Atelier "CHIMIE DES PLASMAS" –

CINÉTIQUE DES ÉTATS EXCITÉS – MISE EN ŒUVRE DE MODÈLES COLLISIONNELS-RADIATIFS (CR)

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Plan

1. **Chimie des états excités *vs* chimie des espèces : identification de constantes de vitesse globale**
2. **Bilan détaillé vrai pour les constantes de vitesse globale ?**
3. **Diagrammes de BOLTZMANN et de SAHA-BOLTZMANN / Elaboration modèle Collisionnel-Radiatif et illustration**

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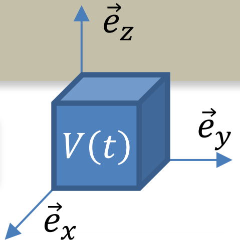
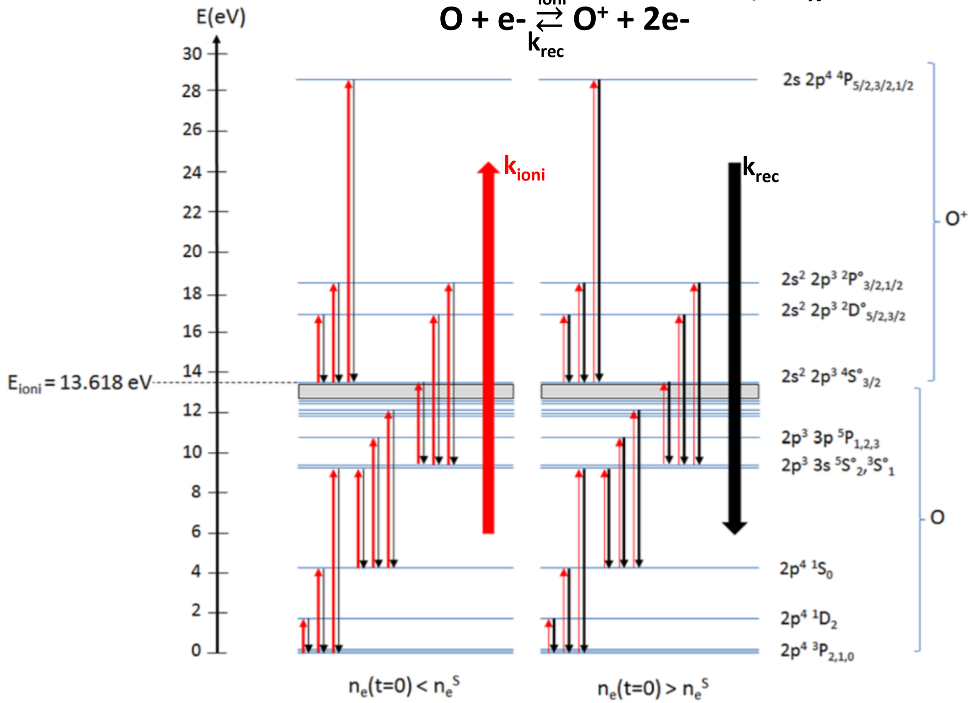
Kinetics – Excited states and species



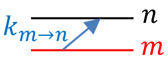
$$k_{m\to n} = \sqrt{\frac{8k_BT_e}{\pi m_e}} \int_{\frac{E_n - E_m}{k_BT_e}}^{+\infty} \sigma_{m\to n}(x)\, x\, e^{-x} dx$$

$$O + e^- \underset{k_{rec}}{\overset{k_{ioni}}{\rightleftarrows}} O^+ + 2e^-$$

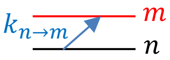


Individual O_m variation rate

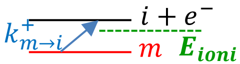
$$\frac{1}{V}\frac{dN_{O_m}}{dt} = -\sum_{n>m} k_{m\to n}\left(1 - \frac{[O_n]}{[O_m]K^B_{n,m}}\right)[O_m]n_e$$



$$+\sum_{n<m} k_{n\to m}\left(1 - \frac{[O_m]}{[O_n]K^B_{m,n}}\right)[O_n]n_e$$



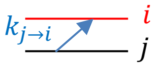
$$-\sum_i k^+_{m\to i}\left(1 - \frac{[O_i^+]n_e}{[O_m]K^S_{i,m}}\right)[O_m]n_e$$



Individual O_i^+ variation rate

$$\frac{1}{V}\frac{dN_{O_i^+}}{dt} = -\sum_{j>i} k_{i\to j}\left(1 - \frac{[O_j^+]}{[O_i^+]K^B_{j,i}}\right)[O_i^+]n_e$$

$$+\sum_{j<i} k_{j\to i}\left(1 - \frac{[O_i^+]}{[O_j^+]K^B_{i,j}}\right)[O_j^+]n_e$$



$$+\sum_m k^+_{m\to i}\left(1 - \frac{[O_i^+]n_e}{[O_m]K^S_{i,m}}\right)[O_m]n_e$$

Global O variation rate

$$\frac{1}{V}\frac{dN_O}{dt} = \sum_m \frac{1}{V}\frac{dN_{O_m}}{dt} = \begin{cases} -k_{ioni}[O]n_e \\ +k_{rec}[O^+]n_e^2 \end{cases}$$

Global O⁺ variation rate

$$\frac{1}{V}\frac{dN_{O^+}}{dt} = \sum_i \frac{1}{V}\frac{dN_{O_i^+}}{dt} = \begin{cases} +k_{ioni}[O]n_e \\ -k_{rec}[O^+]n_e^2 \end{cases}$$

