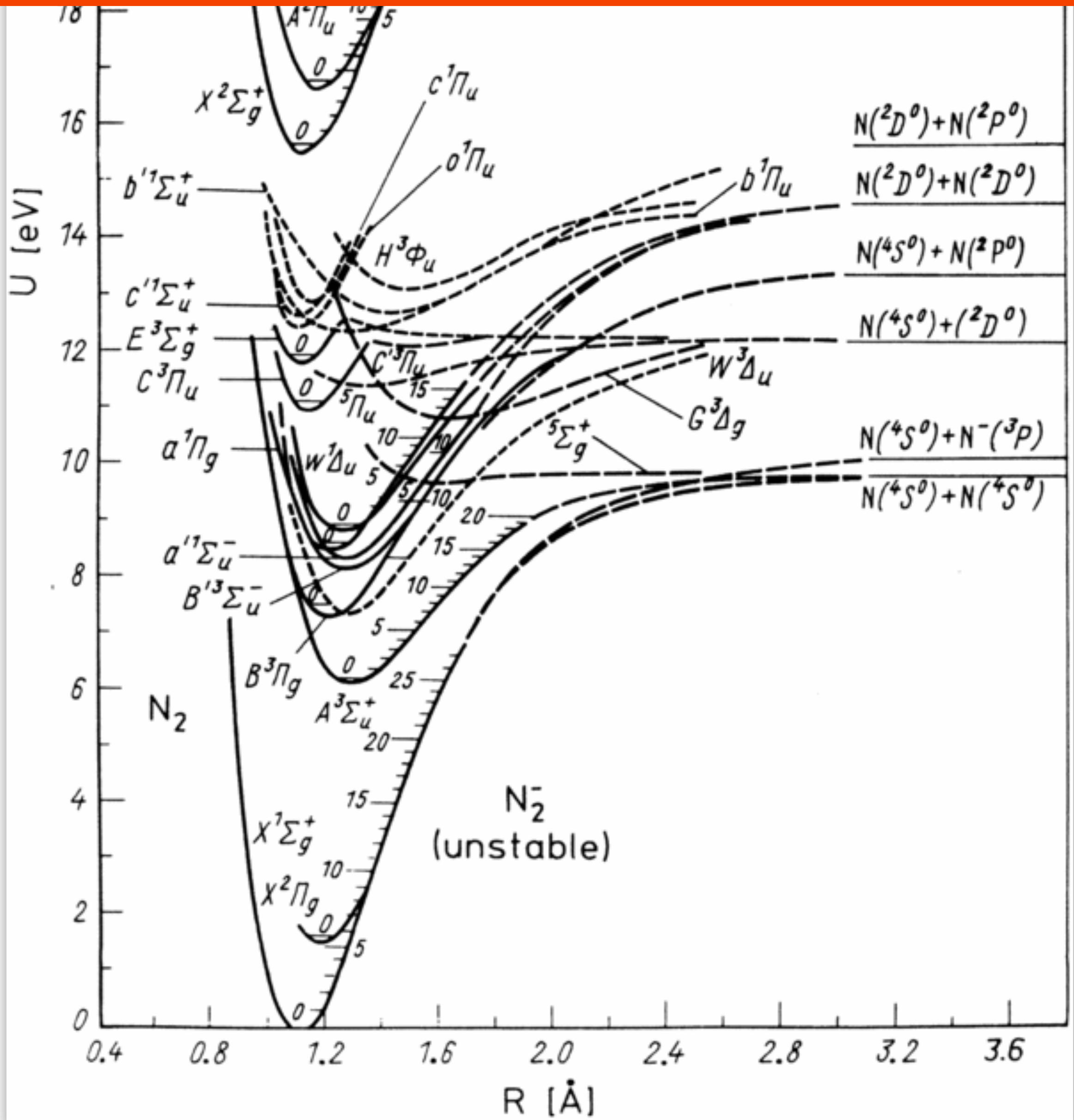
Modeling of nonequilibrium molecular plasmas



The N_2 molecule



Kinetic modeling (N_2-O_2)

- Electron kinetics (electron Boltzmann equation)
- Vibrational kinetics of $N_2(X, 0 \leq v \leq 60)$ and $O_2(X, 0 \leq v \leq 47)$ molecules
- Chemical kinetics of
  - $N_2(A, B, C, B', a', a, w, a'')$
  - $O_2(X, a, b)$
  - $N(^4S, ^2D, ^2P)$, $O(^3P, ^1D)$
  - O_3, O_3^*, $NO(X, A, B)$, $NO_2(X, A)$
- Ion kinetics of N_2^+, N_4^+, O_2^+, O^+, NO^+, O^-

Self-consistent modeling

Input:

- Discharge operating parameters (p, R, P-n_e-I, ω)
- Wall (and often gas) temperature
- Collisional data

Output:

- Electron Energy Distribution Function (EEDF)
- Vibrational Distribution Function (VDF)
- Concentration of excited states, radicals & ions
- (gas temperature)

Physical insight

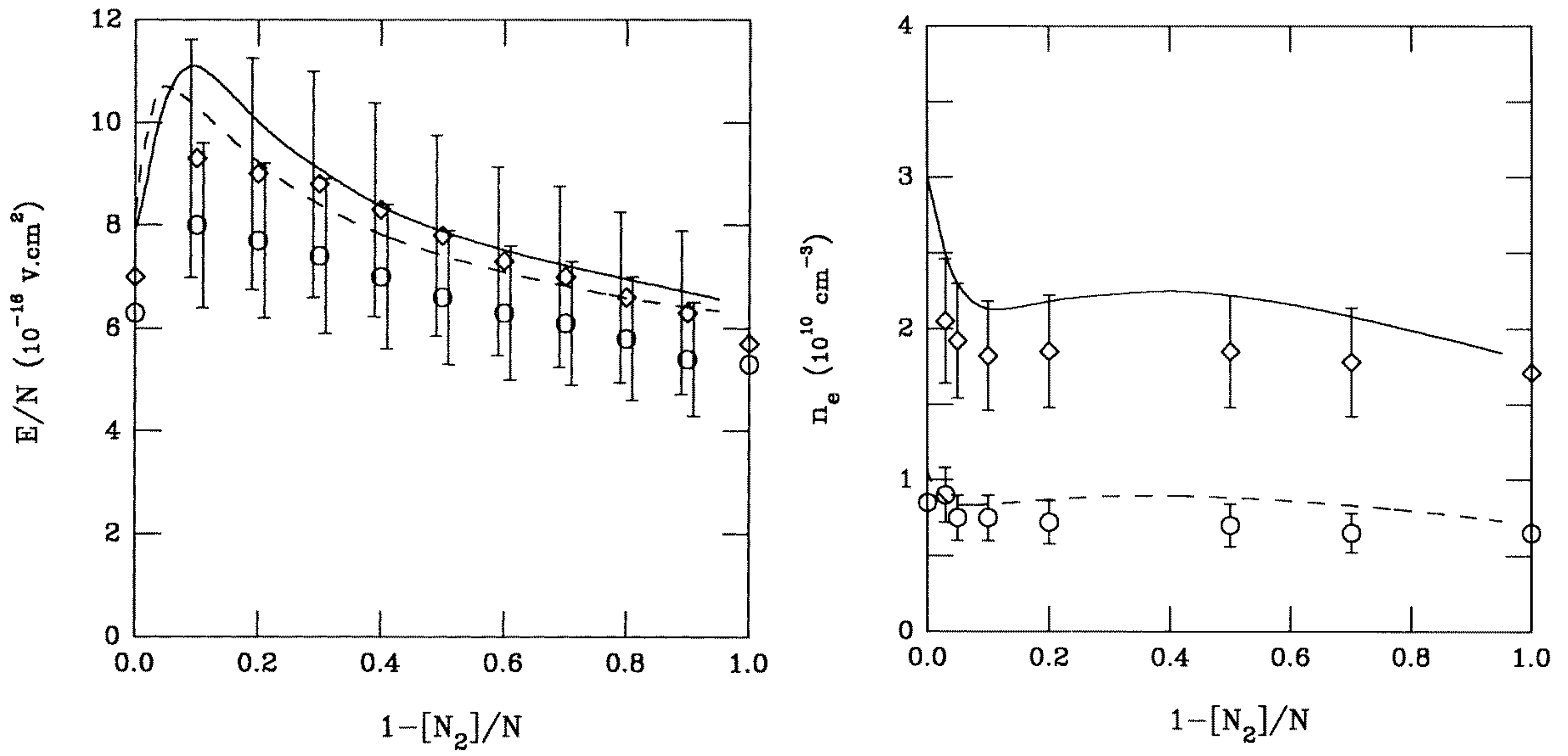
Some lessons from the past

In collaboration with Jorge Loureiro

Plasma Sources Sci. Technol. **6** (1997) 373
Plasma Sources Sci. Technol. **8** (1999) 110
(…)

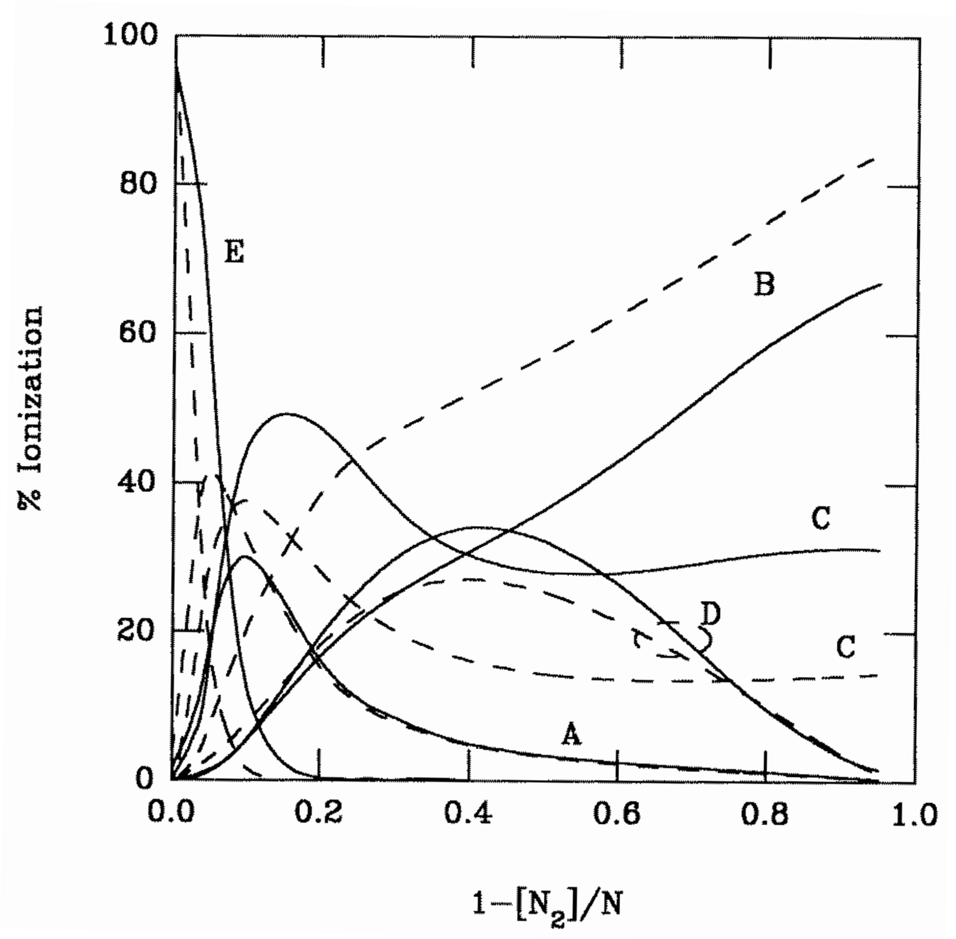
- Focus on ionisation, N, O and NO
- The pure gases are often more complex than the air mixture
- Surface processes may play an important role
- Strong coupling $N_2(X,v)$, NO, N, O, $N_2(A,B)$

Some lessons from the past



p=2 Torr, R=0.8 cm, I=30 & 80 mA

Some lessons from the past



A : $e+N_2 \rightarrow e+e+N_2^+$

B : $e+O_2 \rightarrow e+e+O_2^+$

C : $e+O \rightarrow e+e+O^+$

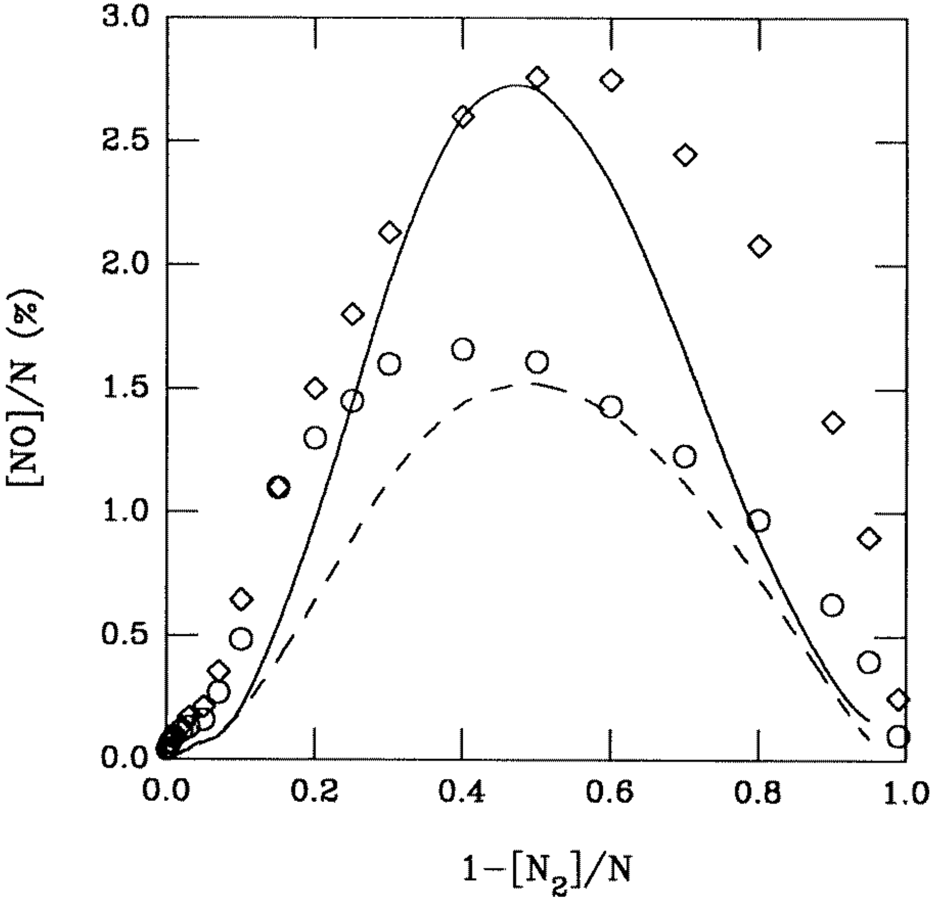
D : $e+NO \rightarrow e+e+NO^+$

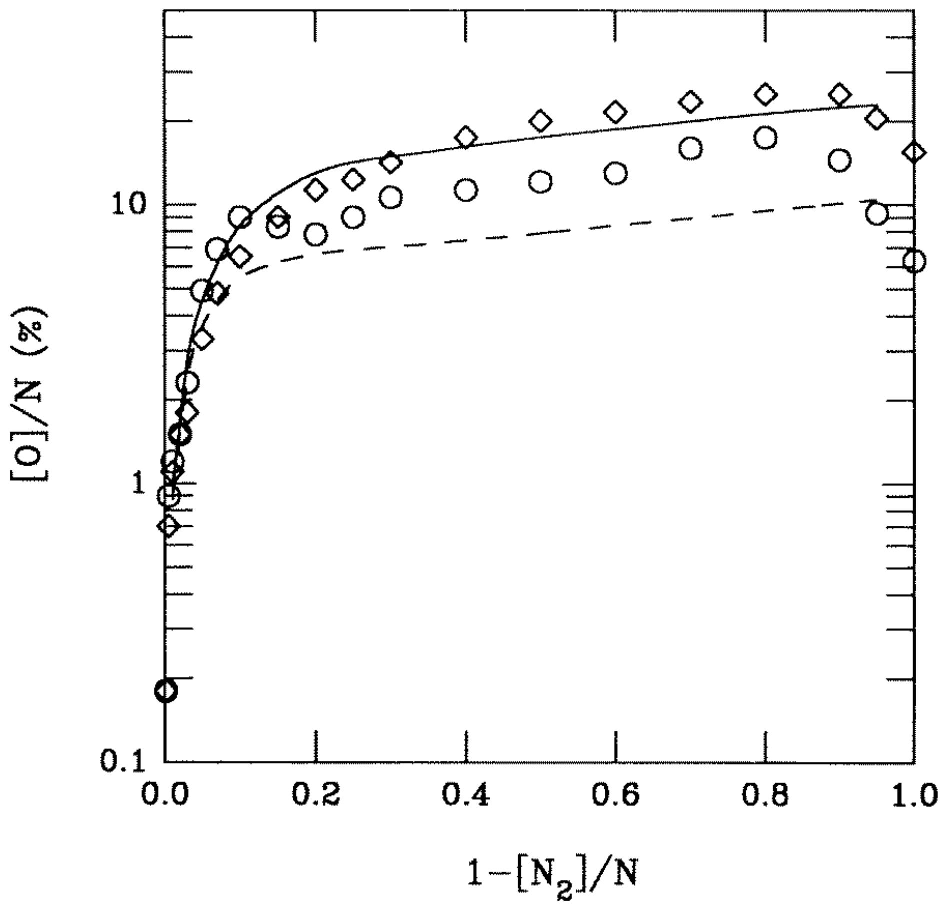
E : $N_2(A,a') + N_2(a') \rightarrow$

$\rightarrow N_4^+ + e$

$N_2(A,a') + O_2 \rightarrow N_2(X) + O + O$

Some lessons from the past





p=2 Torr, *R*=0.8 cm, *I*=30 & 80 mA

Some lessons from the past

NO formation:

$$N_2(X, v \geq 13) + O \rightarrow NO + N$$

$$N_2(A) + O \rightarrow NO + N(^2D)$$

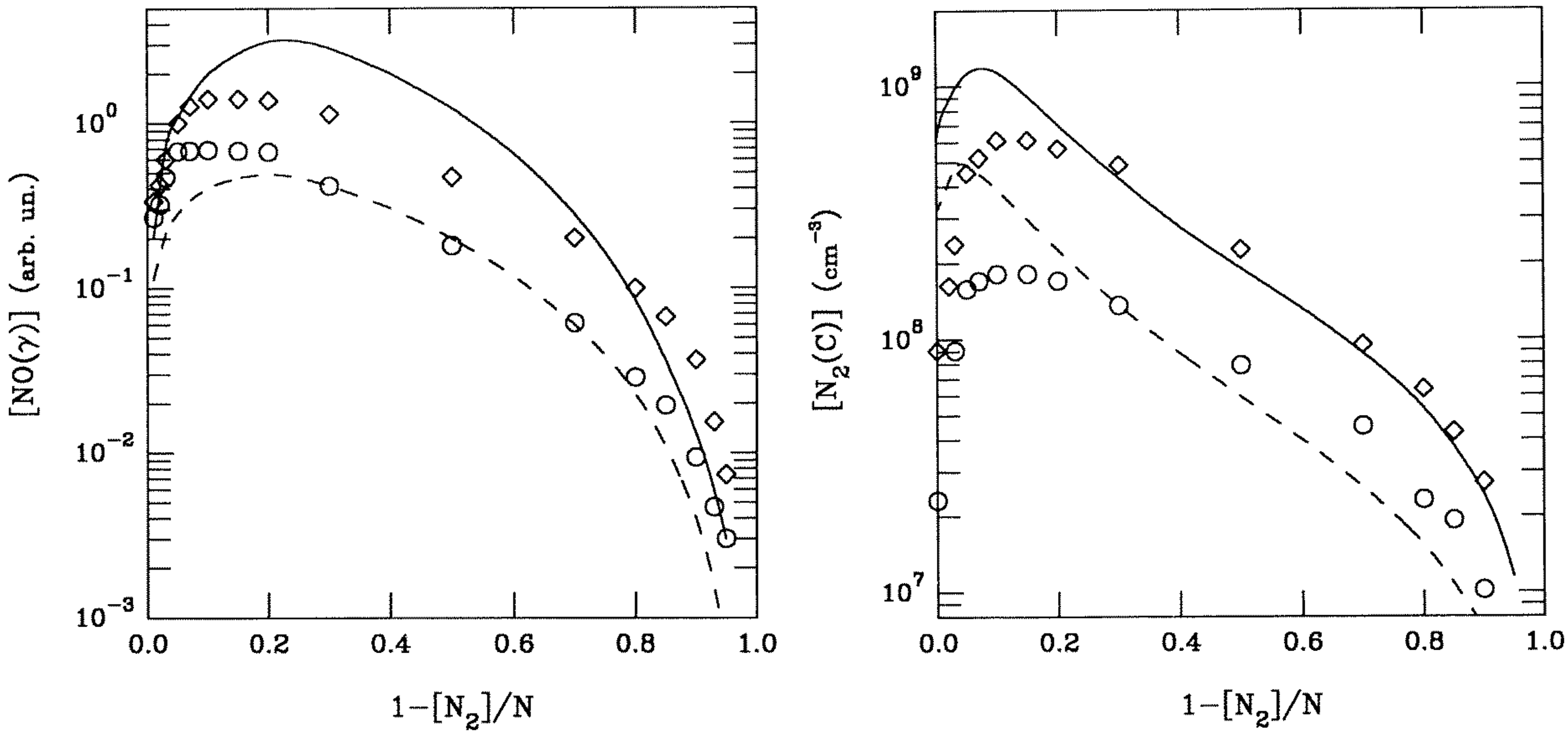
$$N(^2D) + O_2 \rightarrow NO + O$$

O formation:

$$e + O_2 \rightarrow e + O + O$$

$$N_2(B) + O_2 \rightarrow O + O + N_2$$

Some lessons from the past



$N_2(A) + NO \rightarrow NO(\gamma) + N_2$

Successes #1

NO kinetics and gas heating in pulsed discharges

In collaboration with

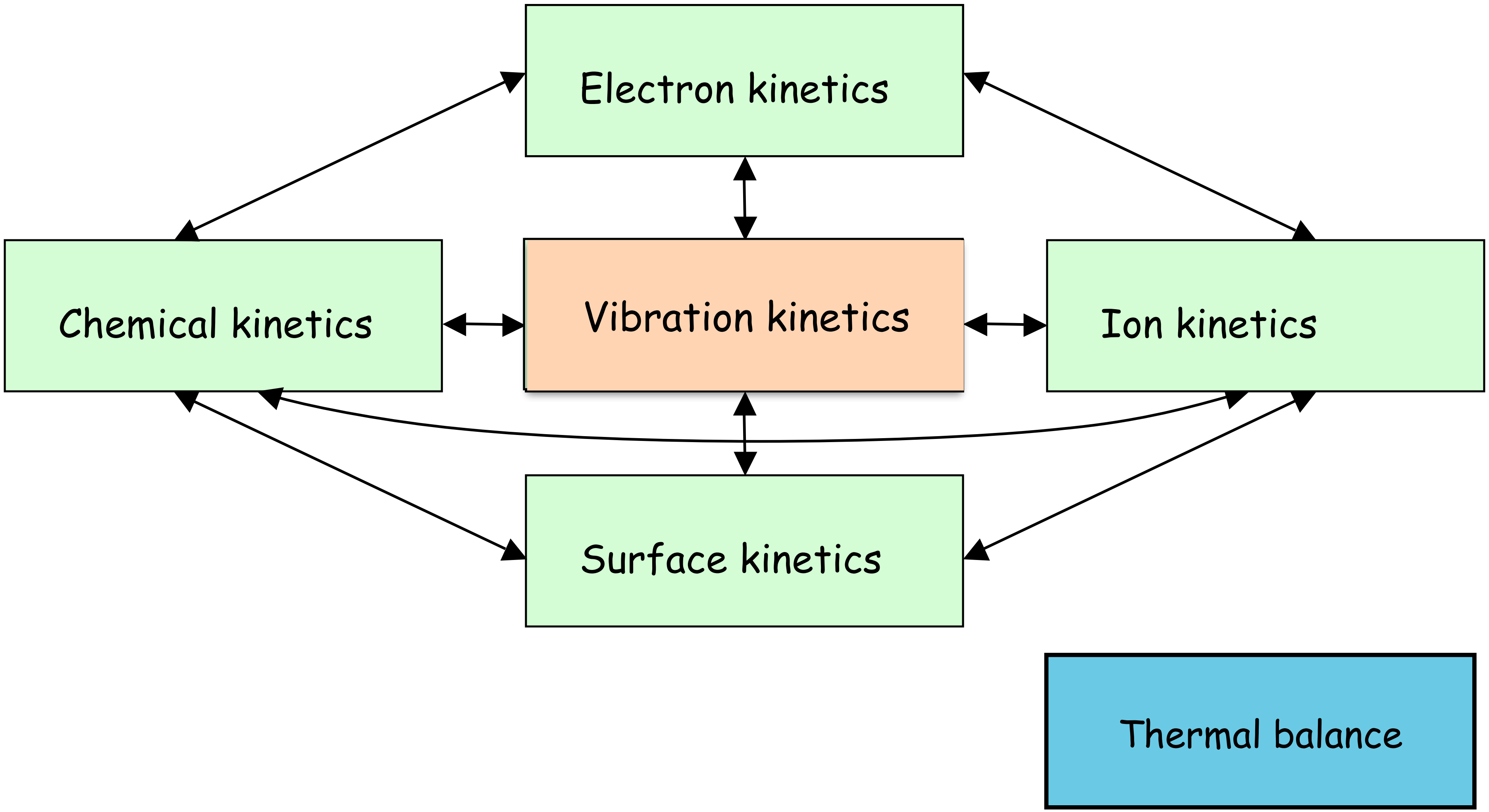
Carlos D. Pintassilgo,[1] Olivier Guaitella[2] and
Antoine Rousseau[1]

[1]Faculdade de Engenharia, Universidade do Porto, Portugal

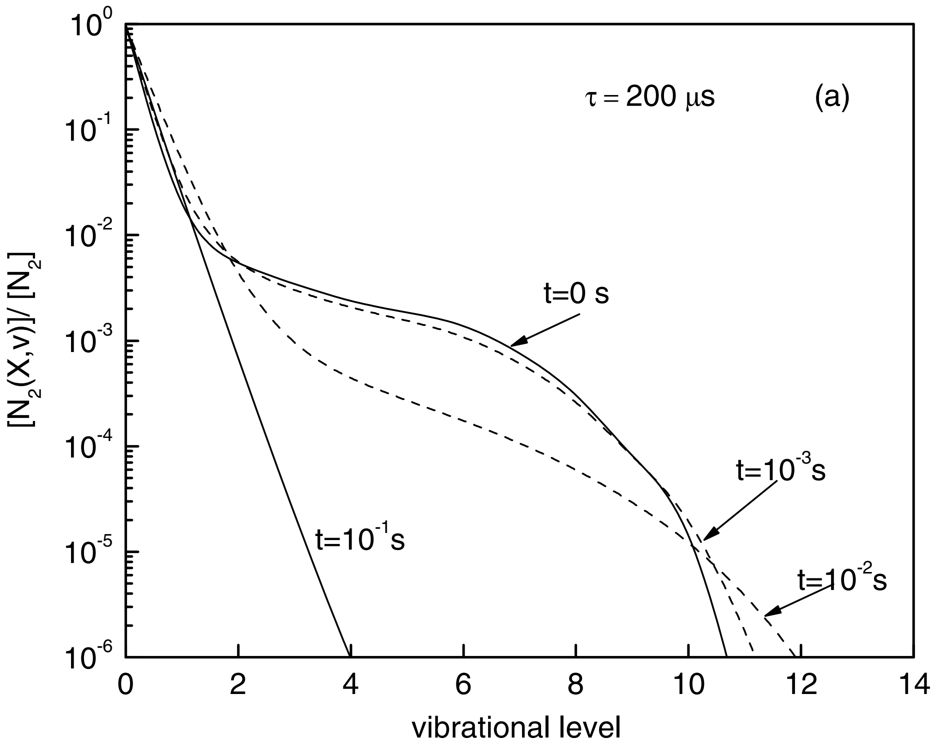
[2]Laboratoire de Physique des Plasmas, Ecole Polytechnique, France

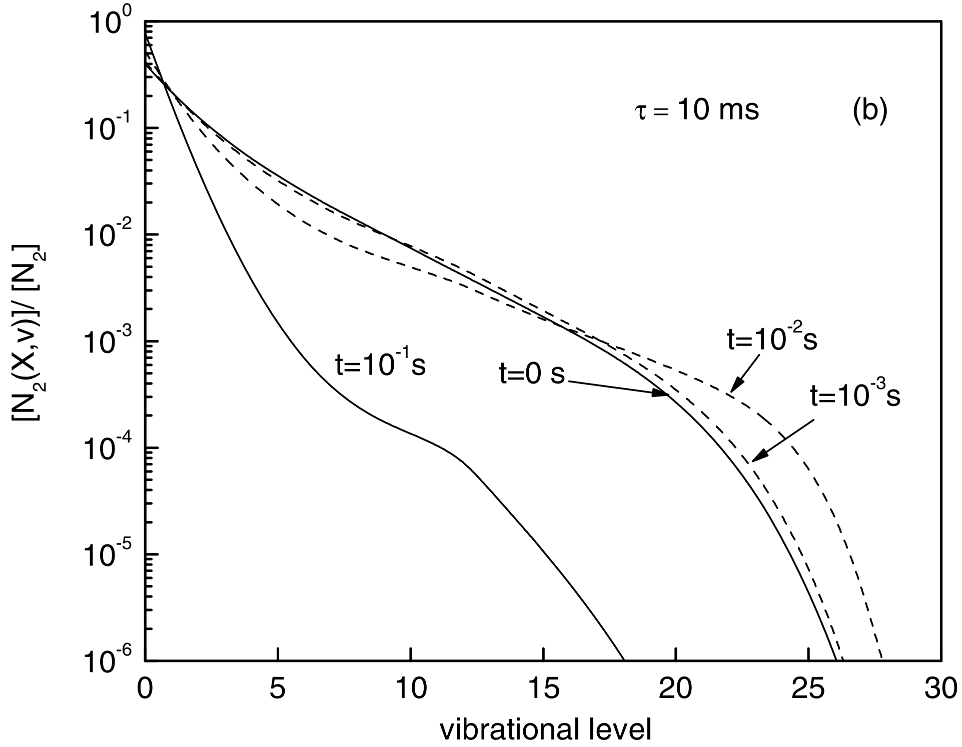
Plasma Sources Sci. Technol. **19** (2010) 055001
Plasma Sources Sci. Technol. **23** (2014) 025006

NO kinetics and gas heating in pulsed discharges



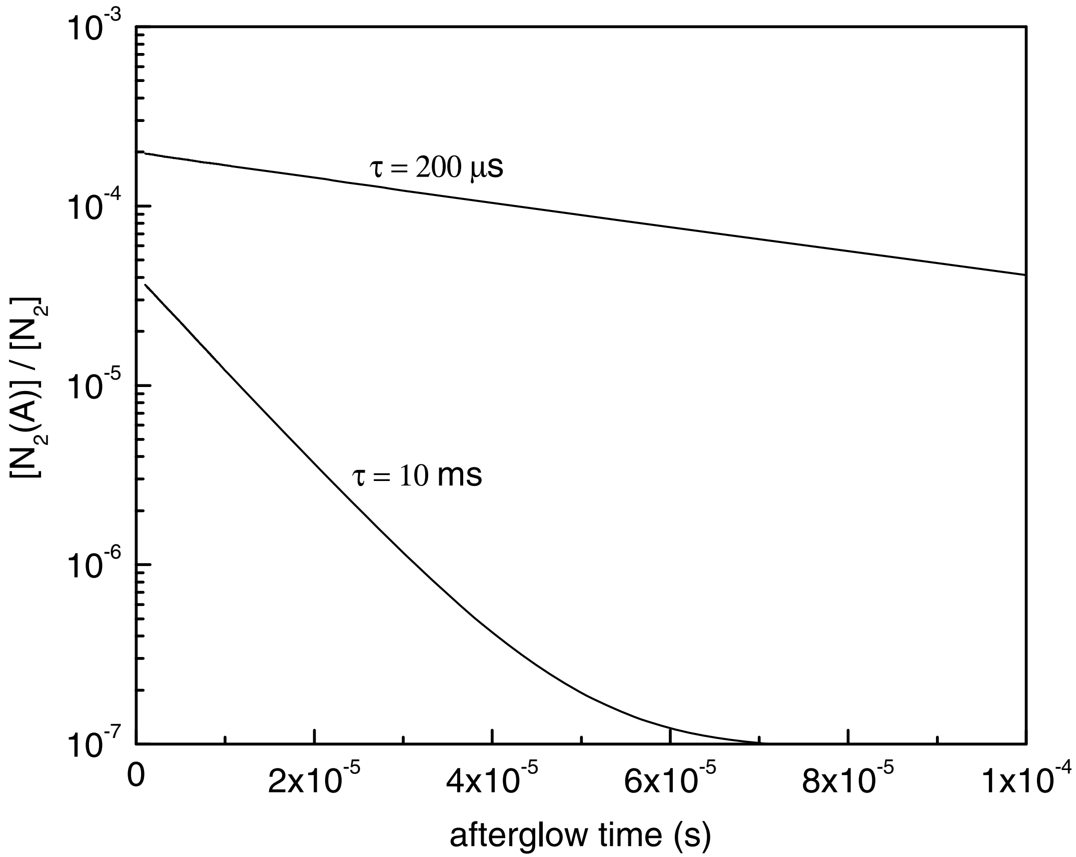
Vibrations need time to build up!





p=1 Torr, R=1.05 cm, I=40 mA

Electron impact excitation is fast



$$N_2(A) + N(^4S) \rightarrow N_2(X,v) + N(^2P)$$

NO formation

NO formation:

$$N_2(X,v \geq 13) + O \rightarrow NO + N$$

$$N_2(A) + O \rightarrow NO + N(^2D)$$

The first reaction gains importance:

- with the pulse length
- with the afterglow time

Gas heating

Early instants

$$e + O_2 \rightarrow e + O_2(B) \rightarrow e + O + O$$

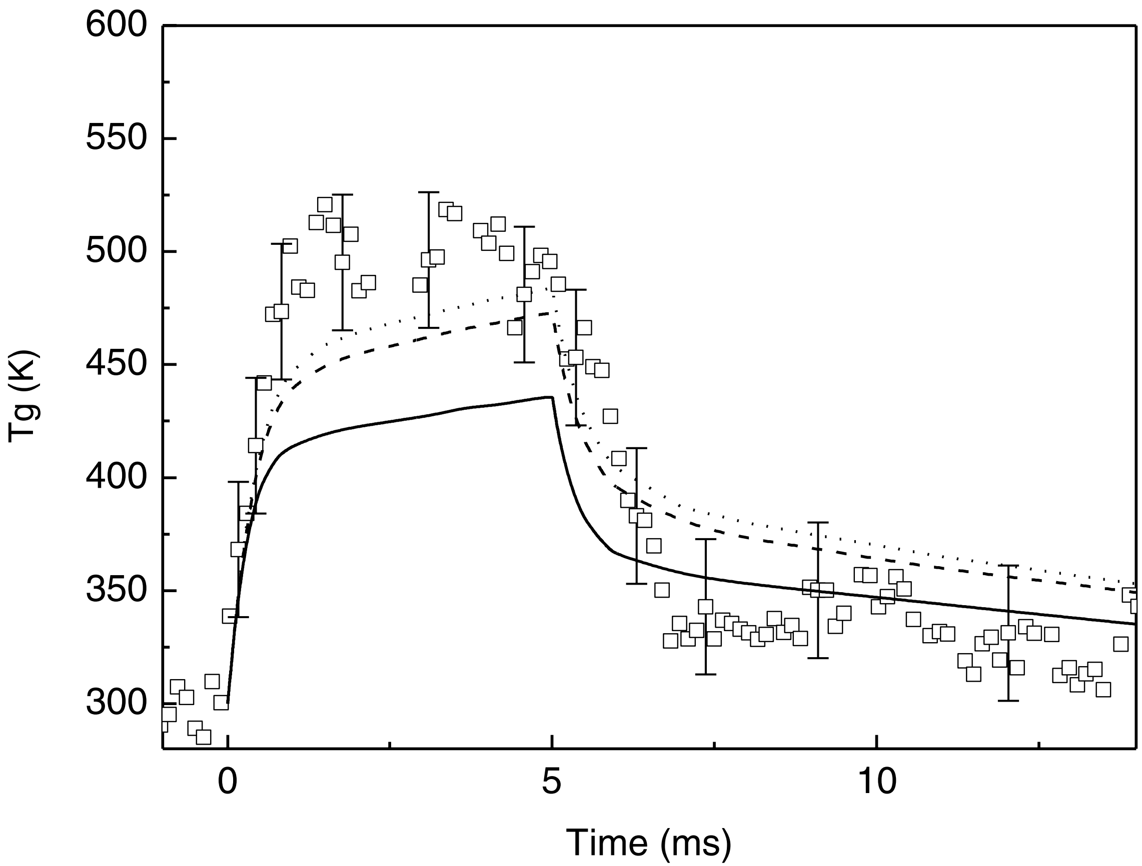
$$N_2(A, B, a', a) + O_2 \rightarrow N_2 + O + O$$

Longer instants

$$N_2(X, v) + O \rightarrow N_2(X, v-1) + O$$

$$O + \text{wall} \rightarrow (1/2) O_2 + \text{wall}$$

Gas heating



p=1 Torr, I=150 mA, τ=5 ms

Measurements by Hubner *et al*, *Meas. Sci. Technol.* **23** (2012) 115602

Successes #2

NO_2 formation on a Pyrex surface

In collaboration with

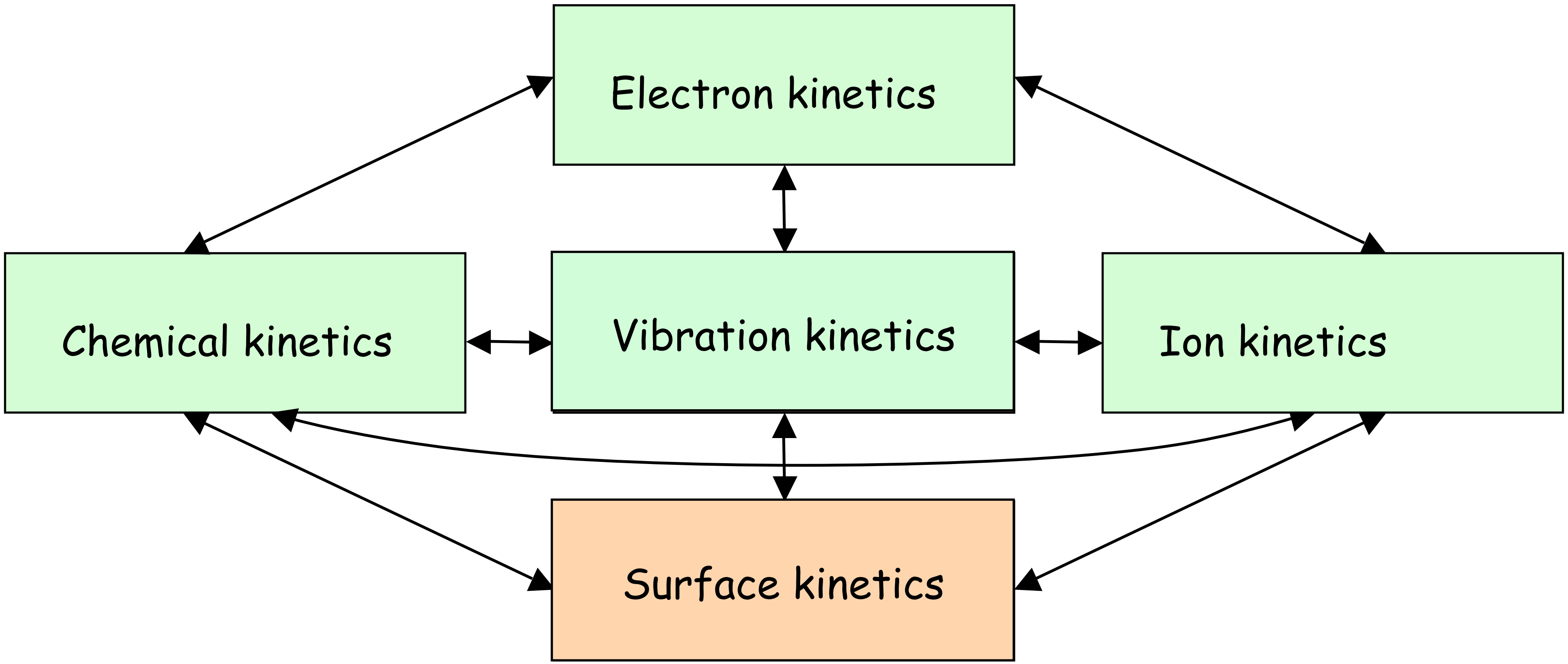
Daniil Marinov, Olivier Guaitella and Antoine Rousseau

Laboratoire de Physique des Plasmas, Ecole Polytechnique, France

See the previous lecture, by Daniil Marinov!!!

J. Phys. D: Appl. Phys. **47** (2014) 224012

NO_2 formation on a Pyrex surface



Motivation

- Molecule formation on surfaces is a relevant issue
- NO, NO_2, N_2O, O_3,...

Major difficulties:

- Good control of the surface conditions
- Reproducibility
- "Unambiguous" interpretation

The garden of the forking paths

Purpose

- System that avoids the major difficulties already identified
- Demonstrate qualitatively and if possibly quantitatively heterogeneous molecule formation (NO oxidation into NO_2)
- Check for a possible distribution of reactivity of the adsorption sites

Experiment

- Pyrex tube, R=1cm, L=60 cm
- Pre-treatment (~1h) with O_2
  - $[O_s]$~$4x10^{14}$ cm^{-2}
- Pumping (~10')
- "Probing"
  - Injection of NO (0.1-4 Torr)
  - Measurement of NO and NO_2 kinetics

D. Marinov, O. Guaitella, A. Rousseau and Y. Ionikh, *J. Phys. D: Appl. Phys.* (2010) **43** 115203
D. Marinov, O. Guaitella, J. P. Booth and A. Rousseau, *J. Phys. D: Appl. Phys.* (2013) **46** 032001

Modeling: surface descriptions

- Macroscopic approach (γ)
- Mesoscopic approach
  - Monte Carlo
  - Continuous in terms of coverage
- Microscopic approach (molecular dynamics)

Model

- 7 types of "chemisorption sites"

  P. F. Kurunczi, J. Guha, and V. M. Donnelly: *J. Phys. Chem. B* **109** (2005) 20989.

- Eley-Rideal "recombination"

$$NO+O_S(i) \rightarrow NO_2+S_V(i)$$

E_R=16 – 41 kJ/mol

- NO_2 adsorption

$$NO_2+S_V(i) \rightarrow (NO_2)_S$$

Rates of the elementary processes

$NO + O_S(i) \rightarrow NO_2 + S_V(i)$

$$r_1(i) = k_1^{0\prime}(i)\varphi_i \frac{\phi_{NO}}{[S_i]} \exp\left(-\frac{E_R(i)}{kT_w}\right) \ \text{site}^{-1}\text{s}^{-1} \ .$$

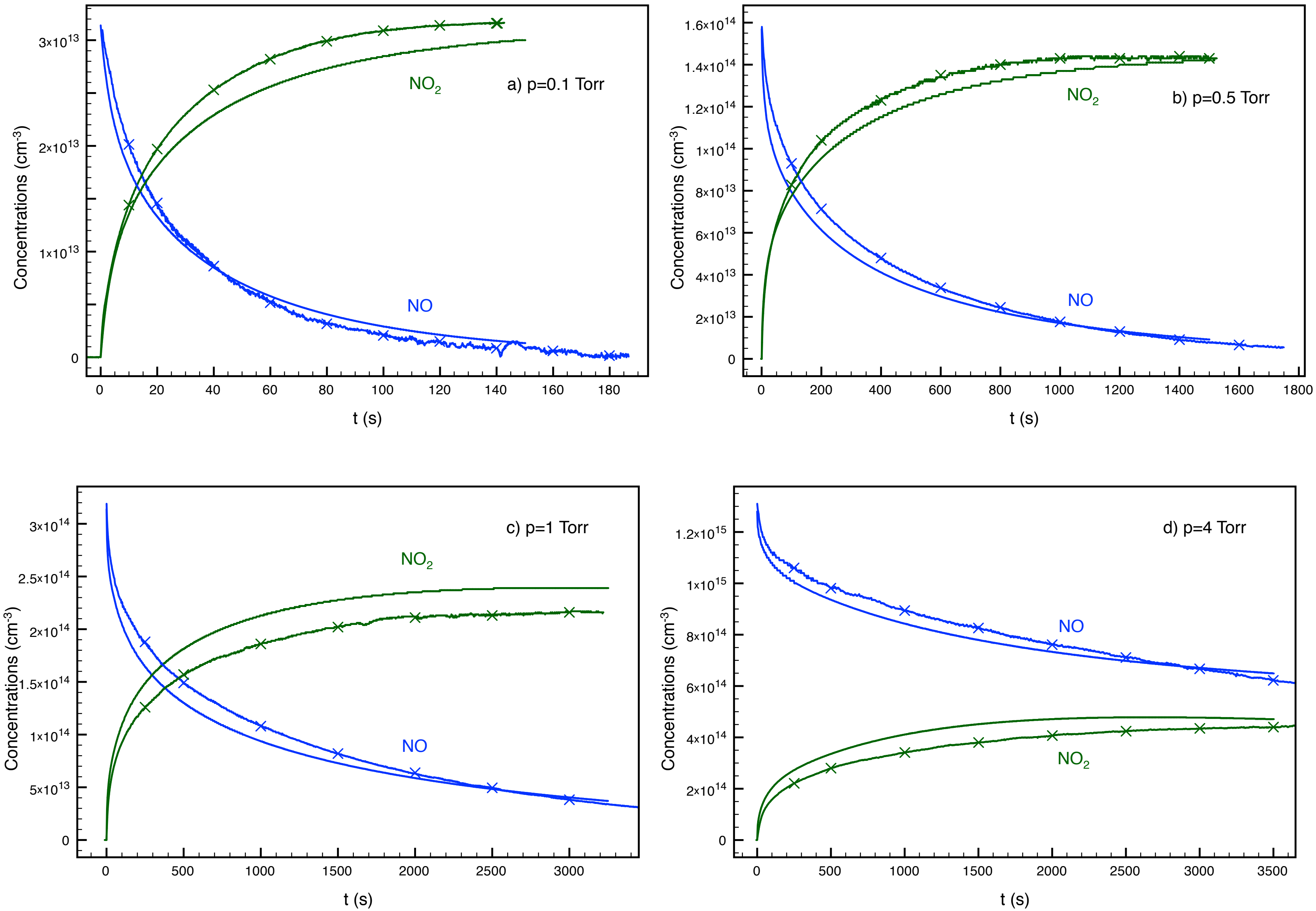
$NO_2 + S_V(i) \rightarrow (NO_2)_S$

$$r_2(i) = k_2^{0\prime}(i)\varphi_i \frac{\phi_{NO}}{[S_i]} \ \text{site}^{-1}\text{s}^{-1}$$

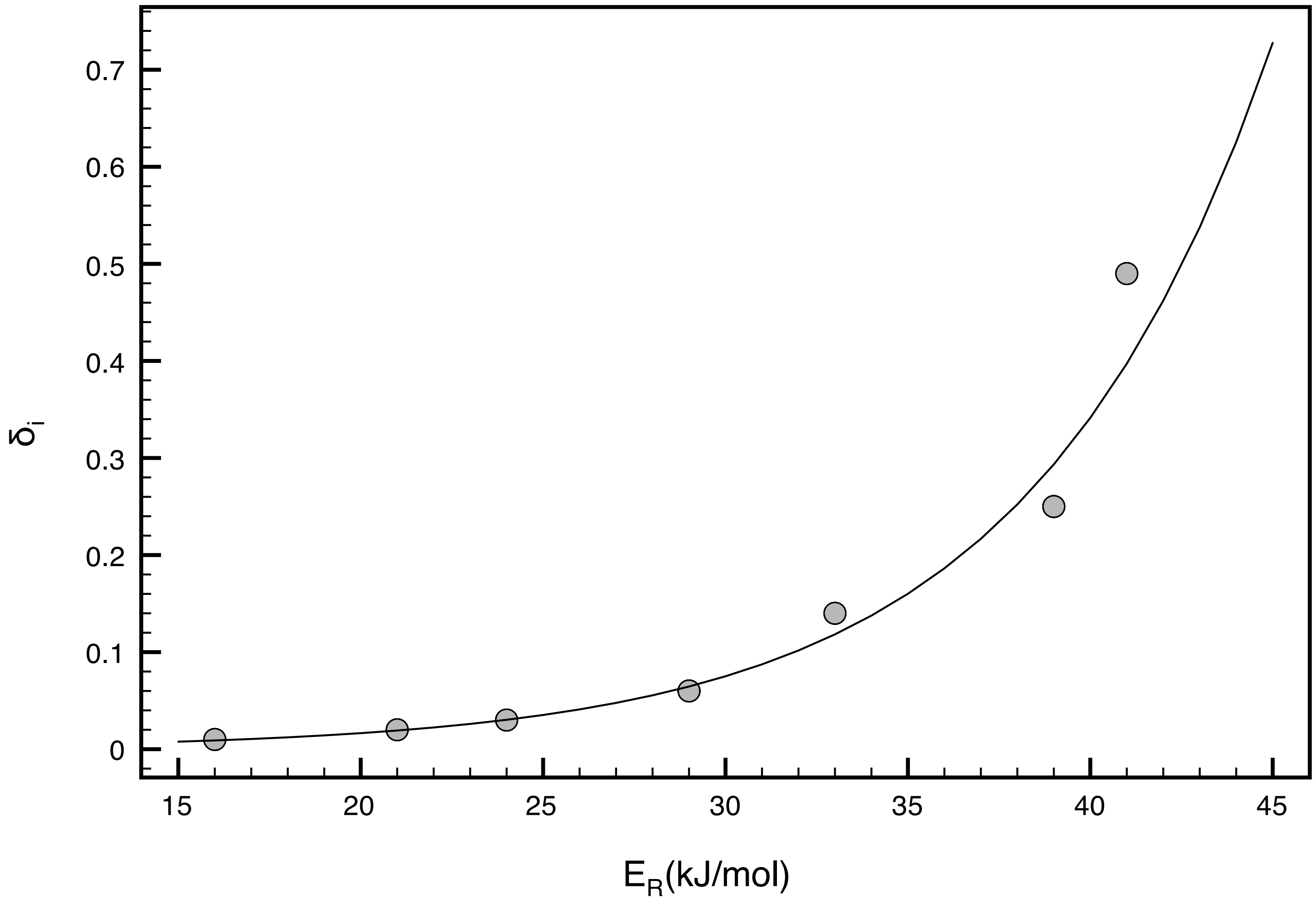
The system of equations

$$
\begin{aligned}
\theta_M(i) &= \frac{[M_S(i)]}{[S_i]} \\
\frac{d\theta_O(i)}{dt} &= -r_1(i)\theta_O(i) \\
\frac{d\theta_{NO_2}(i)}{dt} &= \left[1 - \theta_O(i) - \theta_{NO_2}(i)\right] r_2(i) \\
\frac{d[NO]}{dt} &= -\frac{2}{R}\left(\sum_{i=1}^{7} \theta_O(i)[S_i]r_1(i)\right) \\
\frac{d[NO_2]}{dt} &= \frac{2}{R}\sum_{i=1}^{7} \left\{\theta_O(i)r_1(i) - \left[1 - \theta_O(i) - \theta_{NO_2}(i)\right] r_2(i)\right\} [S_i]
\end{aligned}
$$

