Kinetic modelling of air plasmas
self-consistency, bottlenecks, successes

Vasco Guerra
Instituto Superior Técnico, Instituto de Plasmas e Fusão Nuclear,
Universidade de Lisboa, Portugal
vguerra@ist.utl.pt
Modeling of nonequilibrium molecular plasmas

- Electron kinetics
- Vibration kinetics
- Ion kinetics
- Surface kinetics

- Chemical kinetics
- Wave electrodynamics
- Thermal balance
The \( \text{N}_2 \) molecule
Kinetic modeling (N\textsubscript{2}-O\textsubscript{2})

- Electron kinetics (electron Boltzmann equation)
- Vibrational kinetics of N\textsubscript{2}(X,0\leq v\leq60) and O\textsubscript{2}(X, 0\leq v\leq47) molecules
- Chemical kinetics of
  - N\textsubscript{2}(A, B, C, B’, a’, a, w, a’’)
  - O\textsubscript{2}(X, a, b)
  - N(\textsuperscript{4}S, \textsuperscript{2}D, \textsuperscript{2}P), O(\textsuperscript{3}P, \textsuperscript{1}D)
  - O\textsubscript{3}, O\textsubscript{3}*, NO(X, A, B), NO\textsubscript{2}(X, A)
- Ion kinetics of N\textsubscript{2}\textsuperscript{+}, N\textsubscript{4}\textsuperscript{+}, O\textsubscript{2}\textsuperscript{+}, O\textsuperscript{+}, NO\textsuperscript{+}, O\textsuperscript{-}
Self-consistent modeling

Input:
- Discharge operating parameters \((p, R, P-n_e-l, \omega)\)
- 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)
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 $\text{N}_2(X,v)$, NO, N, O, $\text{N}_2(A,B)$
Some lessons from the past

$p=2 \text{ Torr}, R=0.8 \text{ cm}, I=30 \& 80 \text{ mA}$
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: $N_2(A,a') + N_2(a') \rightarrow N_4^+ + e$

$N_2(A,a') + O_2 \rightarrow N_2(X) + O + O$
Some lessons from the past

\[ p=2 \text{ Torr}, \ R=0.8 \text{ cm}, \ l=30 \ & 80 \text{ mA} \]
Some lessons from the past

NO formation:

\[ \text{N}_2(X,v \geq 13) + O \rightarrow \text{NO} + \text{N} \]
\[ \text{N}_2(A) + O \rightarrow \text{NO} + \text{N}(^2D) \]
\[ \text{N}(^2D) + \text{O}_2 \rightarrow \text{NO} + \text{O} \]

O formation:

\[ \text{e} + \text{O}_2 \rightarrow \text{e} + \text{O} + \text{O} \]
\[ \text{N}_2(B) + \text{O}_2 \rightarrow \text{O} + \text{O} + \text{N}_2 \]
Some lessons from the past

\[
\text{N}_2(A) + \text{NO} \rightarrow \text{NO}(\gamma) + \text{N}_2
\]
In collaboration with

Carlos D. Pintassilgo,\textsuperscript{1} Olivier Guaitella\textsuperscript{2} and Antoine Rousseau\textsuperscript{1}

\textsuperscript{1}Faculdade de Engenharia, Universidade do Porto, Portugal
\textsuperscript{2}Laboratoire de Physique des Plasmas, Ecole Polytechnique, France

\textit{Plasma Sources Sci. Technol.} 23 (2014) 025006
NO kinetics and gas heating in pulsed discharges

Chemical kinetics

Electron kinetics

Vibration kinetics

Ion kinetics

Surface kinetics

Thermal balance
Vibrations need time to build up!

\[ p = 1 \text{ Torr}, R = 1.05 \text{ cm}, I = 40 \text{ mA} \]
Electron impact excitation is fast

\[ \text{N}_2(A) + \text{N}^{(4S)} \rightarrow \text{N}_2(X,v) + \text{N}^{(2P)} \]
NO formation:

- \( \text{NO formation:} \quad N_2(X, v \geq 13) + O \rightarrow NO + N \)
- \( N_2(A) + O \rightarrow NO + N(2D) \)

The first reaction gains importance:

- with the pulse length
- with the afterglow time
Gas heating

Early instants

\[ 
\begin{align*}
e + O_2 & \rightarrow e + O_2(B) \rightarrow e + O + O \\
N_2(A, B, a', a) + O_2 & \rightarrow N_2 + O + O
\end{align*}
\]

Longer instants

\[ 
\begin{align*}
N_2(X, \nu) + O & \rightarrow N_2(X, \nu - 1) + O \\
O + \text{wall} & \rightarrow (1/2)O_2 + \text{wall}
\end{align*}
\]
Gas heating

\[ p=1 \text{ Torr}, \; I=150 \text{ mA}, \; \tau=5 \text{ ms} \]

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!!!