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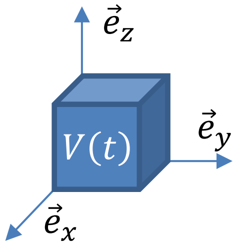
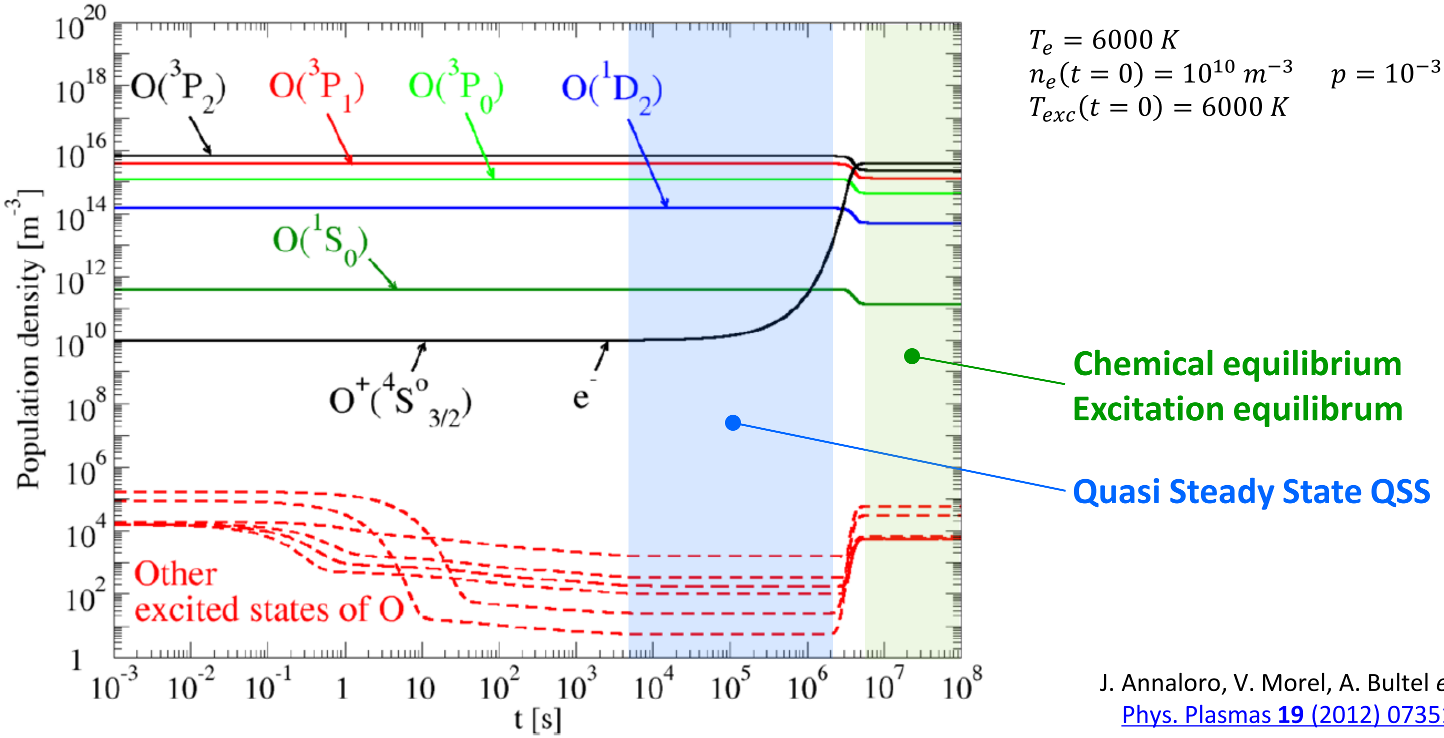
Kinetics of ionization – Example



For ionization:

$$n_e(t=0) < n_e^S = K^S\left(\sqrt{1+\frac{p}{K^S k_B T_e}}-1\right)$$

0D simulation



$T_e = 6000\ K$
$n_e(t=0) = 10^{10}\ m^{-3}$ $p = 10^{-3}\ Pa$
$T_{exc}(t=0) = 6000\ K$

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Identification of global rate coefficient

Global O variation rate

$$\frac{1}{V}\frac{dN_O}{dt} = \sum_m \frac{1}{V}\frac{dN_{O_m}}{dt} = \begin{cases} -k_{ioni}[O]n_e \\ +k_{rec}[O^+]n_e^2 \end{cases}$$

Global O⁺ variation rate

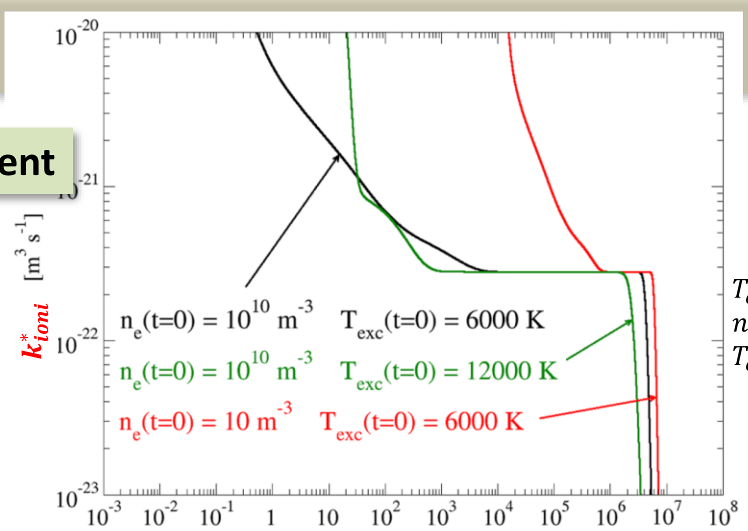
$$\frac{1}{V}\frac{dN_{O^+}}{dt} = \sum_i \frac{1}{V}\frac{dN_{O_i^+}}{dt} = \begin{cases} +k_{ioni}[O]n_e \\ -k_{rec}[O^+]n_e^2 \end{cases}$$