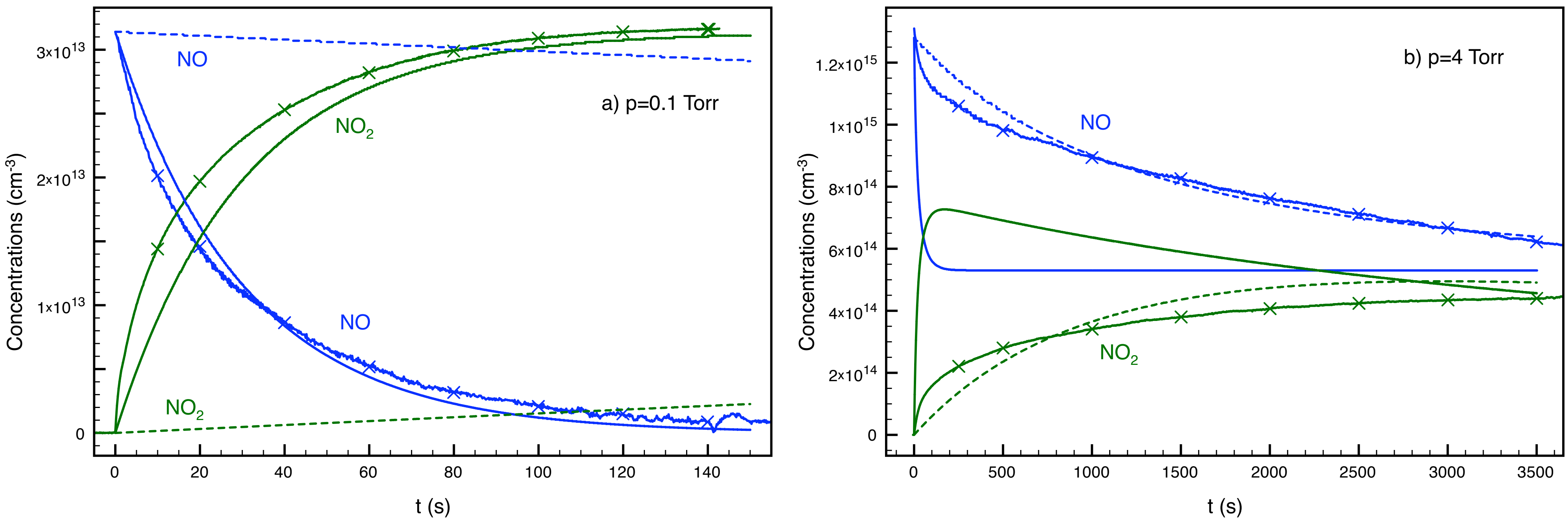
Results: NO and NO_2



Results: distribution of sites

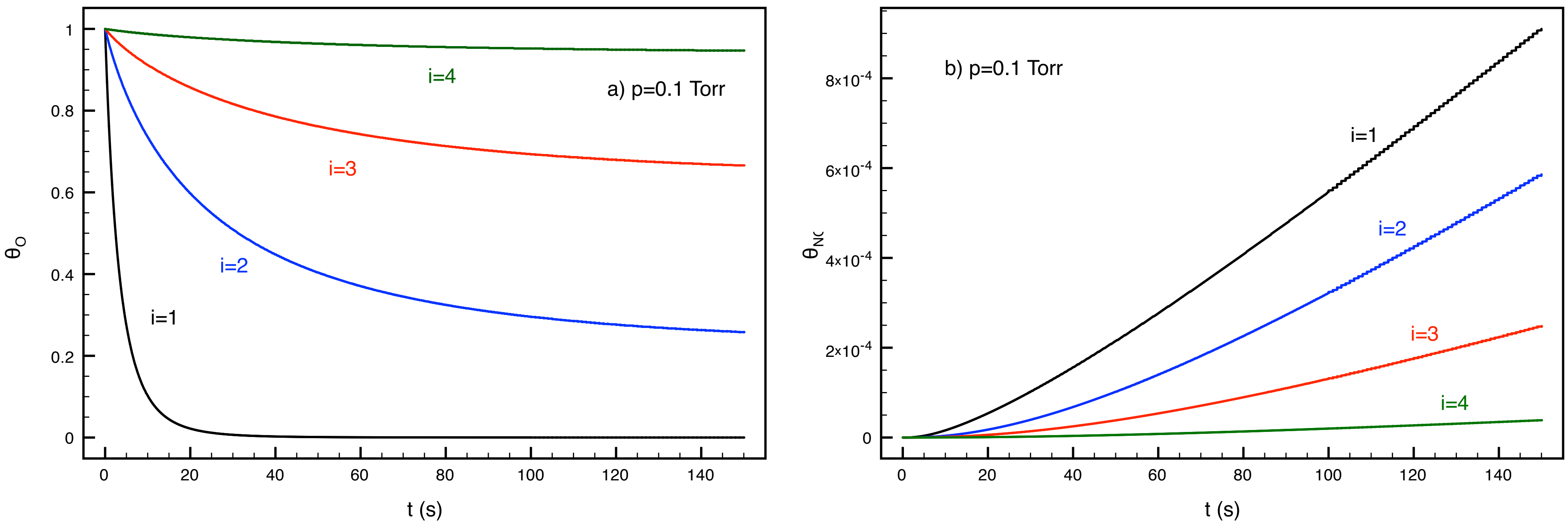


Results: NO and NO_2



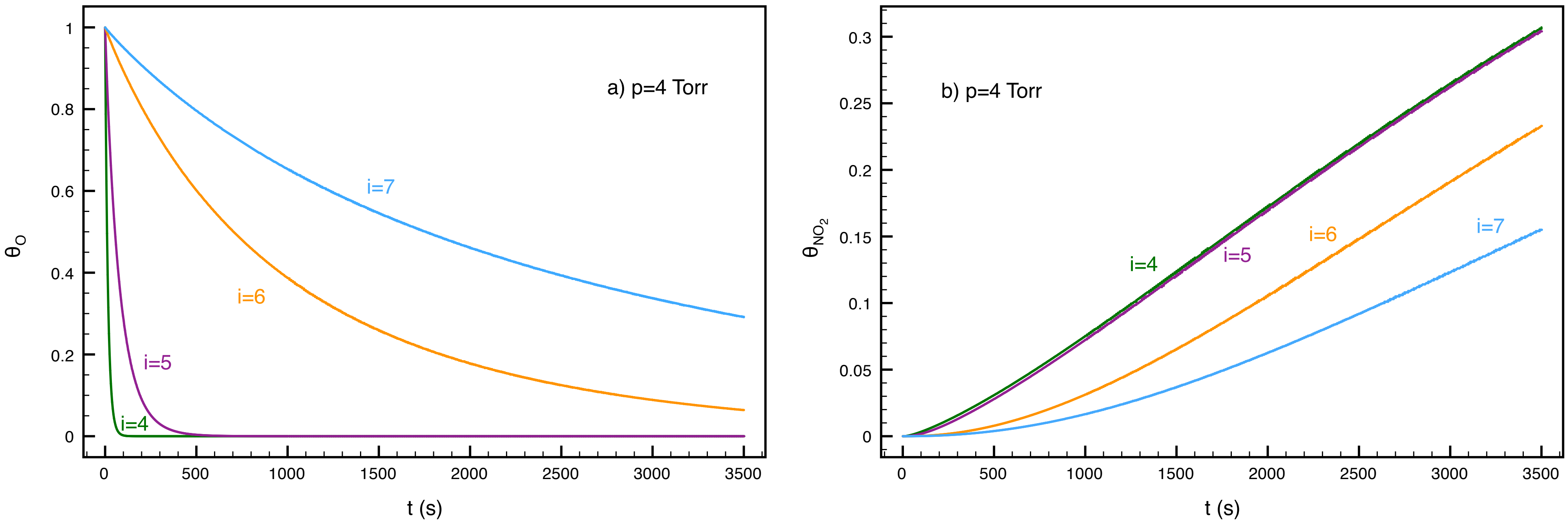
Different timescales require a distribution of $E_R(i)$

Results: coverage of O_s and NO_{2s}



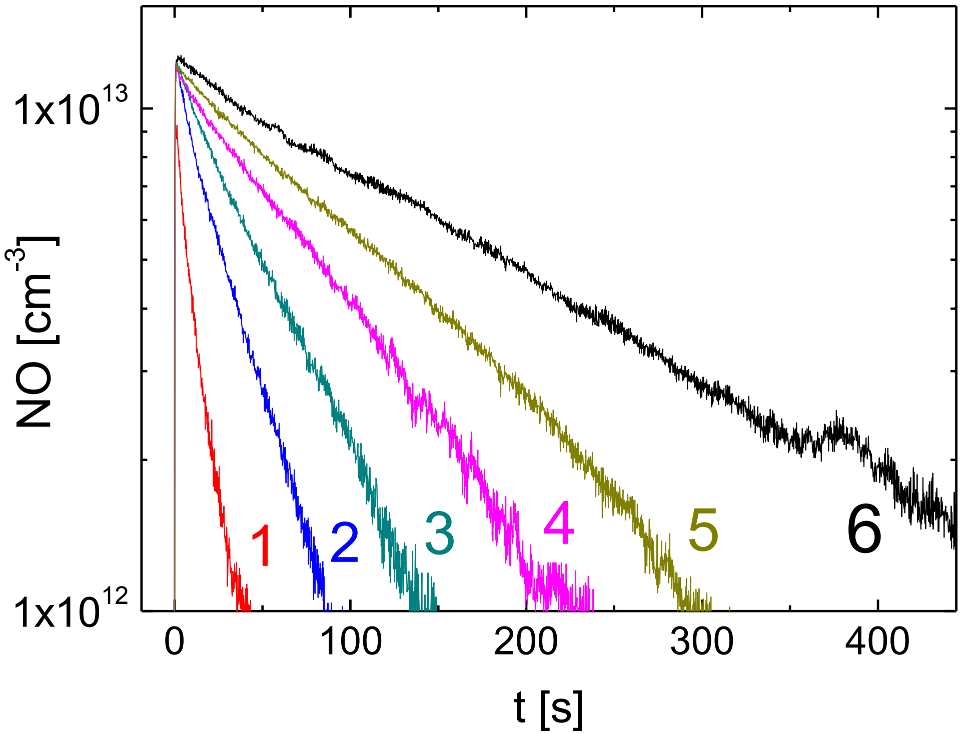
p = 0.1 Torr

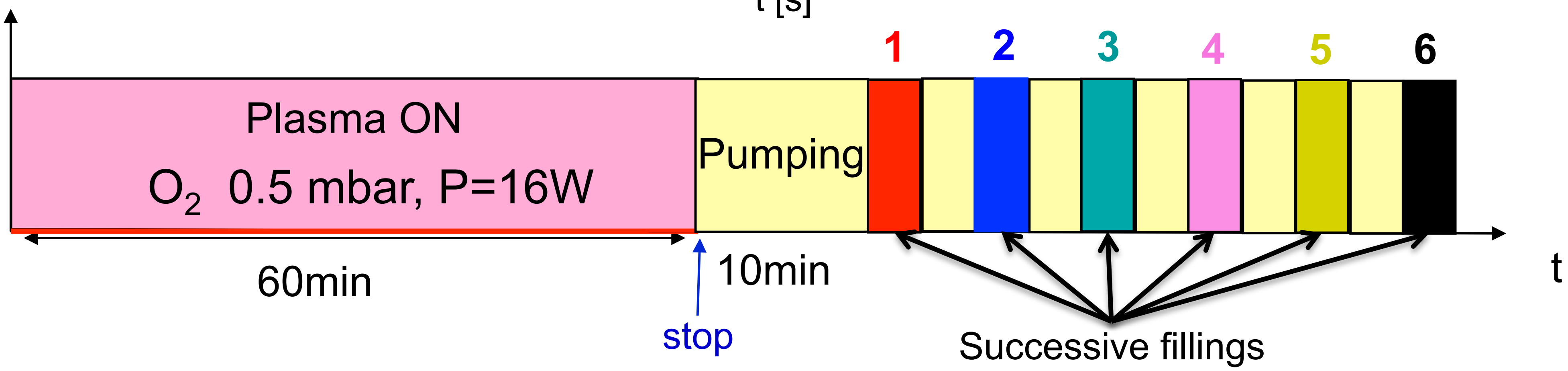
Results: coverage of O_s and NO_{2s}



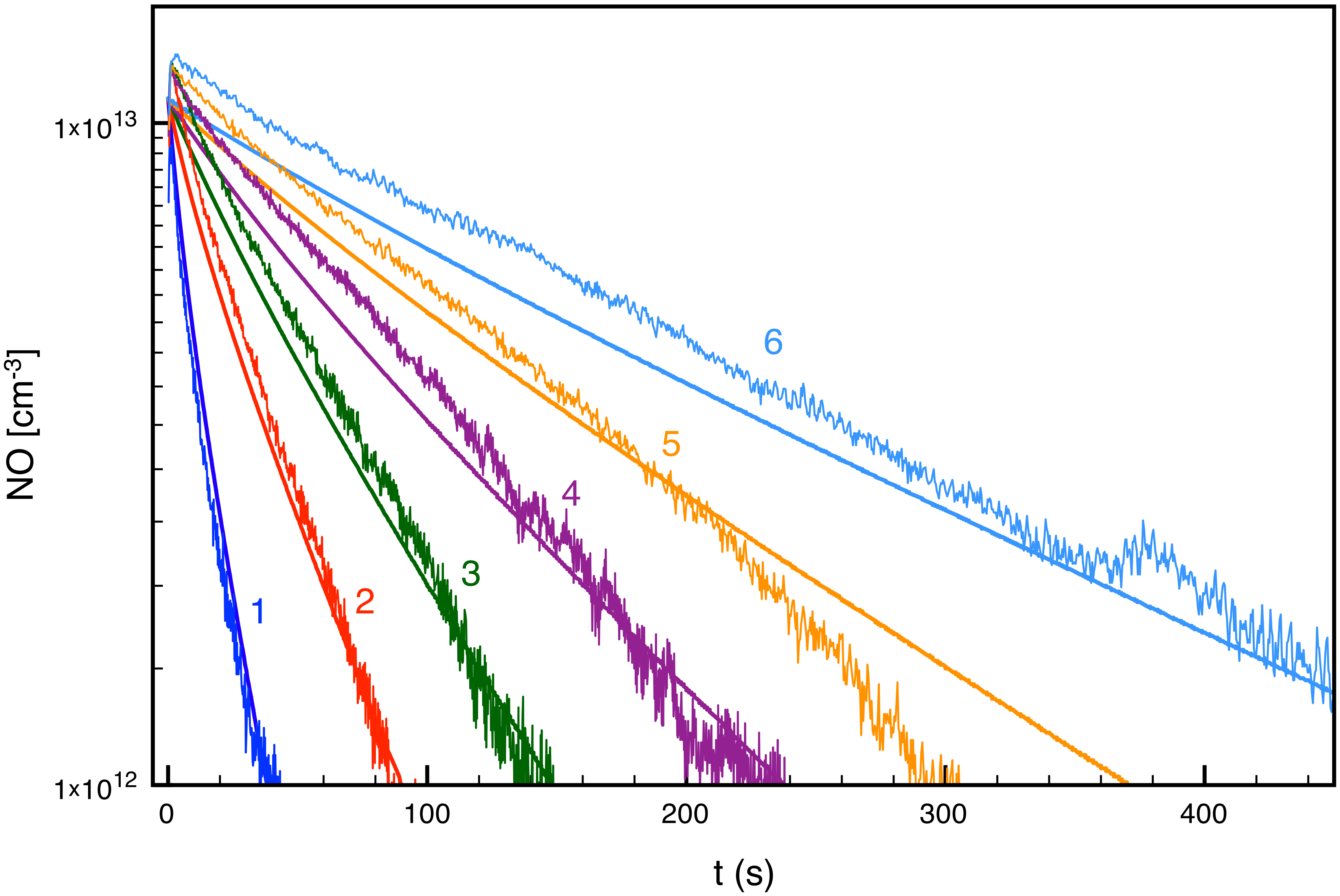
p = 5 Torr

Results: successive NO fillings





Results: successive NO fillings

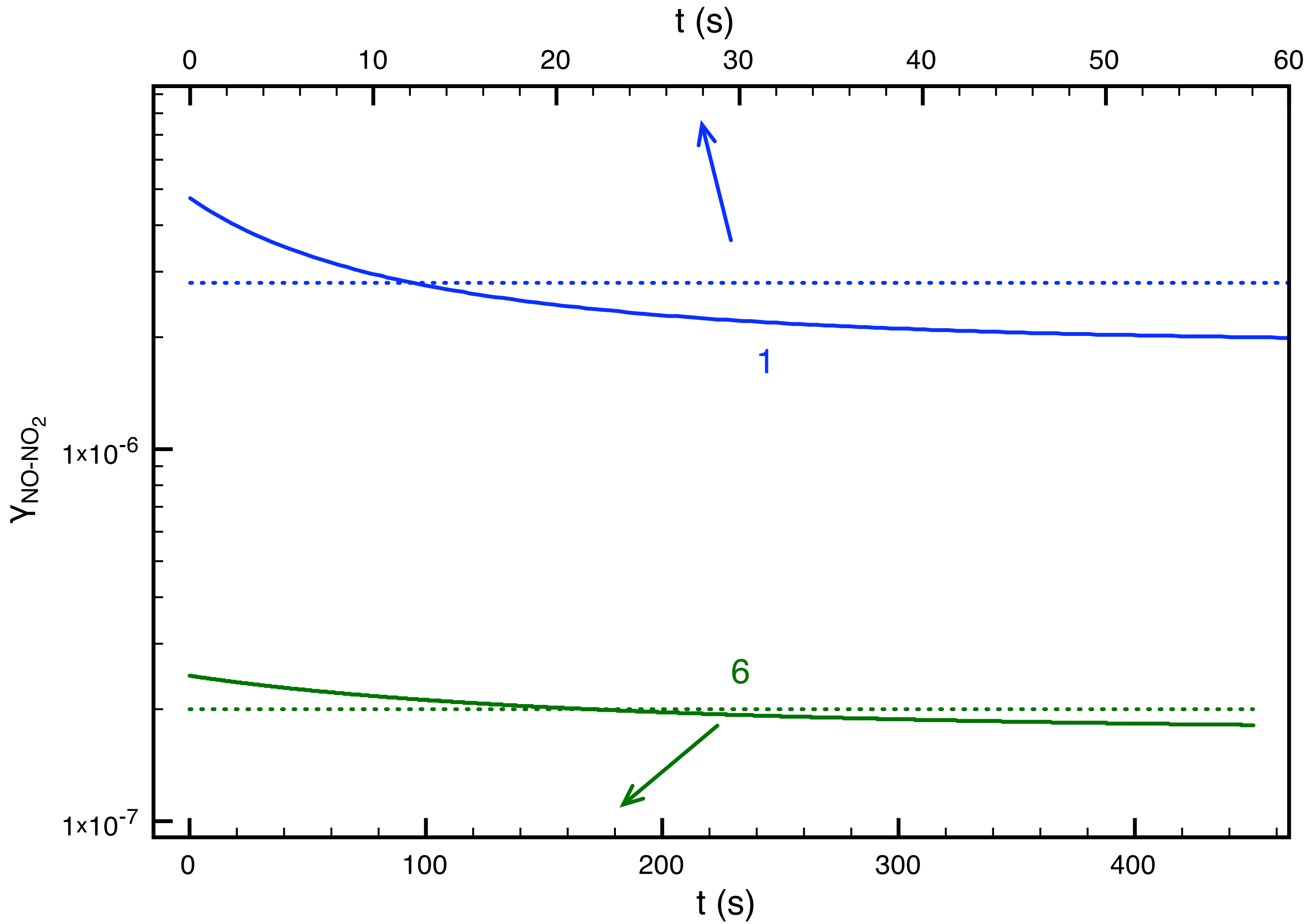


Results: effective $\gamma_{NO\text{-}NO2}$

$$\left(\frac{d[NO]}{dt}\right)_{wall} = -\frac{\langle v_{NO}\rangle \gamma_{NO\rightarrow NO_2}}{2R}[NO]$$

$$\gamma_{NO\rightarrow NO_2} = \frac{1}{\phi_{NO}} \sum_{i=1}^{7} \theta_S(i)[S_i] r_1(i)$$