As perguntas fundamentais

O que é um plasma?

NO₂ formation on a Pyrex surface

Electron kinetics

Chemical kinetics

Vibration kinetics

Ion kinetics

Surface kinetics

Chemical kinetics

Vibration kinetics

Ion kinetics

Surface kinetics

Chemical kinetics

Vibration kinetics

Electron kinetics

Ion kinetics

Surface kinetics

Vibration kinetics
Motivation

• Molecule formation on surfaces is a relevant issue
• \( \text{NO, NO}_2, \text{N}_2\text{O, O}_3,... \)

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, \( R = 1 \text{ cm}, \ L = 60 \text{ cm} \)
- Pre-treatment (\( \sim 1 \text{ h} \)) with \( \text{O}_2 \)
  - \([\text{O}_s]\sim 4 \times 10^{14} \text{ cm}^{-2}\)
- Pumping (\( \sim 10' \))
- “Probing”
  - Injection of NO (0.1-4 Torr)
  - Measurement of NO and NO\(_2\) kinetics

Modeling: surface descriptions

- Macroscopic approach ($\gamma$)
- Mesoscopic approach
  - Monte Carlo
  - Continuous in terms of coverage
- Microscopic approach (molecular dynamics)
Model

• 7 types of “chemisorption sites”

• Eley-Rideal “recombination”

  \[ \text{NO} + \text{O}_S(i) \rightarrow \text{NO}_2 + \text{S}_V(i) \]

  \[ E_R = 16 - 41 \text{ kJ/mol} \]

• NO₂ adsorption

  \[ \text{NO}_2 + \text{S}_V(i) \rightarrow (\text{NO}_2)_S \]
Rates of the elementary processes

$$\text{NO} + \text{O}_s(i) \rightarrow \text{NO}_2 + \text{S}_v(i)$$

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

$$\text{NO}_2 + \text{S}_v(i) \rightarrow (\text{NO}_2)_s$$

$$r_2(i) = k_2'(i) \varphi_i \frac{\phi_{NO}}{[S_i]} \text{site}^{-1}\text{s}^{-1}.$$
The system of equations

\[
\begin{align*}
\theta_M(i) &= \frac{[M_S(i)]}{[S_i]} \\
\frac{d\theta_O(i)}{dt} &= -r_1(i)\theta_O(i) \\
\frac{d\theta_{NO_2}(i)}{dt} &= [1 - \theta_O(i) - \theta_{NO_2}(i)] r_2(i) \\
\frac{d[NO]}{dt} &= -\frac{2}{R} \left( \sum_{i=1}^{7} \theta_O(i) [S_i] r_1(i) \right) \\
\frac{d[NO_2]}{dt} &= \frac{2}{R} \sum_{i=1}^{7} \left\{ \theta_O(i) r_1(i) - [1 - \theta_O(i) - \theta_{NO_2}(i)] r_2(i) \right\} [S_i]
\end{align*}
\]
Results: NO and NO₂

a) $p=0.1$ Torr

b) $p=0.5$ Torr

c) $p=1$ Torr

d) $p=4$ Torr
Results: distribution of sites

\[ \delta_i \]

\[ E_R (kJ/mol) \]
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 $NO_2s$

\[ p = 5 \text{ Torr} \]
Results: successive NO fillings

Plasma ON

O₂ 0.5 mbar, P=16W

60min

10min

stop

Successive fillings
Results: successive NO fillings

![Graph showing successive NO fillings with time](image-url)
Results: effective $\gamma_{NO-NO_2}$

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

\[
\gamma_{NO\rightarrow NO_2} = \frac{1}{\phi_{NO}} \sum_{i=1}^{7} \theta_S(i) [S_i] r_1(i)
\]
Results: effective $\gamma_{\text{NO-NO2}}$

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.
• 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 \((O_3 \text{ formation at the wall})\)
  - Role of vibrationally excited ozone \((O_3^*)\)
Ozone formation at the wall

Jansen and Tuzson \cite{Jansen2010}
- “Isotope Evidence for Ozone Formation on Surfaces”

Lopaev et al \cite{Lopaev2011}
- DC discharges \( p = 10\text{-}50 \text{ Torr} \)
- \( \gamma(O_3) \) increases with pressure: \(~10^{-3} \text{ at } 10 \text{ Torr}; \)
  \(~5 \times 10^{-4} \text{ at } 5 \text{ Torr} \)
Vibrationally excited ozone