For ionization, we follow:

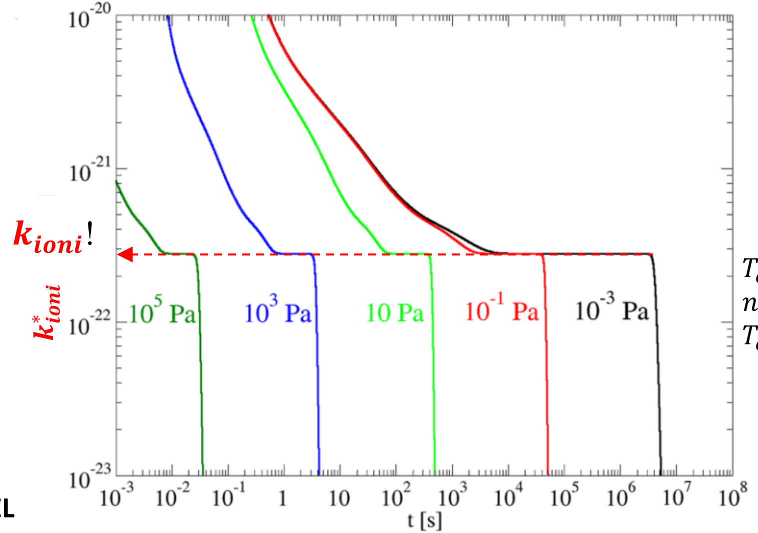
$$k_{ioni}^* = -\frac{1}{V[O]\,n_e}\frac{dN_O}{dt} = +\frac{1}{V[O]\,n_e}\frac{dN_{O^+}}{dt}$$

For recombination, we follow:

$$k_{rec}^* = +\frac{1}{V[O^+]n_e^2}\frac{dN_O}{dt} = -\frac{1}{V[O^+]n_e^2}\frac{dN_{O^+}}{dt}$$



$T_e = 6000\ K$
$n_e(t=0) = ???\ m^{-3}$
$T_{exc}(t=0) = ???\ K$
$p = 10^{-3}\ Pa$



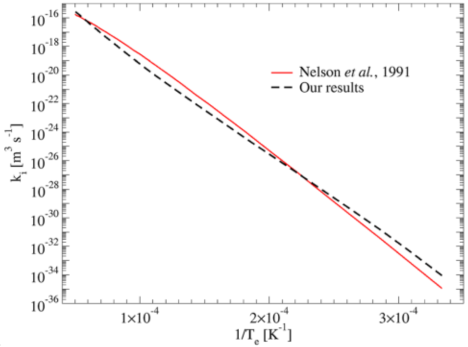
$T_e = 6000\ K$
$n_e(t=0) = 10^{10}\ m^{-3}$
$T_{exc}(t=0) = 6000\ K$
$p = ???\ Pa$

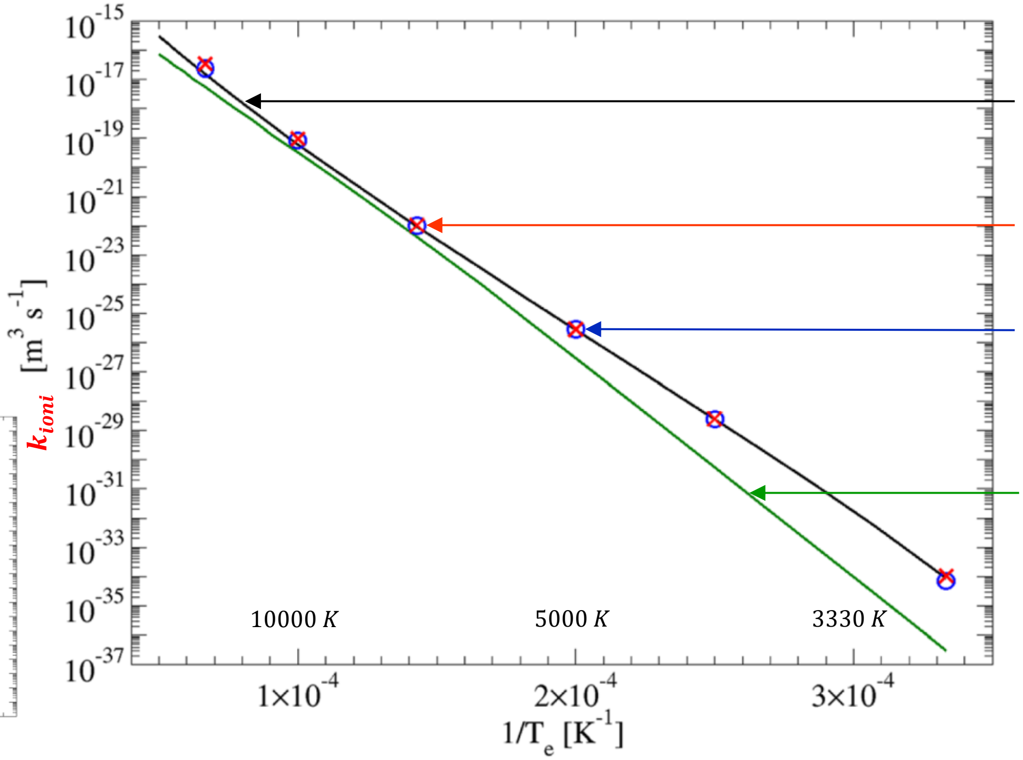
Influence of temperature and energy diagram

$$Ar + e^- \underset{k_{rec}}{\overset{k_{ioni}}{\rightleftarrows}} Ar^+ + 2e^-$$