Results: effective γ_{NO-NO2}



M. Castillo, V. Herrero, I. Mendez, and I. Tanarro, *PSST* (2004) **13** 343: 2×10^{-7}

Conclusions #2

- Formation of NO_2 by oxidation of NO with previously grafted O atoms on a Pyrex surface was established
- The complex time dependent kinetics observed is a manifestation of a distribution of reactivity among adsorption sites
- This was interpreted as a distribution of activation energies...
- ... which we assign to a distribution of binding energies of adsorbed O atoms

Conclusions #2

- The number and variety of time-dependent experiments imposes severe constraints on the model
- Several (7) types of chemisorption sites, with activation energies for recombination in the range 16-41 kJ/mol

Successes #3

Ozone kinetics in low-pressure discharges

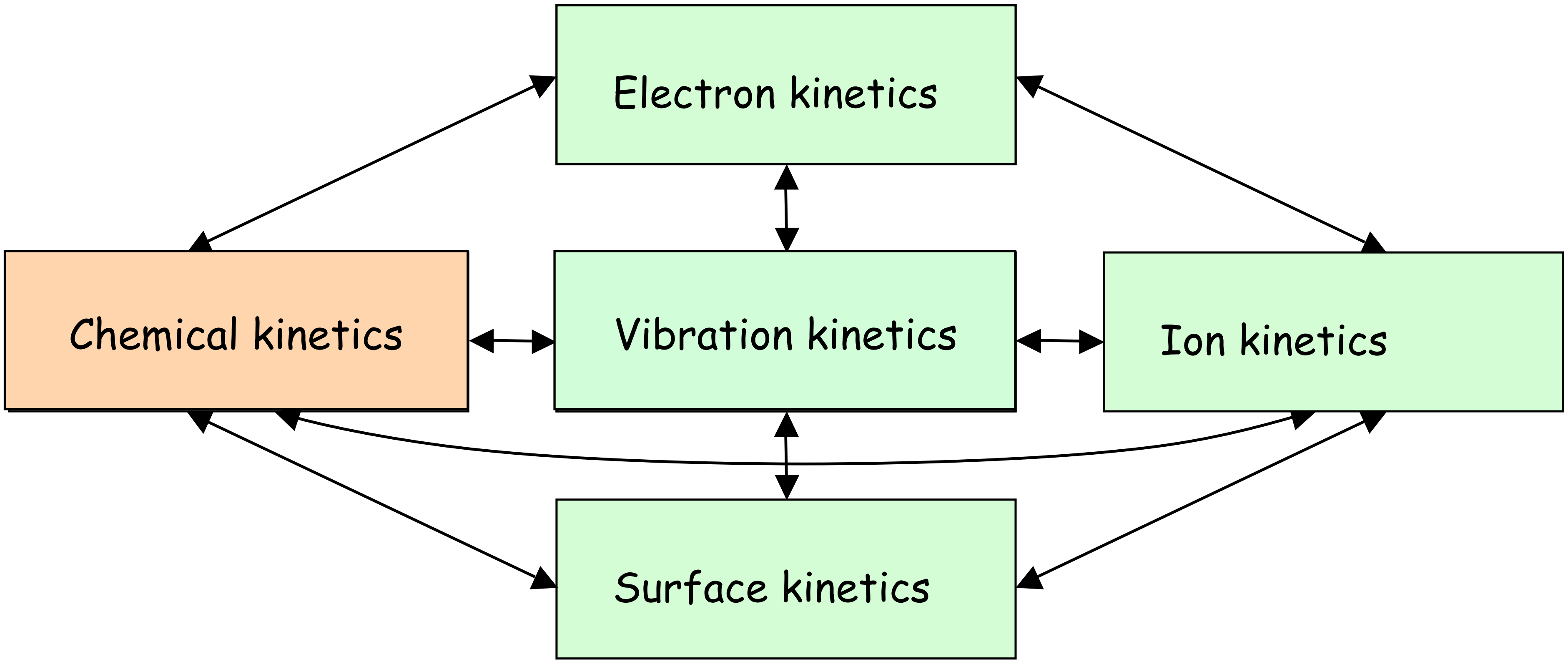
In collaboration with

Daniil Marinov, Jean-Paul Booth, Olivier Guaitella
and Antoine Rousseau

Laboratoire de Physique des Plasmas, Ecole Polytechnique, France

Plasma Sources Sci.Technol. **22** (2013) 055018

Ozone kinetics in low-pressure discharges



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 [*J. Phys. Chem. A* (2010) **114** 9709]

- "Isotope Evidence for Ozone Formation on Surfaces"

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

- DC discharges p=10-50 Torr
- $\gamma(O_3)$ increases with pressure: ~10^{-3} at 10 Torr; ~5×10^{-4} at 5 Torr)

Vibrationally excited ozone

Rawlins *et al* [*J. Geophys. Res.* **90** (1985) 283]

- O_3^* is mainly formed on the asymmetric stretching mode ν_3 (00*v*)

Eliasson et al 1987, Eliasson and Kogelschatz 1990 [J. Phys. D: Appl. Phys. 20 (1987) 1421]

- $O_2+O_2+O \rightarrow O_3+O_2$ 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

Lopaev *et al* 2011

- Model with 5 vibration levels of O_3

Experiment

- DC discharge with short pulses (~1 ms)
- Silica tube, R=1cm, p=1-5 Torr
- Time-resolved measurements of [O] (TALIF)
- Time-resolved measurements of [O_3] (UV absorption)

Modeling

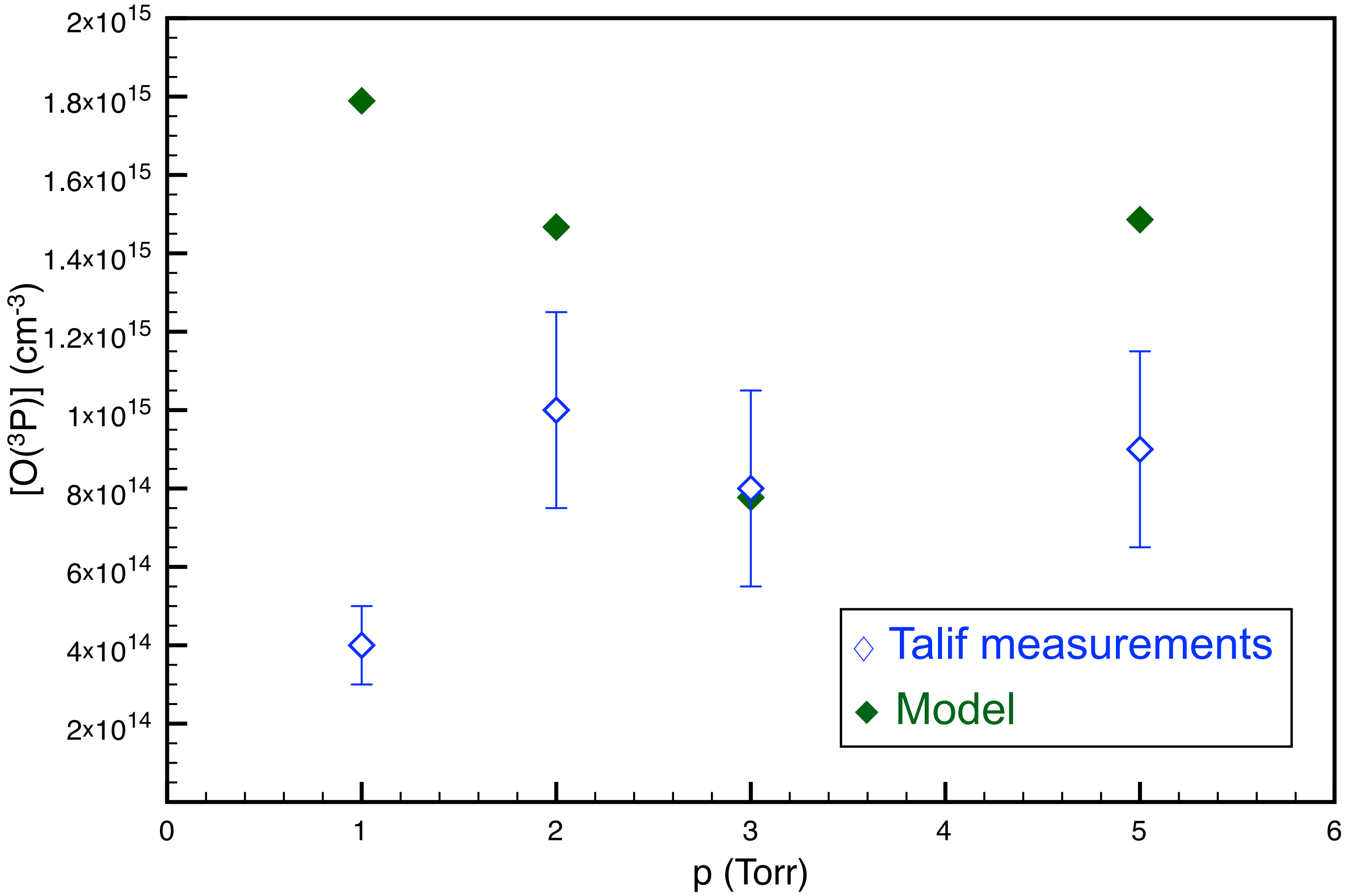
- Self-consistent kinetic model (Boltzmann, $O_2(X, a, b)$, $O(^3P, ^1D)$, O_3, O_3^*, O^+, O_2^+, O^-)
- Input: p, I, R, Δt, T_g=300 K
- Discharge + afterglow

- 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^*

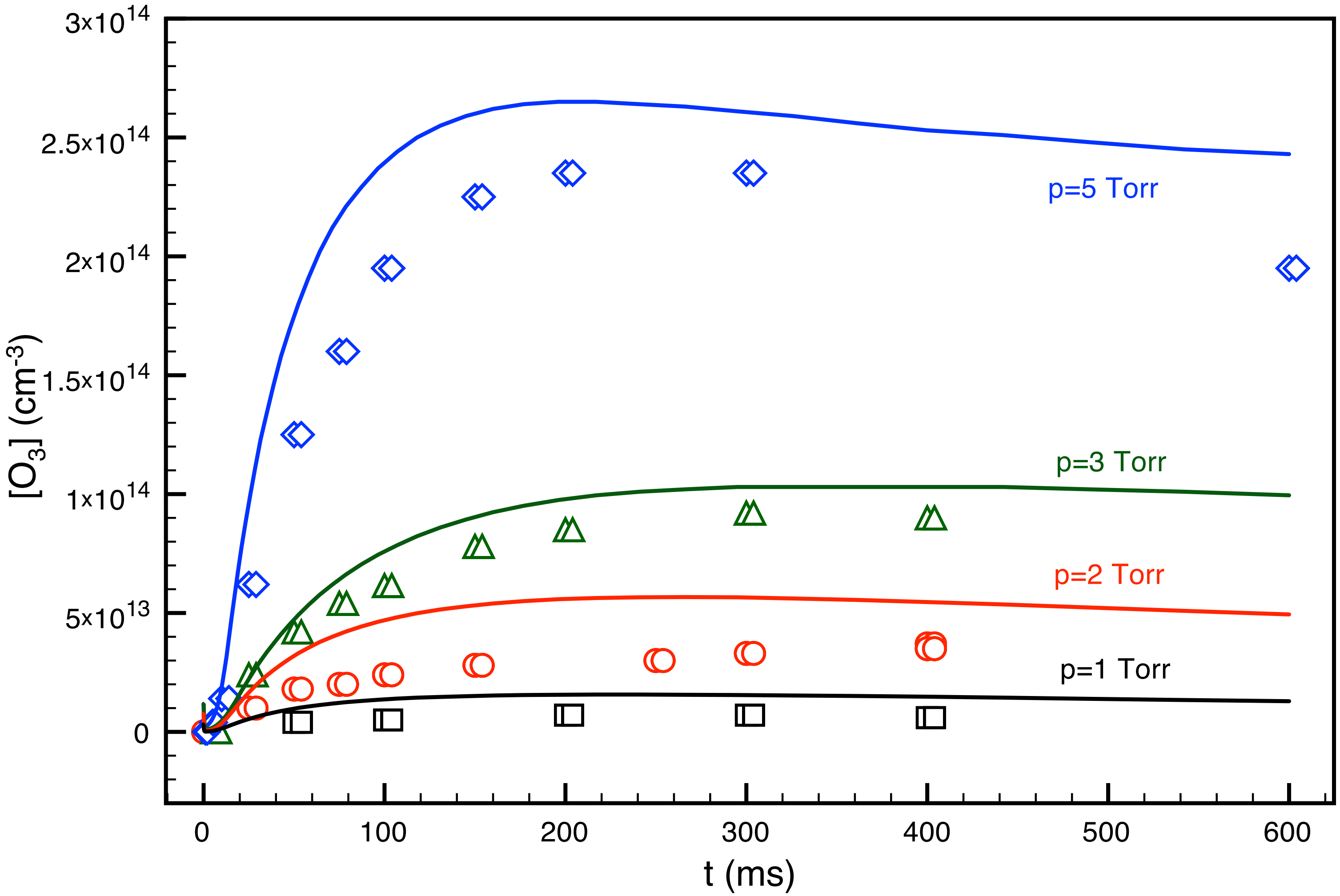
O_3^* kinetics

Formation
$O_2+O_2+O \rightarrow O_3^*+O_2$
Destruction
$O_3^*+O \rightarrow O_2+O_2$
$O_3^*+O_2(a) \rightarrow O_2+O_2+O$
$O_3^*+O_2 \rightarrow O_3+O_2$
$O_3^*+O \rightarrow O_3+O$
$O_3^*+Wall \rightarrow O_3+Wall$