Rawlins et al [J. Geophys. Res. 90 (1985) 283]
- $\text{O}_3^*$ is mainly formed on the asymmetric stretching mode $\nu_3 \ (00\nu)$

- $\text{O}_2 + \text{O}_2 + \text{O} \rightarrow \text{O}_3 + \text{O}_2$ produces $\text{O}_3$ mainly in an excited state
- $\text{O}_3^*$ decreases the absolute value of $[\text{O}_3]$
- $\text{O}_3^*$ increases the characteristic time for ozone formation

Lopaev et al 2011
- Model with 5 vibration levels of $\text{O}_3$
Experiment

- DC discharge with short pulses (~1 ms)
- Silica tube, $R=1\text{ cm}$, $p=1-5\text{ Torr}$
- 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: $p$, $I$, $R$, $\Delta t$, $T_g=300$ 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 $O_3^*$
As perguntas fundamentais

O que é um plasma?

O3* kinetics

Formation

\[ \text{O}_2 + \text{O} + \text{O} \rightarrow \text{O}_3^* + \text{O}_2 \]

Destruction

\[ \text{O}_3^* + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \]

\[ \text{O}_3^* + \text{O}_2(a) \rightarrow \text{O}_2 + \text{O}_2 + \text{O} \]

\[ \text{O}_3^* + \text{O}_2 \rightarrow \text{O}_3 + \text{O}_2 \]

\[ \text{O}_3^* + \text{O} \rightarrow \text{O}_3 + \text{O} \]

\[ \text{O}_3^* + \text{Wall} \rightarrow \text{O}_3 + \text{Wall} \]
Results: O atoms

\[
\begin{align*}
\text{[O}^3\text{P}] (\text{cm}^{-3}) & = 2 \times 10^{15} \\
& \quad \times 10^{14} \\
& \quad \times 10^{15} \\
& \quad \times 10^{15} \\
& \quad \times 10^{15} \\
& \quad \times 10^{15} \\
\end{align*}
\]
Results: $\text{O}_3$ molecules

![Graph showing the concentration of $\text{O}_3$ molecules over time for different pressures (p=1 Torr, p=2 Torr, p=3 Torr, p=5 Torr). The graph plots [O$_3$] (cm$^{-3}$) against t (ms).]
Results: role of $O_3^*$
Results: O atoms decay

\[ \gamma_O = 2 \times 10^{-4} \]
Results: species concentrations

![Graph showing species concentrations over time](image_url)

- $\text{O}_2(X)$
- $\text{O}^3P$
- $\text{O}_2(a)$
- $\text{O}_2(b)$
- $\text{O}_3$
- $\text{O}_3(\ast)$

$[\text{Concentrations}] (\text{cm}^{-3})$

$t (\text{ms})$

$p = 5 \text{ Torr}$
Results: $\gamma(O_3)$

$p=1$ Torr; $\gamma(O_3)<10^{-5}$
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 \([\text{N}_2(A)]\) in the \(\text{N}_2\) 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
RF discharge, $p = 8 \text{ Torr}$, $P = 100 \text{ W}$, $Q = 1 \text{ slm}$, $R_1 = 0.3 \text{ cm}$, $R_2 = 1.1 \text{ cm (quartz)}$, gas mixture $N_2$ - (0-1)\%O$_2$. 

The nitrogen afterglows
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

\[ \text{N} + \text{N} + \text{N}_2 \rightarrow \text{N}_2(B,v' = 11) + \text{N}_2 \]

\[ \text{N}_2(B) \rightarrow \text{N}_2(A) + \text{hv} \]
• 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(\(^4\)S)
  - O(\(^3\)P)
  - N\(_2\)(A)

in the nitrogen afterglow.

• Bonus: experimental estimation of the rate coefficient of reaction

\[ \text{N}_2(X, v \geq 13) + \text{O} \rightarrow \text{NO} + \text{N} \]

at room temperature
Determination of $[N]$

Experimental determination of $[N]$:

- Measurement of the $1^{+}$ intensity at 580 nm
- Pseudo-stationary concentration $[\text{N}_2(B)]$ determined from:

  1. $N + N + N_2 \rightarrow \text{N}_2(B, \nu' = 11) + N_2$
  2. $\text{N}_2(B, \nu' = 11) \rightarrow \text{N}_2(A, \nu'' = 7) + h\nu (580\,nm)$
  3. $\text{N}_2(B) + N_2 \rightarrow \text{N}_2(A, X) + N_2$
  4. $\text{N}_2(B) + O_2 \rightarrow \text{N}_2(A, X) + O + O$

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

- Requires calibration (NO titration) and early-late “mixing coefficient”
Determination of [O]

Experimental determination of [O]:

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

(5) $N + O + N_2 \rightarrow NO(B, \nu' = 0) + N_2$

(6) $NO(B, \nu' = 0) \rightarrow NO(X, \nu'' = 8) + h\nu(320\,\text{nm})$

(7) $NO(B) + N_2 \rightarrow \text{products}$

(8) $NO(B) + O_2 \rightarrow \text{products}$

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

\[
(8) \quad N_2(A) + N_2(A) \rightarrow N_2(C, \nu' = 1) + N_2(X) \\
(9) \quad N_2(C, \nu' = 1) \rightarrow N_2(B, \nu'' = 0) + h\nu(316 \text{ nm}) \\
(10) \quad N_2(C) + N_2 \rightarrow \text{products}
\]

\[
\frac{I(320)}{I(316)} \sim \frac{A_{320}}{A_{316}} \left( \frac{k_5[N][O][N_2]}{k_8[N_2(A)]^2} \right) \left( \frac{\nu_9 + k_{10}[N_2]}{\nu_6 + k_7[N_2]} \right)
\]
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 temperature (!)
Results: summary

Concentrations (cm$^{-3}$) vs. % O$_2$ graph showing:
- N(4S)
- O(3P)
- N$_2$(A)

Commentary:
- (-, *, Pink afterglow)
- (..., o) Late afterglow
N$_2$(B) state

$p=8$ Torr, $P=100$ W
$N_2(B)$ state

$N+N+N_2 \rightarrow N_2(B)+N_2$

$N_2(A)+N_2(X,v) \rightarrow N_2(B)+N_2$

$N_2(a')+N_2 \rightarrow N_2(B)+N_2$

$p=8$ Torr, $P=100$ W
$[N_2(A)]$ can be determined from different line ratios:

<table>
<thead>
<tr>
<th>Species</th>
<th>Lines</th>
<th>Industrial N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[N_2(A)]$</td>
<td>$I_\gamma(259)/I_\beta(262)$</td>
<td>$1.1 \times (10^9 - 10^{11})$</td>
</tr>
<tr>
<td>$[N_2(A)]$</td>
<td>$I_{2+}(316)/I_\beta(320)$</td>
<td>$2.4 \times 10^{11}$</td>
</tr>
<tr>
<td>$[N_2(A)]$</td>
<td>$I_{1+}(580)/I_{2+}(316)$</td>
<td>$7.3 \times 10^{10}$</td>
</tr>
</tbody>
</table>

**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 methods 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:
  \[
  N_2(X, \nu \geq 13) + O \rightarrow NO + N \text{ at room temperature}
  \]
In collaboration with

Philippe Coche,¹ Luís Lemos Alves,¹ Olivier Leroy,² Gabi Stancu,³ Philippe Leprince² and Tiberiu Minea²

¹ IPFN, Instituto Superior Técnico, Universidade de Lisboa, Portugal
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

- Wave electrodynamics
- Chemical kinetics
- Vibration kinetics
- Surface kinetics
- Electron kinetics
- Ion kinetics
Surface waves in capillary tubes

- $f=2.45 \text{ GHz}$, $p=2 \text{ Torr}$, $R=0.345 \text{ mm}$
- 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

![Graph showing the relationship between electron temperature ($T_e$), electric field to number density ratio ($E/N$), and radius ($R$). The graph compares classical ambipolar theory and self and Ewald theory. The x-axis represents the radius in centimeters ($R (cm)$), the y-axis represents the electron temperature in electron volts ($T_e (eV)$), and the z-axis represents the electric field to number density ratio in Thomson scattering units ($E/N$) and torr-degrees ($T_d$).]
Surface waves in capillary tubes

• NO kinetics:

\[ \text{N}(^2D)+\text{O}_2 \rightarrow \text{N}+\text{NO} \]
\[ \text{e}+\text{NO} \rightarrow \text{e}+\text{e}+\text{NO}^+ \]
\[ \text{NO}^++\text{wall} \rightarrow \text{e}+\text{NO} \]
Summary

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

Bottlenecks / challenges

• State-to-state reliable collisional data

• $T_g$ dependence of the rate coefficients
  
  $[N_2(X,v \geq 13) + O \rightarrow NO + N$ at low $T_g,$
  Several data at high $T_g$ (ester, http://ester.ist.utl.pt/)]
Summary


and upper atmospheric chemistry. 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-
Summary

• Breakthrough measurements
  – $\text{N}_2$ singlets

• Role of V-E energy exchanges
  [Mário Lino da Silva & J. Loureiro, *ICPIG 2013* PSI-113]

• Surface characteristics and surface processes
  [Daniil Marinov, this master class]
Conferences @ Lisboa!

You just don’t want to miss them! 😊