Arrhenius-type rate coefficient

$$k_{ioni}(T_e) = A\, T_e^{\alpha}\, e^{-\frac{E_A}{k_B T_e}}$$





NIST database (previous approach)

NIST database
+ Rydberg states with $g_k = 1$

NIST database
+ Rydberg states with $g_k = 2n_k^2$

Vleck energy diagram

J. Vlcek, J. Phys. D: Appl. Phys. 22 (1989) 623

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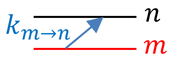
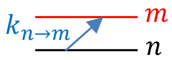
Detailed balance

Individual O_m variation rate

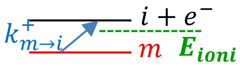
$$\frac{1}{V}\frac{dN_{O_m}}{dt} = -\sum_{n>m} k_{m\to n}\left(1-\frac{[O_n]}{[O_m]K^B_{n,m}}\right)[O_m]n_e$$



$$+\sum_{n<m} k_{n\to m}\left(1-\frac{[O_m]}{[O_n]K^B_{m,n}}\right)[O_n]n_e$$



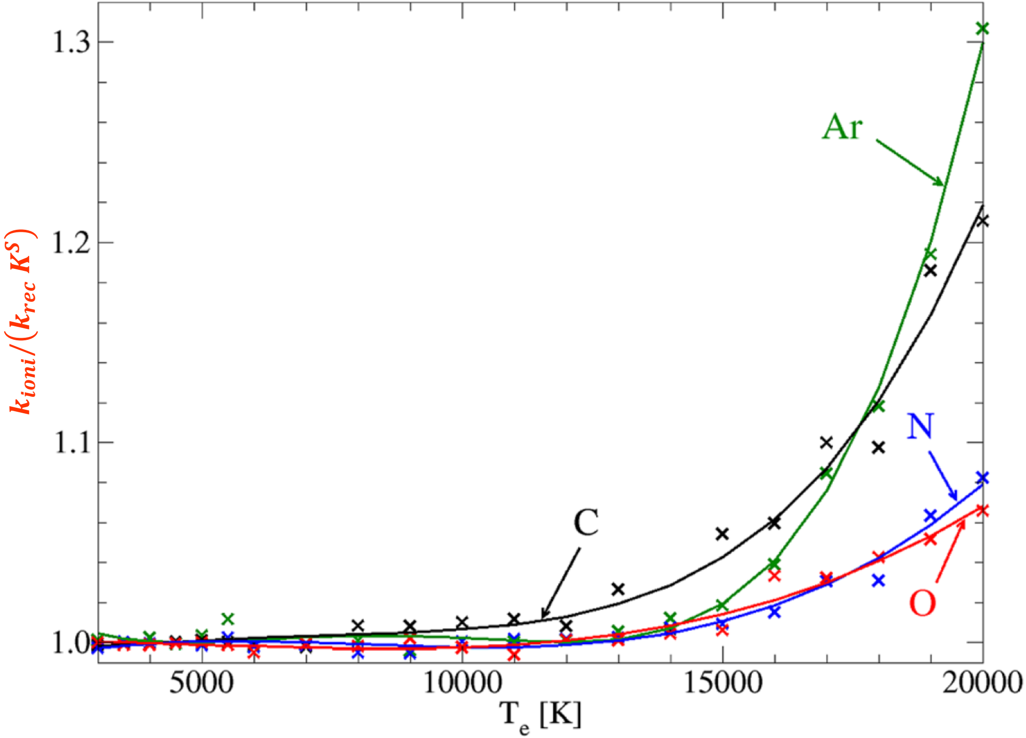
$$-\sum_i\ k^+_{m\to i}\left(1-\frac{[O_i^+]n_e}{[O_m]K^S_{i,m}}\right)[O_m]n_e$$



Boltzmann equilibrium constant $K^B_{n,m} = \frac{g_n}{g_m}\, e^{-\frac{E_n-E_m}{k_BT_e}}$

Saha equilibrium constant $K^S_{i,m} = \frac{2\,g_i^+}{g_m}\left(\frac{2\pi\, m_e k_B T_e}{h^2}\right)^{3/2} e^{-\frac{E_i-E_m}{k_BT_e}}$

Species Saha equilibrium constant $K^S = \frac{2\,Z^+}{Z}\left(\frac{2\pi\, m_e k_B T_e}{h^2}\right)^{3/2} e^{-\frac{E_{ioni}}{k_BT_e}}$



O + e- $\underset{k_{rec}}{\overset{k_{ioni}}{\rightleftarrows}}$ O⁺ + 2e-

$$\frac{1}{V}\frac{dN_{O^+}}{dt} = k_{ioni}[O]n_e - k_{rec}[O^+]n_e^2 \xrightarrow{\text{Chemical eq.}} K^S = \frac{n_e[O^+]}{[O]} = \frac{k_{ioni}}{k_{rec}} \Rightarrow \frac{k_{ioni}}{k_{rec}\,K^S} = 1$$