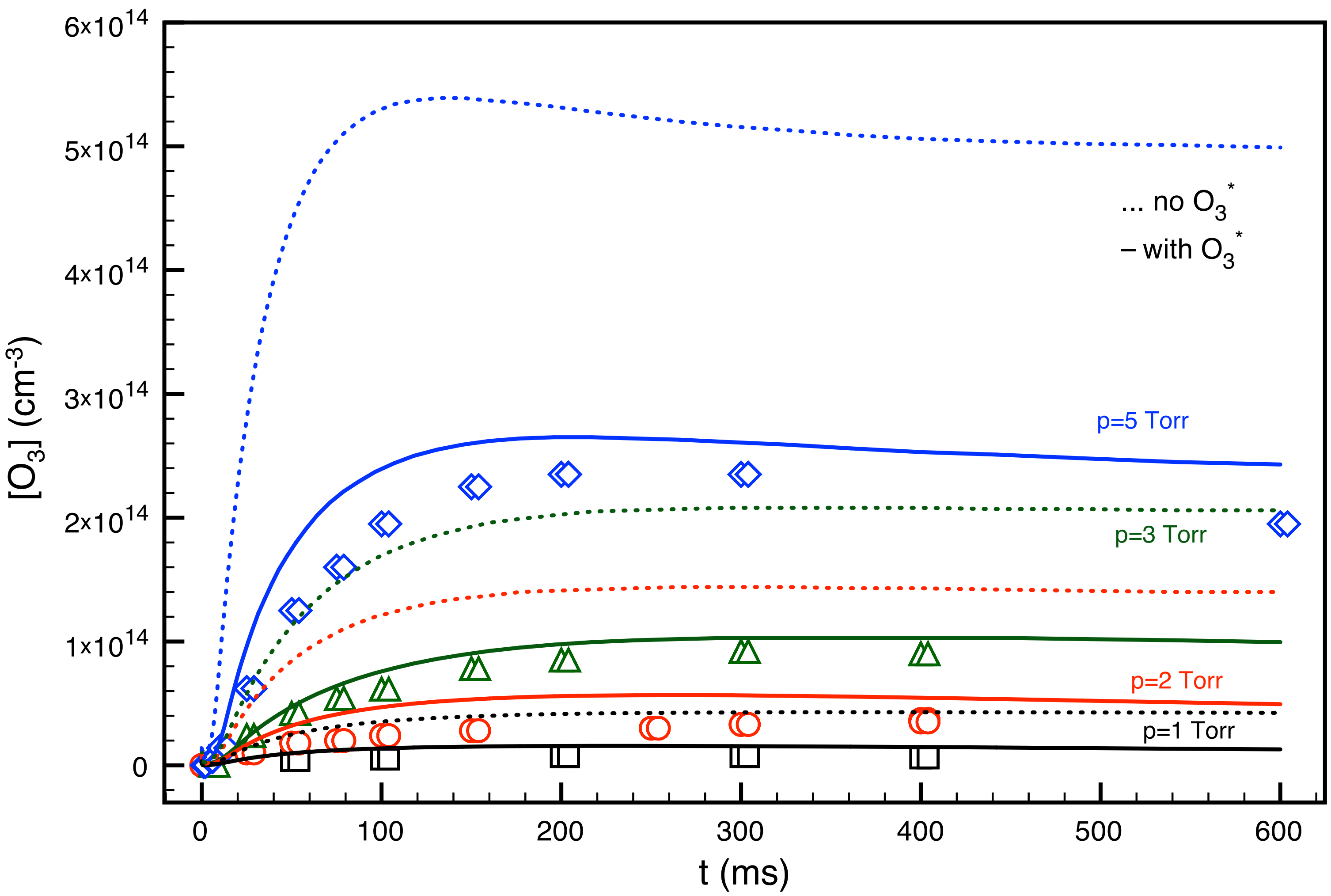
Results: O atoms



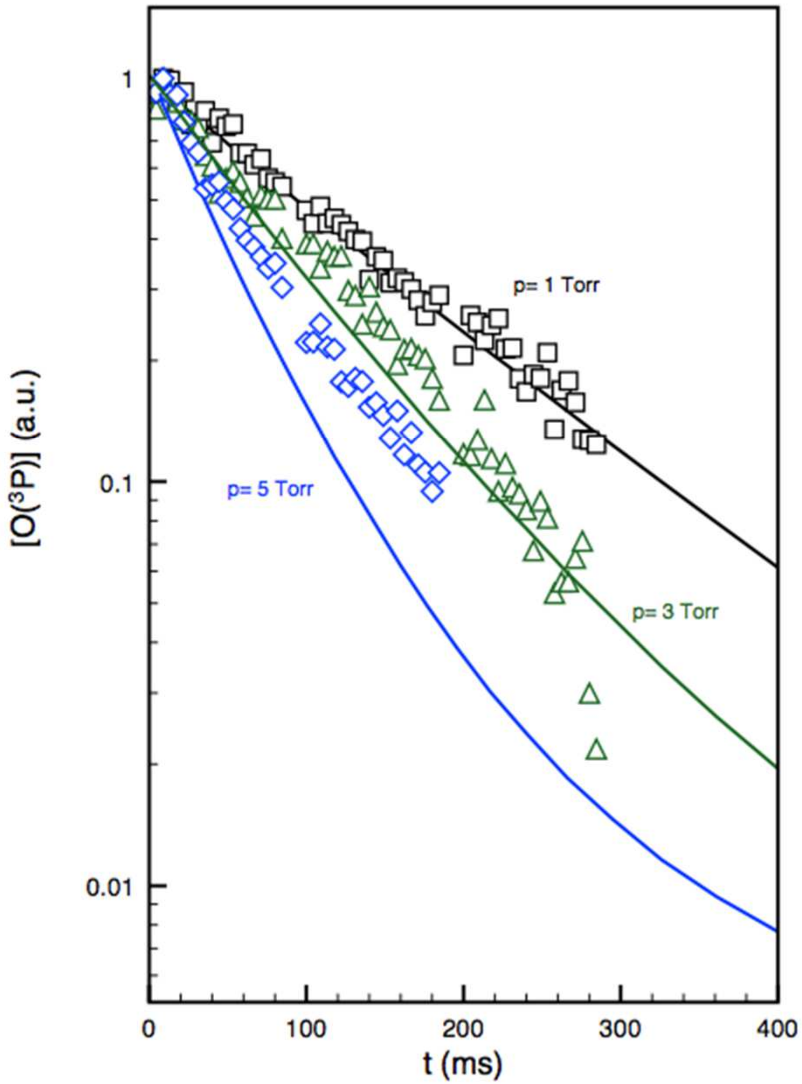
Results: O_3 molecules



Results: role of O_3^*

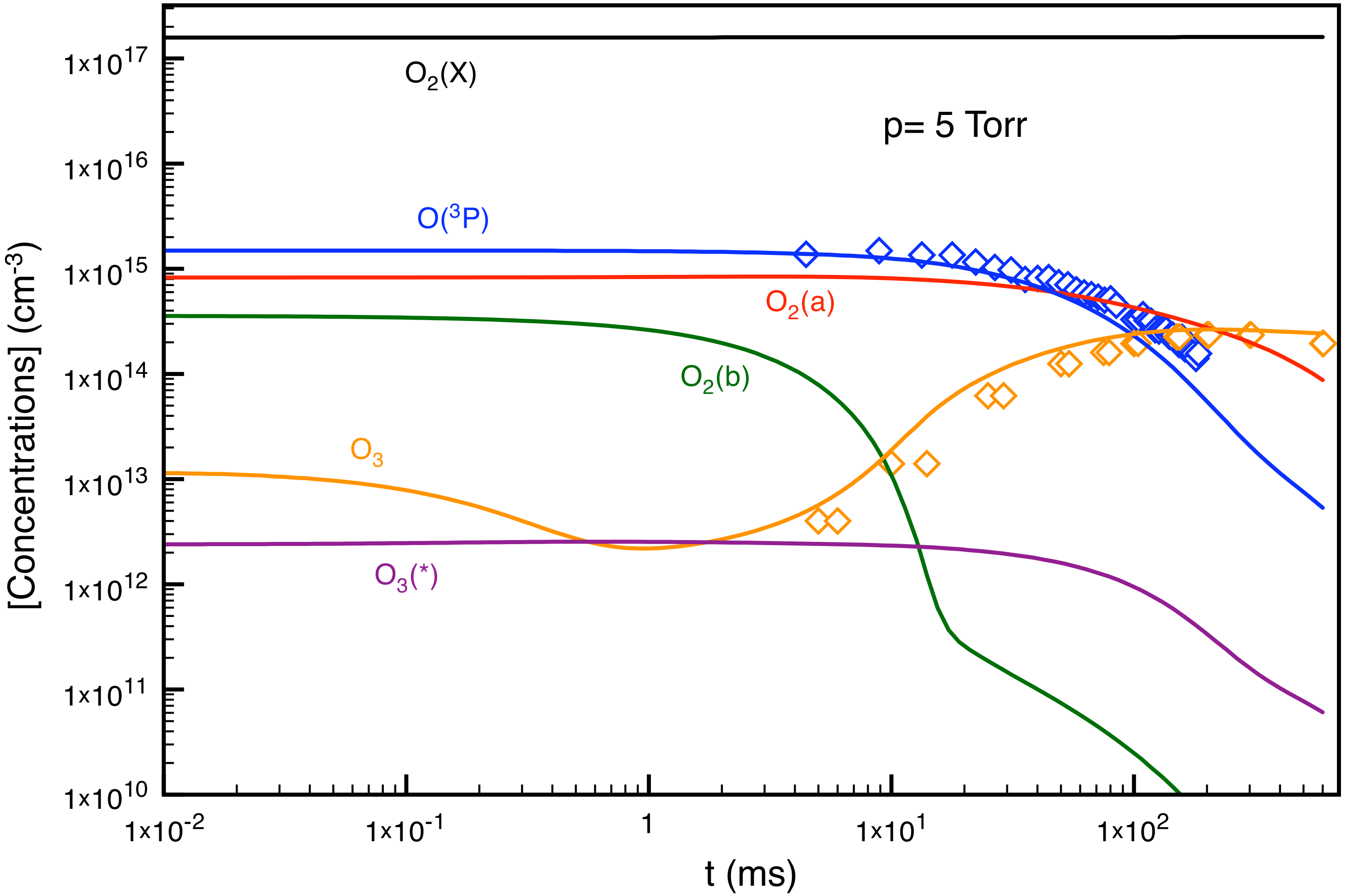


Results: O atoms decay

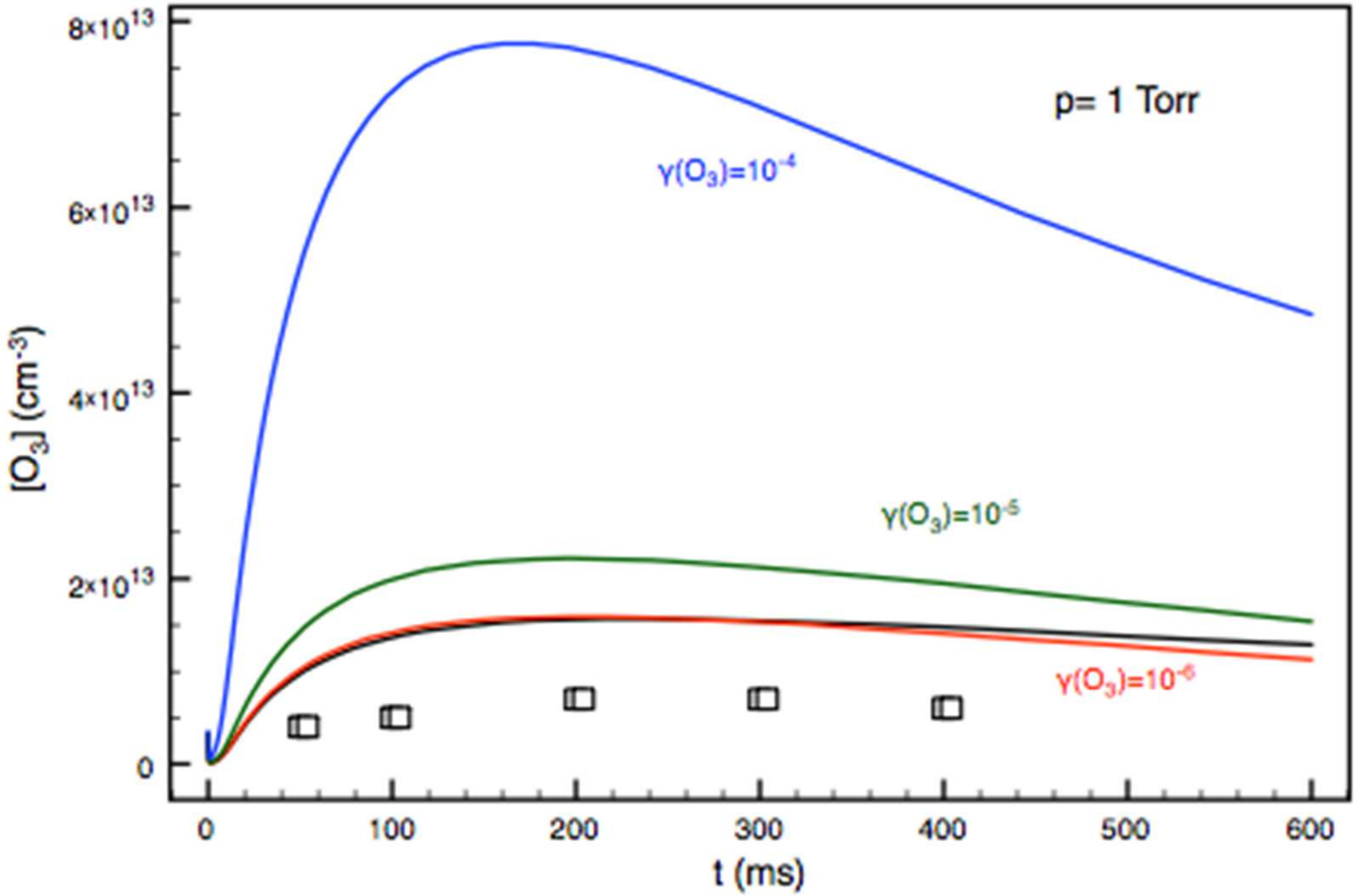


$\gamma_O = 2 \times 10^{-4}$

Results: species concentrations

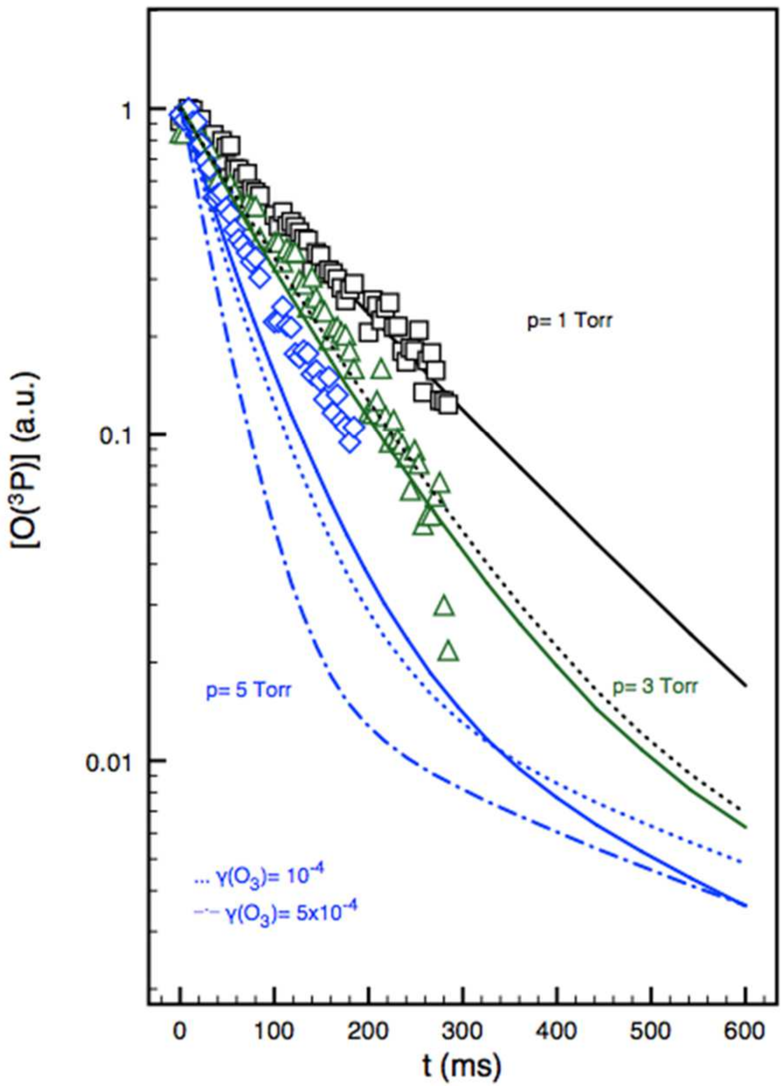


Results: $\gamma(O_3)$



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

Results: $\gamma(O_3)$



p=5 Torr

$\gamma(O_3) < 10^{-4}$

Conclusions #3

- Good agreement between measurements and model calculations
- 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

Successes #4

Line-ratio determination of [N_2(*A*)] in the N_2 afterglow

In collaboration with

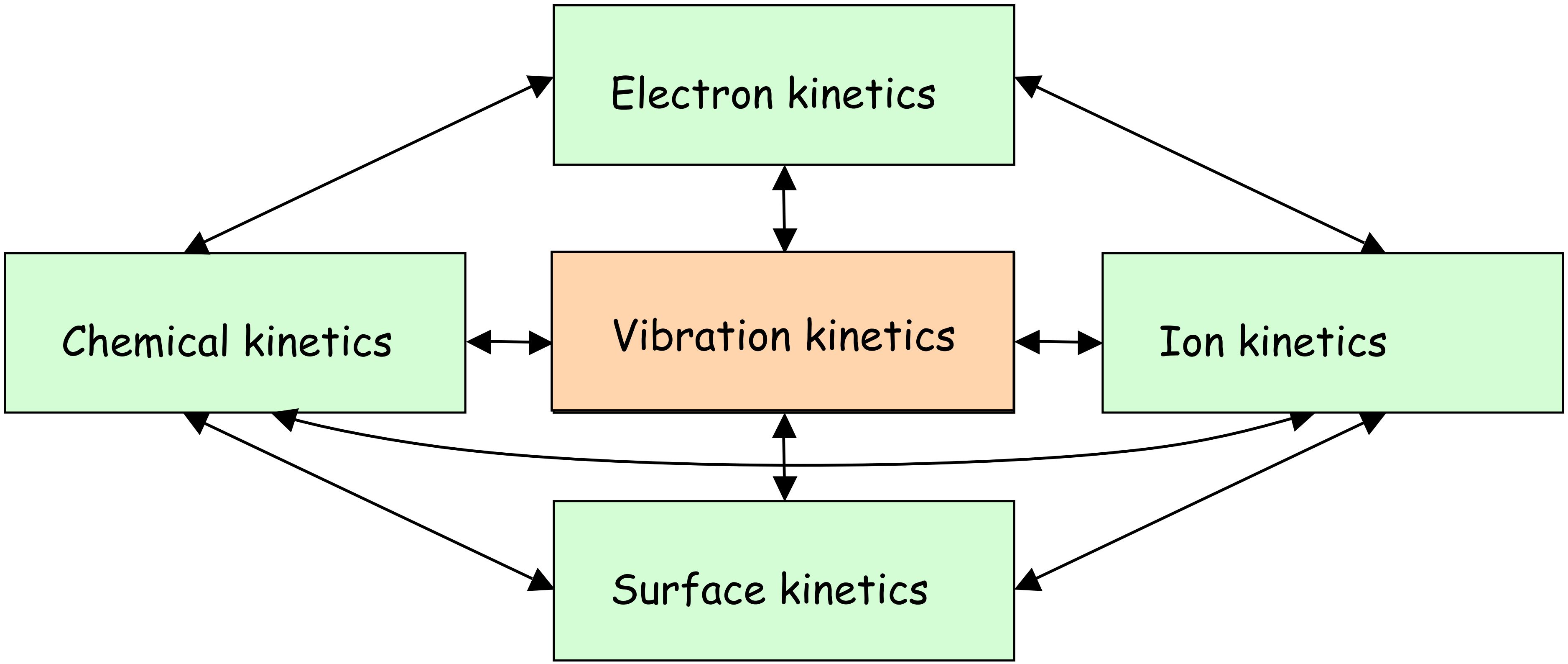
André Ricard[1] and Soo-ghee Oh[2]