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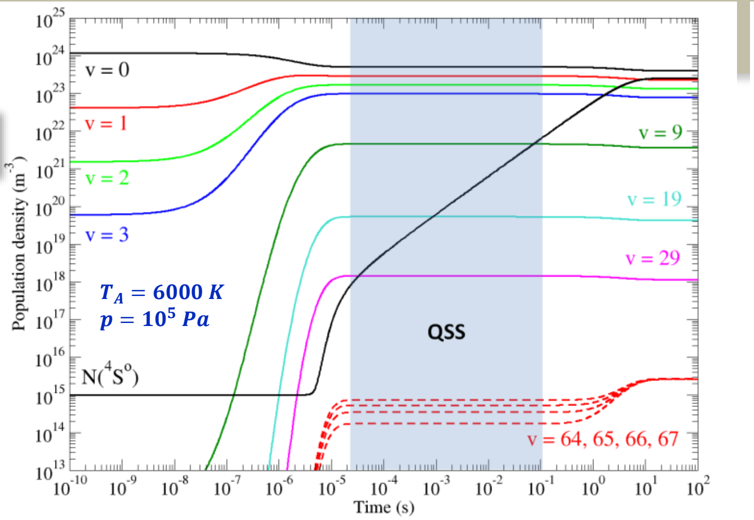
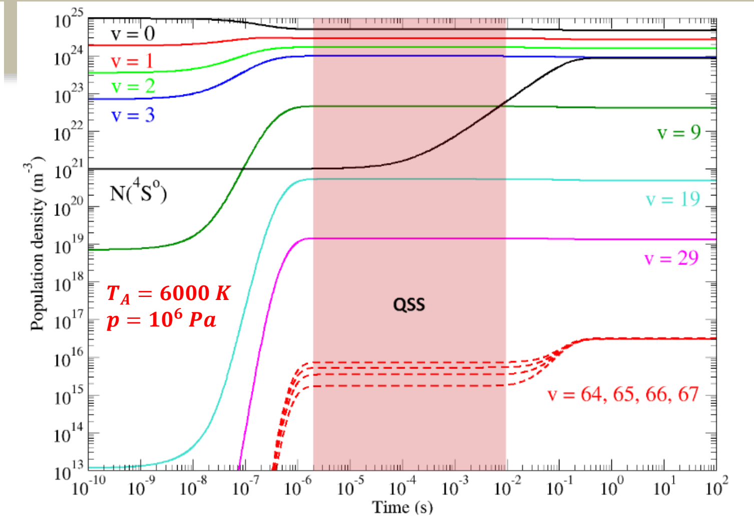
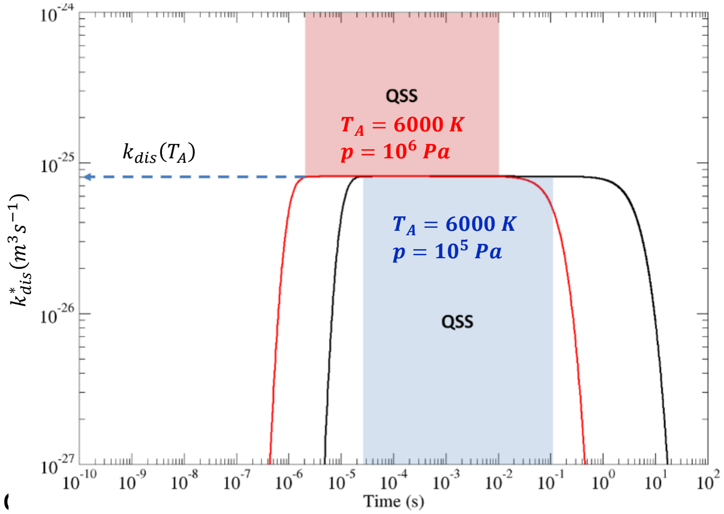
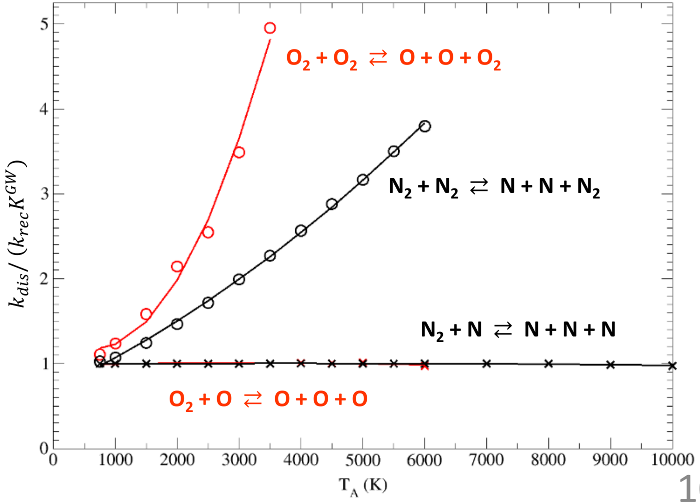
Detailed balance

$$N_2 + N_2 \underset{k_{rec}}{\overset{k_{dis}}{\rightleftarrows}} N + N + N_2$$









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Influence of radiation?

External argon at p_{atm}

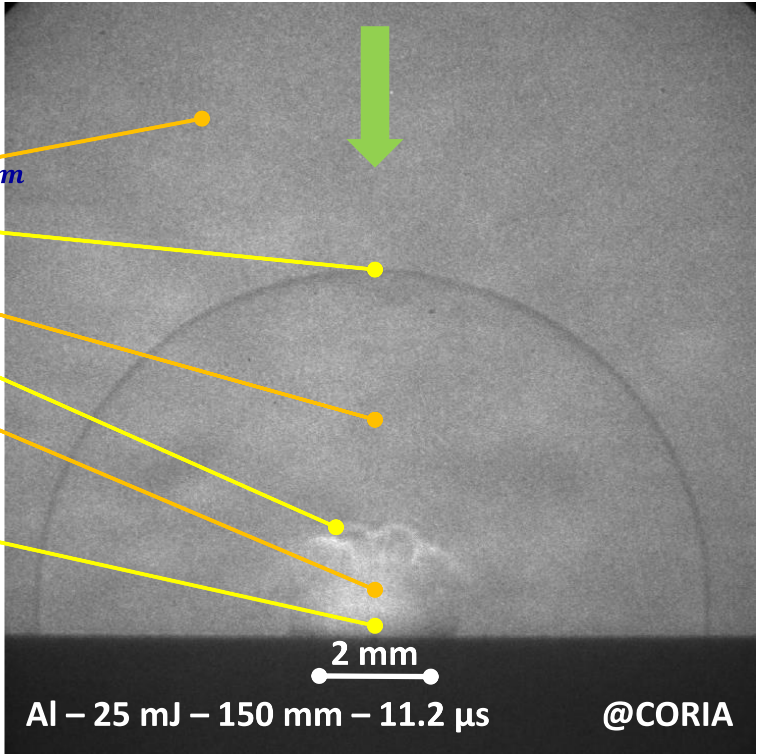
Shockwave

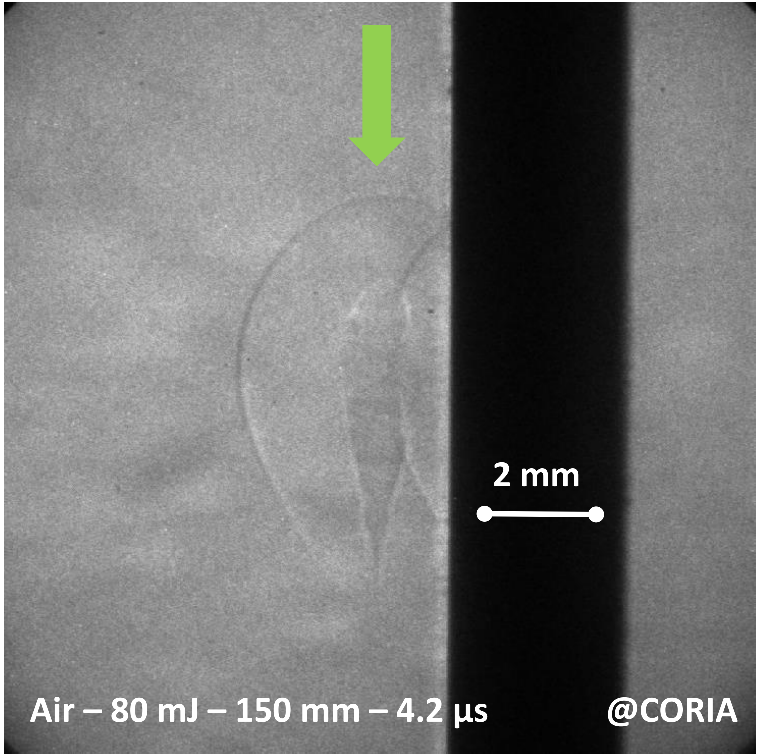
Shock layer

Contact surface

Ablated aluminum

Expanding dense aluminum





The ECHREM* code

*Eulerian CHemically REactive Multi-component plasma code

Horizon 2020 FR FCM EMC energy materials & clean combustion center

V. Morel, A. Bultel *et al.* Spectrochim. Acta B **127** (2017) 7-19

Shock layer - *Argon*

Collisional-Radiative model CoRaM-RG

Ar (5 lev.)
Ar^+ (1 lev.)
Ar_2^+ (1 lev.)

$Ar + e^- \rightleftarrows Ar^* + e^-$	Exc. Elec. Impact
$Ar + Ar \rightleftarrows Ar^* + Ar$	Exc. Elec. Impact
$Ar + e^- \rightleftarrows Ar^+ + 2\,e^-$	Ioni. Elec. Impact
$Ar^* + e^- \rightleftarrows Ar^+ + 2\,e^-$	Ioni. Elec. Impact
$Ar + Ar \rightleftarrows Ar^+ + e^- + Ar$	Ioni. Heavy Impact
$Ar^* + Ar \rightleftarrows Ar^+ + e^- + Ar$	Ioni. Heavy Impact
$Ar^* + Ar^* \rightleftarrows Ar^+ + e^- + Ar$	Penning Ioni.
$Ar_2^+ + e^- \rightleftarrows Ar^*\,ou\;Ar + Ar$	Disso. Recomb.
$Ar^+ + e^- \rightarrow Ar^*\,ou\;Ar + h\nu$	Rad. Recomb.
$Ar_j \rightarrow Ar_{i<j} + h\nu$	Spont. Emiss.

500 elementary processes

Collisional Database

$$k_i(T_{A,e}) = \sqrt{\frac{8\,k_B\,T_{A,e}}{\pi\,\mu}} \int_{x_0}^{+\infty} x\,e^{-x}\,\sigma_i(x)\,dx$$ with

- $\sigma_i(x)$ collisional cross section and
- $x = \frac{\varepsilon}{k_B\,T_{A,e}}$ reduced collision energy

Backward rate coefficient deduced from the ***Detailed Balance***

Central plasma - *Aluminum*

Al (80 lev.)
Al^+ (170 lev.)
Al^{2+} (1 lev.)