[1]Universite de Toulouse, LAPLACE, France

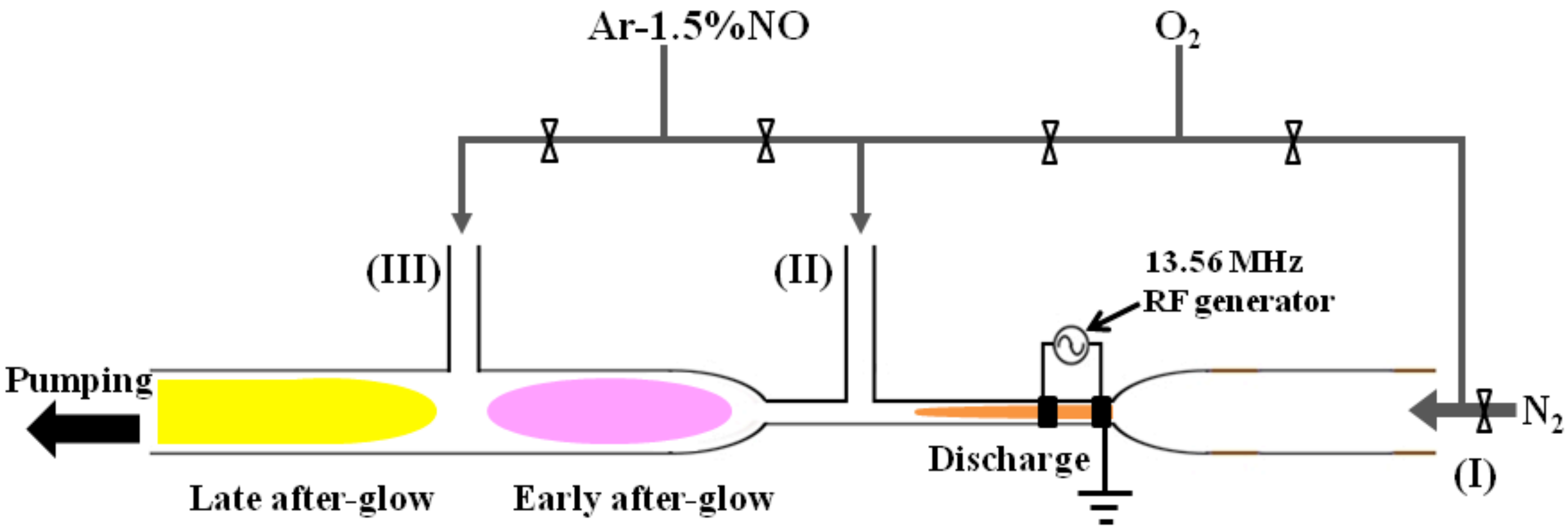
[2]Division of Energy Systems Research, Ajou University, Suwon, South Korea

Plasma Sources Sci. Technol. **22** (2013) 035009

Line-ratio determination of $N_2(A)$ in the nitrogen afterglow



The nitrogen afterglows



RF discharge, p = 8 Torr, P = 100 W, Q = 1 slm,

R_1 = 0.3 cm, R_2 = 1.1 cm (quartz), gas mixture N_2 -(0-1)%O_2.

Origin of the pink afterglow

- V-E transfers involving $N_2(X,v>30)$

- Local production of $N_2(A)$ and $N_2(a')$

$$N_2(X,v\geq 39)+N(^4S) \rightarrow N_2(A)+N(^2D)$$

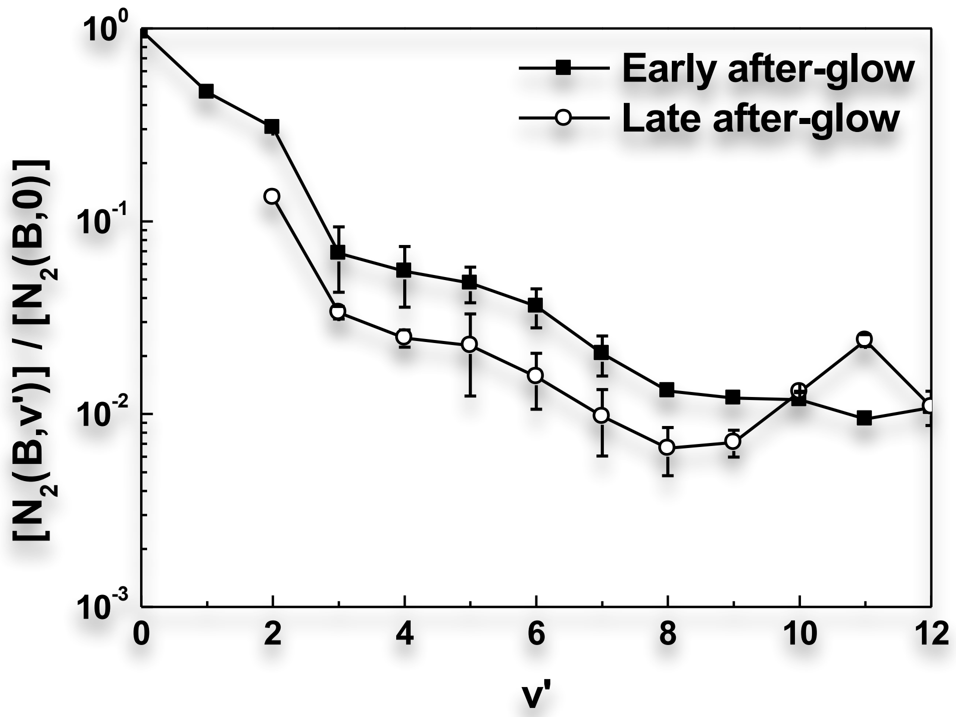
$$N_2(X,v\geq 38)+N(^4S) \rightarrow N_2(a')+N(^4S)$$

Origin of the yellow afterglow

- Three-body nitrogen atomic recombination

$$N+N+N_2 \rightarrow N_2(B, v'=11)+N_2$$

$$N_2(B) \rightarrow N_2(A)+h\nu$$



Diagnostics: actinometry / line-ratio

- The pink afterglow in pure nitrogen has been systematically studied ~10 years ago
- Optical emission spectroscopy is relatively simple to use and inexpensive
- Large expansion of "actinometric" or "line-ratio" methods, usually for the active discharge
- Development of sophisticated kinetic models extension of line-ratio methods for quite different situations!

Diagnostics: actinometry / line-ratio

- A new variant is proposed: determination of the absolute densities of
  - $N(^4S)$
  - $O(^3P)$
  - $N_2(A)$

  in the nitrogen afterglow.
- Bonus: experimental estimation of the rate coefficient of reaction

$$N_2(X, v \geq 13) + O \rightarrow NO + N$$

  at room temperature

Determination of [N]

Experimental determination of [N]:

- Measurement of the 1^+ intensity at 580 nm
- Pseudo-stationary concentration $[N_2(B)]$ determined from:

$$
\begin{array}{ll}
(1) & N + N + N_2 \rightarrow N_2(B, v' = 11) + N_2 \\
(2) & N_2(B, v' = 11) \rightarrow N_2(A, v'' = 7) + h\nu(580nm) \\
(3) & N_2(B) + N_2 \rightarrow N_2(A, X) + N_2 \\
(4) & N_2(B) + O_2 \rightarrow N_2(A, X) + O + O
\end{array}
$$

$$a_{NN} I(580) \simeq k c(580) A_{580} \frac{k_1}{k_3} [N]^2$$

- Requires calibration (NO titration) and early-late "mixing coefficient"

Determination of [O]

Experimental determination of [O]:

- Measurement of the NO_β intensity at 320 nm
- Line-ratio $I(1^+)/I(NO_\beta)$
- Pseudo-stationary concentration [NO(B)] determined from:

$$
\begin{array}{lr}
(5) & N + O + N_2 \rightarrow NO(B, v' = 0) + N_2 \\
(6) & NO(B, v' = 0) \rightarrow NO(X, v'' = 8) + h\nu(320nm) \\
(7) & NO(B) + N_2 \rightarrow \text{products} \\
(8) & NO(B) + O_2 \rightarrow \text{products}
\end{array}
$$

$$\frac{a_{NN} I(580)}{I(320)} \simeq \frac{c(580)}{c(320)} \frac{A_{580}}{A_{320}} \frac{(k_1/k_3)[N]}{k_5[O][N_2]} (\nu_6 + k_7[N_2])$$

Determination of $[N_2(A)]$

Experimental determination of $[N_2(A)]$:

- Measurement of the 2^+ intensity at 316 nm
- Line-ratio $I(NO_\beta)/I(2^+)$
- Pseudo-stationary concentration $[N_2(C)]$ determined from:

$$
\begin{aligned}
(8) \quad & N_2(A) + N_2(A) \rightarrow N_2(C, v' = 1) + N_2(X) \\
(9) \quad & N_2(C, v' = 1) \rightarrow N_2(B, v'' = 0) + h\nu(316nm) \\
(10) \quad & N_2(C) + N_2 \rightarrow \text{products}
\end{aligned}
$$

$$
\frac{I(320)}{I(316)} \simeq \frac{A_{320}}{A_{316}} \frac{k_5[N][O][N_2]}{k_8[N_2(A)]^2} \frac{\nu_9 + k_{10}[N_2]}{\nu_6 + k_7[N_2]}
$$

Bonus: determination of $[N_2(A)]$ #2

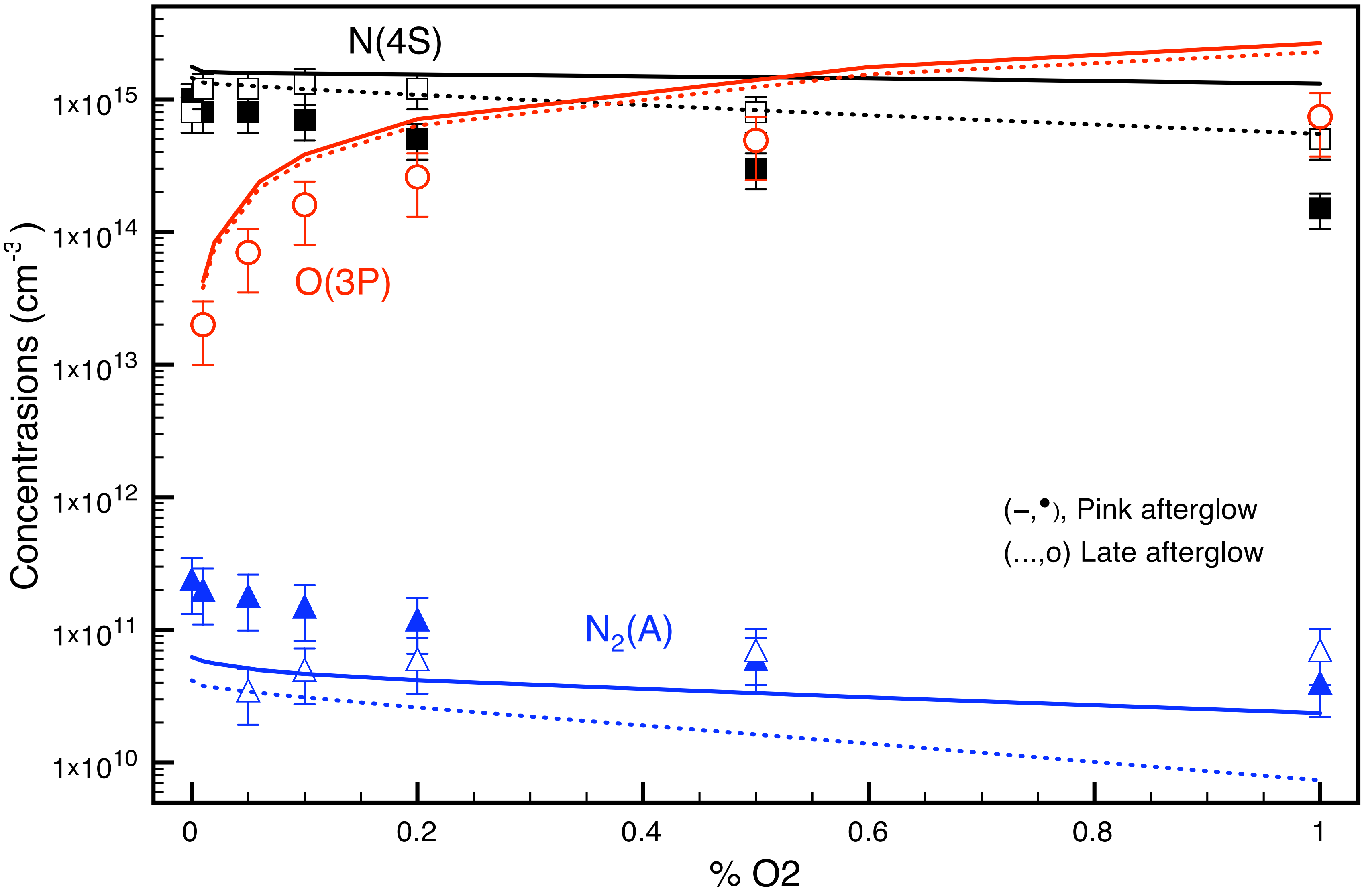
$[N_2(A)]$ can be additionally determined from:

- the $I(2^+)/I(1^+)$ ratio
- the $I(NO_\beta)/I(NO_\gamma)$ ratio
- [Ricard *et al*, *Plasma Sources Sci. Technol.* **22** (2013) 035009]
- the $I(NO_\beta)/I(NO_\gamma)$ ratio provides the first experimental estimation of the rate coefficient of

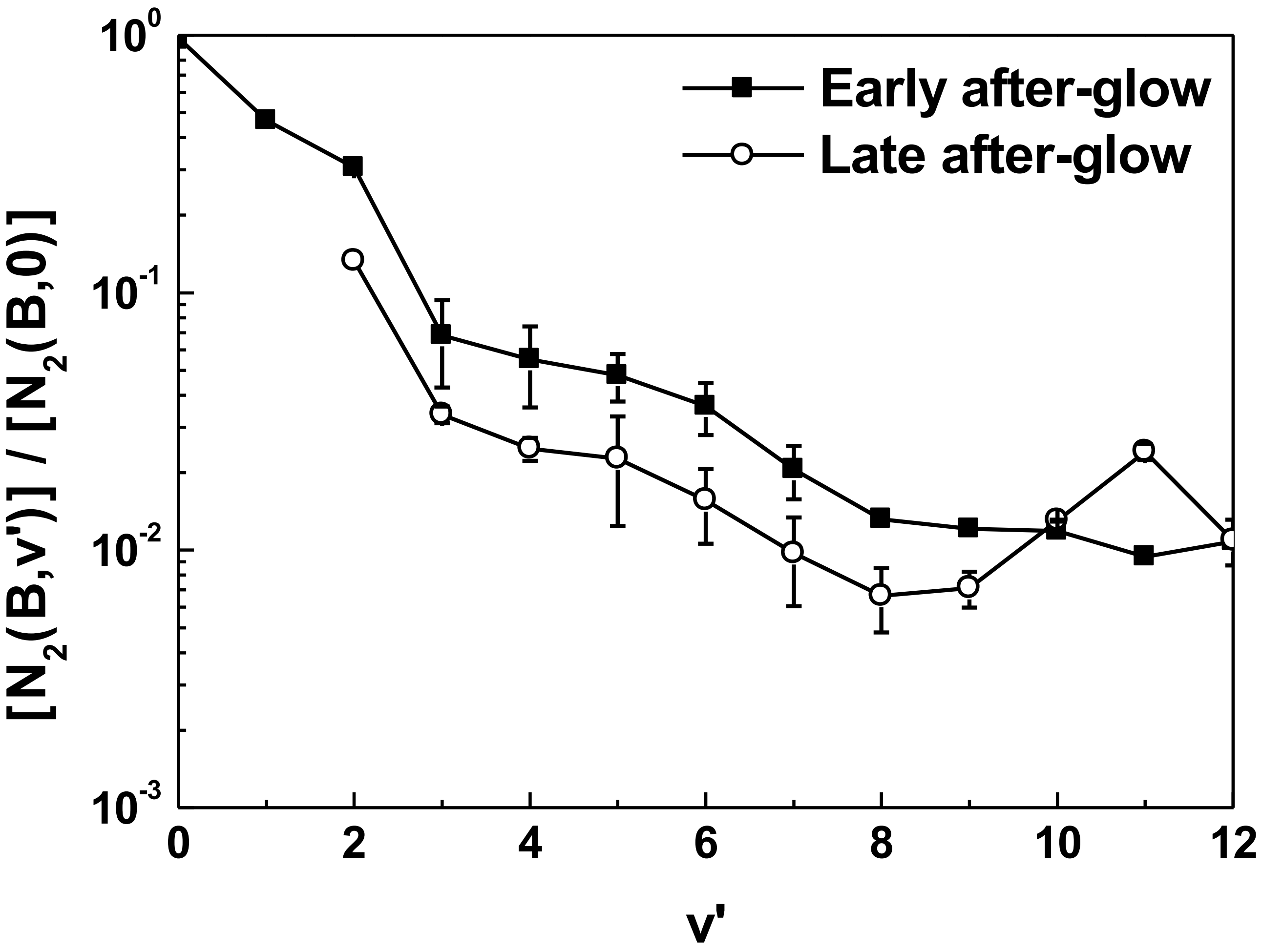
$$N_2(X, v \geq 13) + O \rightarrow NO + N$$

at low tempereature (!)