Collisional-Radiative model CoRaM-Al

$Al_i + e^- \rightleftarrows Al_{j>i} + e^-$
$Al_i^+ + e^- \rightleftarrows Al_{j>i}^+ + e^-$
$Al_i + \Sigma_{i,Z} Al_i^{Z+} \rightleftarrows Al_{j>i} + \Sigma_{i,Z} Al_i^{Z+}$
$Al_i^+ + \Sigma_{i,Z} Al_i^{Z+} \rightleftarrows Al_{j>i}^+ + \Sigma_{i,Z} Al_i^{Z+}$
$Al_i + e^- \rightleftarrows Al_j^+ + 2e^-$
$Al_j^+ + e^- \rightleftarrows Al^{2+} + 2e^-$
$Al_i + \Sigma_{i,Z} Al_i^{Z+} \rightleftarrows Al_j^+ + e^- + \Sigma_{i,Z} Al_i^{Z+}$
$Al_j^+ + \Sigma_{i,Z} Al_i^{Z+} \rightleftarrows Al^{2+} + e^- + \Sigma_{i,Z} Al_i^{Z+}$
$Al^{2+} + e^- \rightleftarrows Al_j^+ + h\nu$
$Al_j^+ + e^- \rightleftarrows Al_i + h\nu$
$Al_j^+ \rightarrow Al_{i<j}^+ + h\nu$
$Al_j \rightarrow Al_{i<j} + h\nu$
Thermal Bremsstrahlung

65 000 elementary processes

Radiative Database

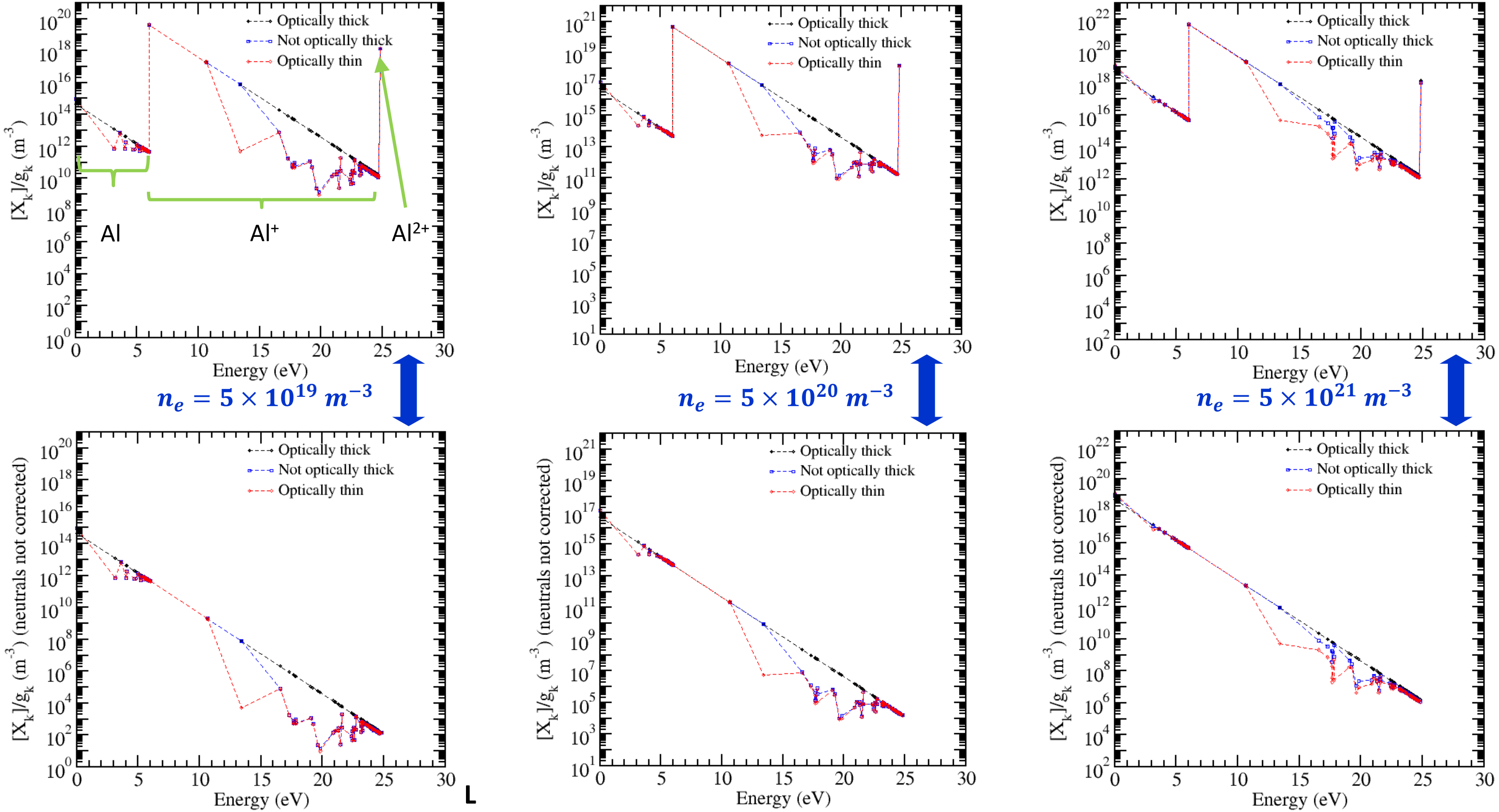
NIST, Atomic Line List, ADAS, HULLAC…

- Recombination under almost constant n_e
- Constant temperature $T_e = 10\ 000\ K$ (order of magnitude for **laser-induced Aluminum plasma**)
- Constant radius $R = 1\ mm$ (order of magnitude for **laser-induced Aluminum plasma**)
- BOLTZMANN and SAHA-BOLTZMANN plots at $t = 1\ \mu s$