Results: summary

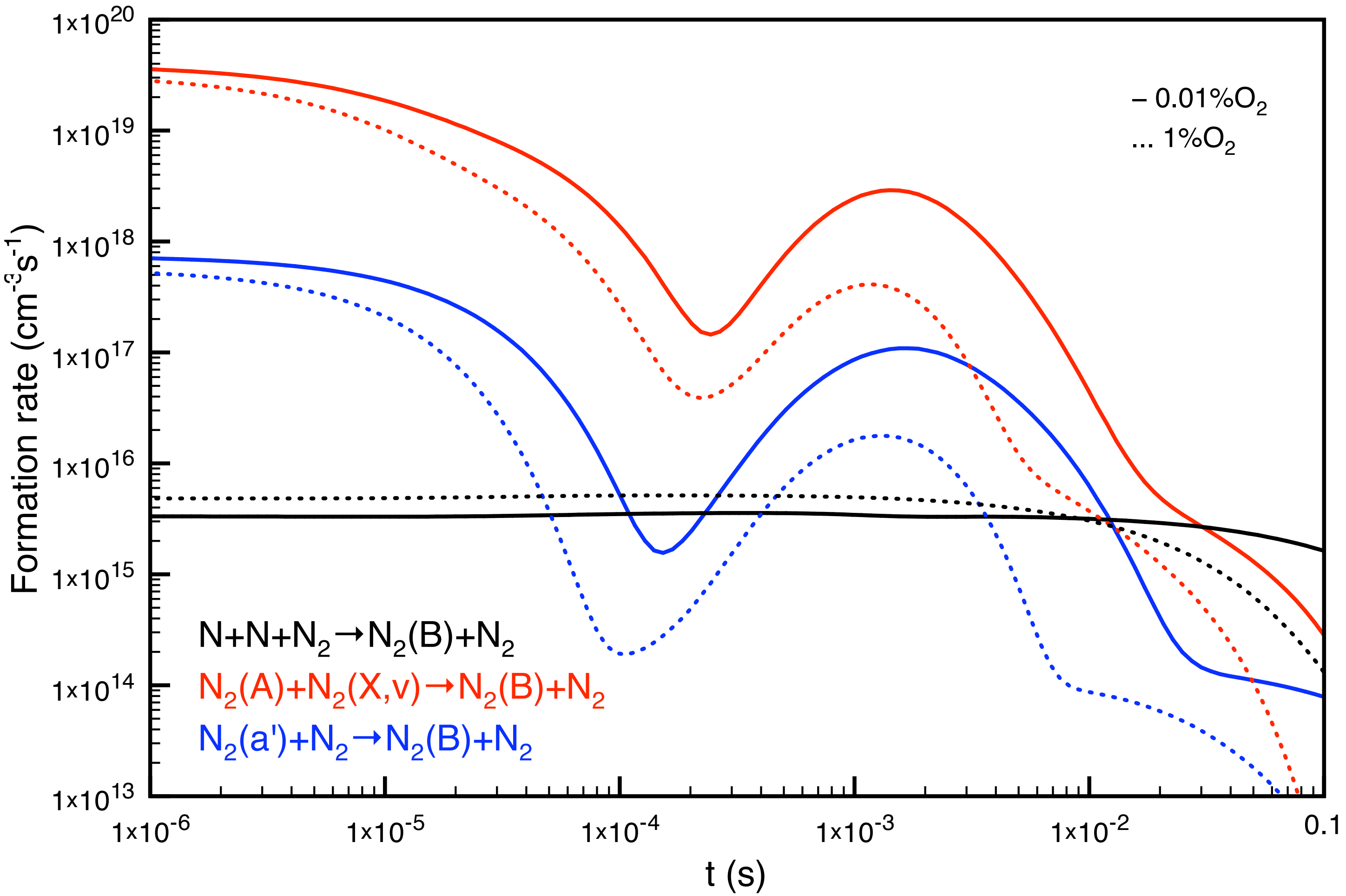


$N_2(B)$ state



p=8 Torr, *P*=100 W

$N_2(B)$ state



p=8 Torr, P=100 W

$N_2(A)$ concentration

$[N_2(A)]$ can be determined from different line ratios:

Species	Lines	Industrial N_2
$[N_2(A)]$	$I_\gamma(259)/I_\beta(262)$	$1.1 \times (10^9 - 10^{11})$
$[N_2(A)]$	$I_{2+}(316)/I_\beta(320)$	2.4×10^{11}
$[N_2(A)]$	$I_{1+}(580)/I_{2+}(316)$	7.3×10^{10}

Table: Absolute densities in cm^{-3} estimated in the late afterglow: $p = 8$ Torr, $Q = 1$ Slm, $P = 100$ W.

Conclusions #4

- OES line-ratio methods are powerful and can be extended far beyond their typical domain of application
- [N], [O] and [N_2(*A*)] were experimentally determined
- Different method for estimation of [N_2(*A*)] give consistent results
- The present work opens the door for a first experimental (indirect) determination of the rate coefficient of the NO formation reaction $N_2(X,v\geq 13)+O \rightarrow NO+N$ at room temperature

Successes #5
Surface waves in capillary tubes

In collaboration with

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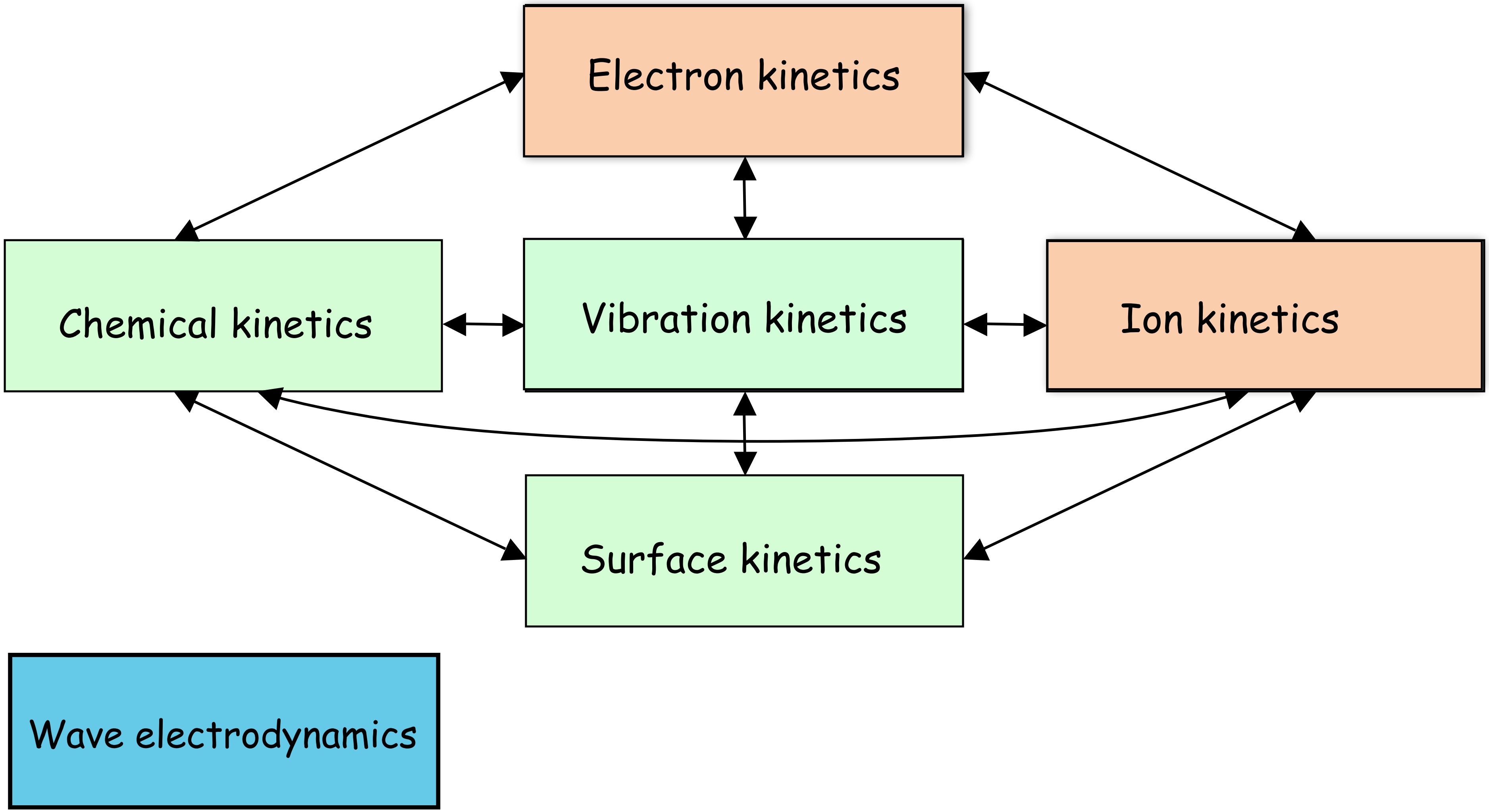
[2] LPGP, Université Paris Sud XI, Orsay, France

[3] Ecole Centrale de Paris, France

Proceedings of the ESCAMPIG XXII, Greifswald, July 2014

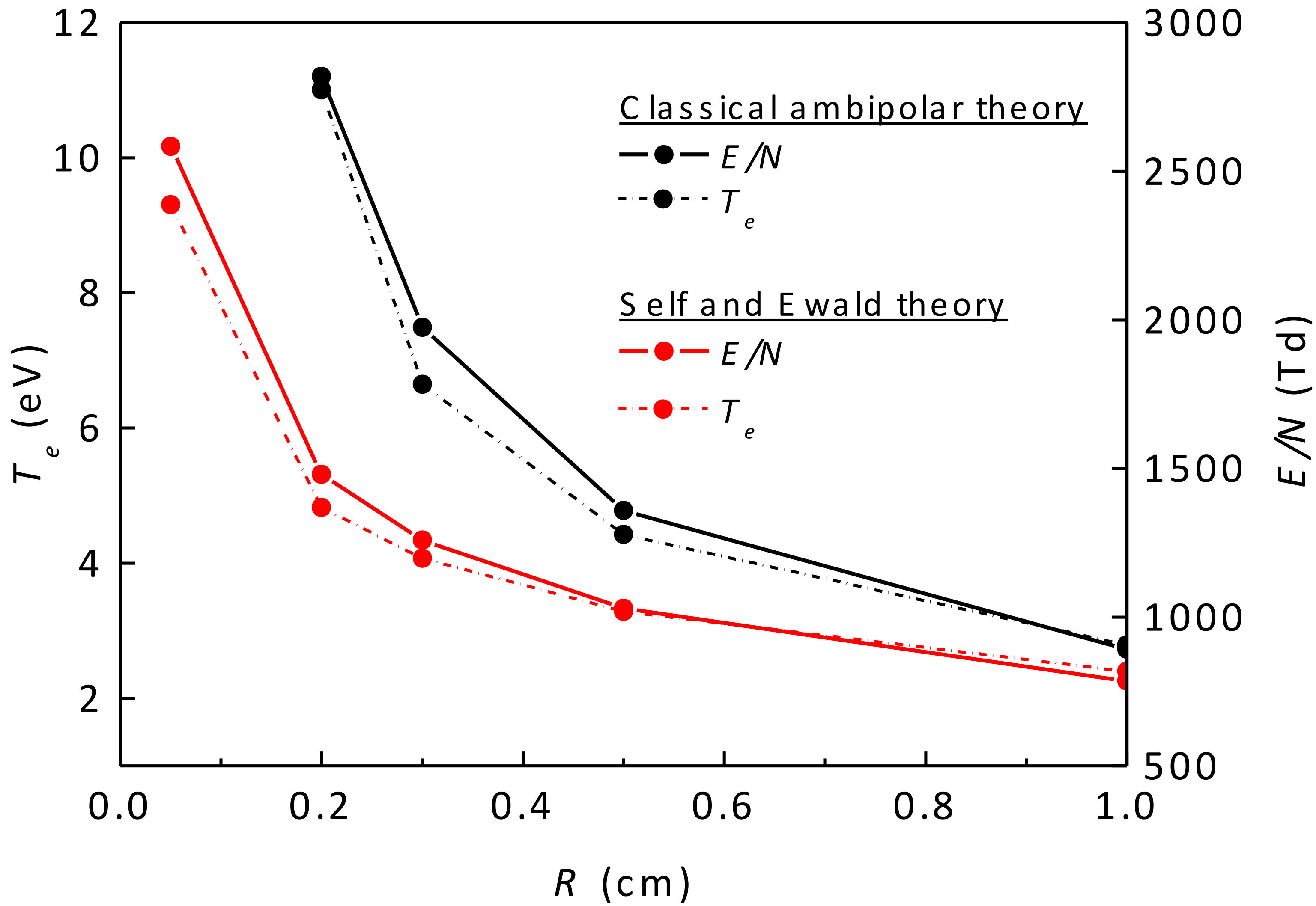
Surface waves in capillary tubes



Surface waves in capillary tubes

- f=2.45 GHz, p=2 Torr, R=0.345 mm
- The global behaviour is strongly dominated by electron impact processes and transport losses
- ▸ Need for the Self & Ewald transport theory
- Heterogeneous atomic recombination is important

Surface waves in capillary tubes



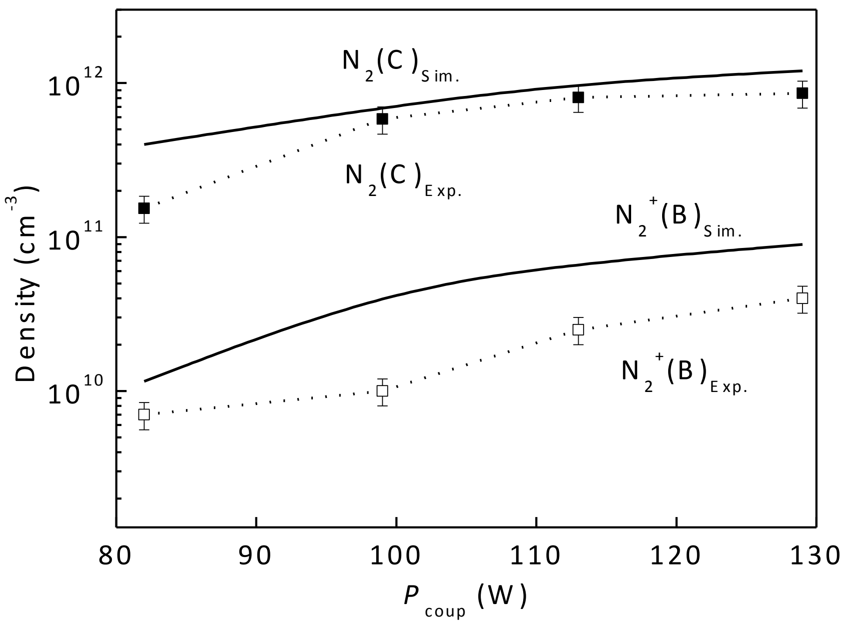
Surface waves in capillary tubes

- NO kinetics:

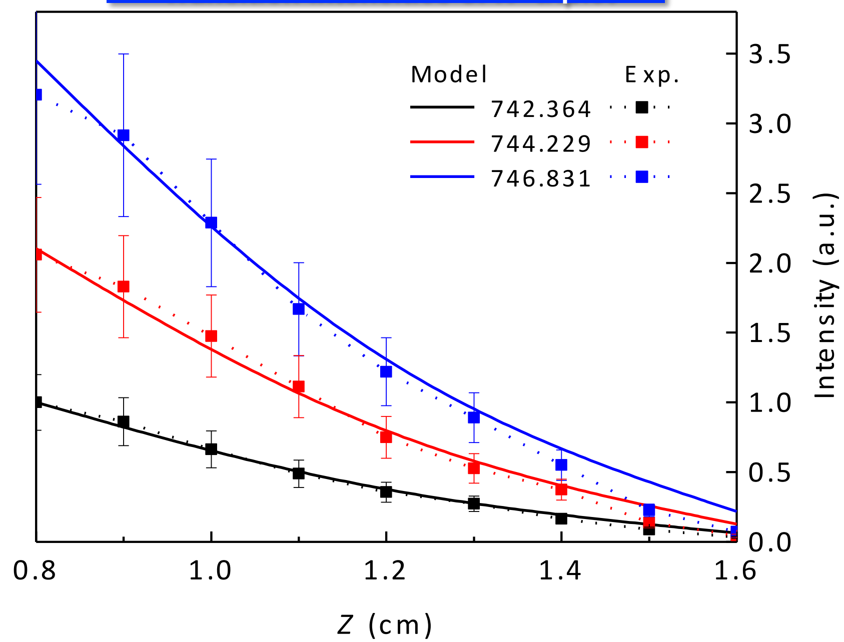
$$N(^2D)+O_2 \rightarrow N+NO$$

$$e+NO \rightarrow e+e+NO^+$$

$$NO^+ + wall \rightarrow e+NO$$



Transition intensities of N* triplet



Summary

- Self-consistent model for air validated for a wide range of operating conditions

Bottlenecks / challenges

- State-to-state reliable collisional data

[Shakhatov & Lebedev, *High Energy Chem.* 42 (2008) 170;
Annarita Laricchiuta, this Master class]

- T_g dependence of the rate coefficients

[$N_2(X,v\geq 13)+O \rightarrow NO+N$ at low Tg,
Several data at high Tg (esther, http://esther.ist.utl.pt/)]

Summary

and upper atmospheric chemistry.[5] Determining the role of N_2 (X,v) in these various processes is difficult, however, due to N_2 (X,v)'s diabolical resistance to detection. A number of laser-based techniques for detecting N_2 (X,v) have been de-

L. G. Piper, *J. Chem. Phys.* **97** (1992) 270

Summary

- Breakthrough measurements
  - N_2 VDF [one measurement at v=18; Macko *et al*, *J. Phys. D: Appl. Phys* **34** (2001) 1807]
  - N_2 singlets
- Role of V-E energy exchanges

  [Mário Lino da Silva & J. Loureiro, *ICPIG 2013* PS1-113]
- Surface characteristics and surface processes

  [Daniil Marinov, this master class]

Conferences @ Lisboa!

You just don't want to miss them! 😉