BOLTZMANN and SAHA-BOLTZMANN plots

BOLTZMANN plots

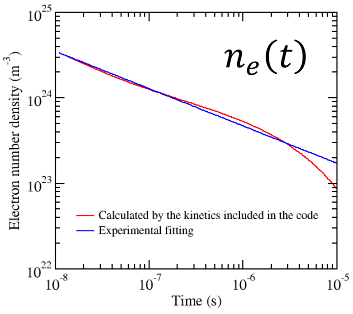
SAHA-BOLTZMANN plots

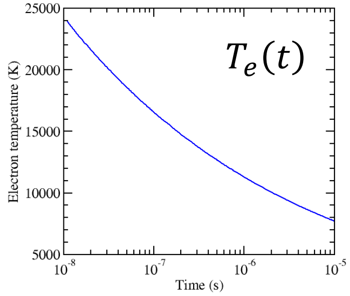


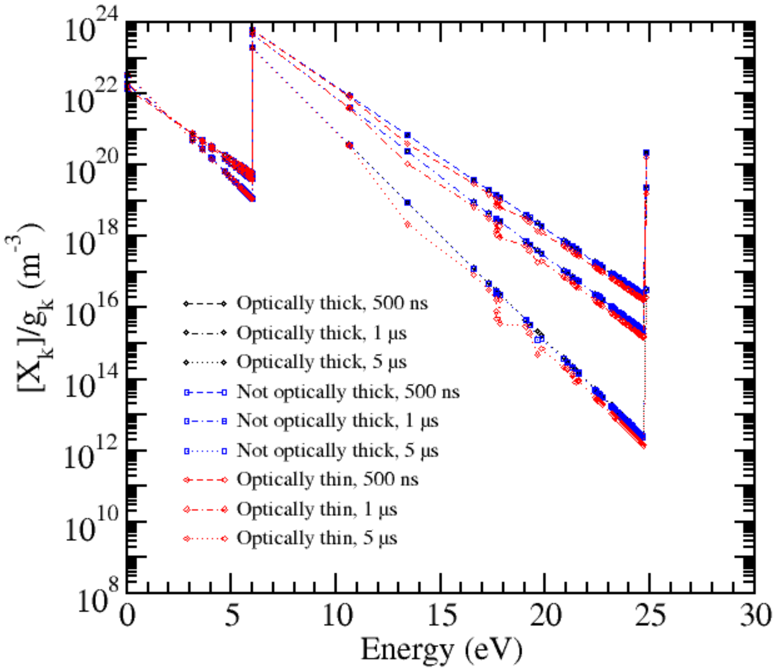
BOLTZMANN and SAHA-BOLTZMANN plots

EXPERIMENTAL TIME-EVOLUTION (typical conditions for a **laser-induced Aluminum plasma**)

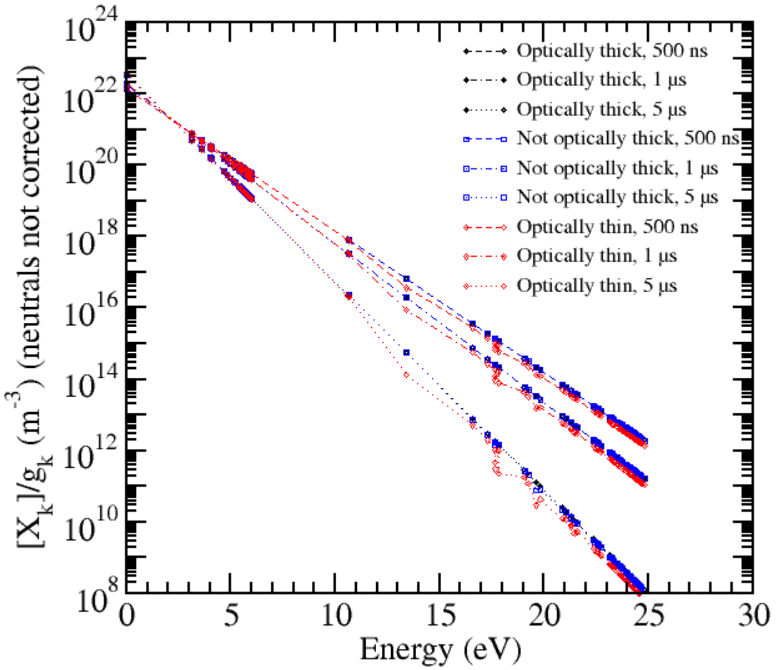
- Electron density $n_e(t) = 3.5 \times 10^{24} \left(\frac{t[ns]}{10}\right)^{-0.436} m^{-3}$ for $t > 10\ ns$
- Electron temperature $T_e(t) = 24\,270 \left(\frac{t[ns]}{10}\right)^{-0.166} K$ for $t > 10\ ns$
- Plasma radius $R(t) = 0.63 \left(\frac{t[ns]}{10}\right)^{0.1} mm$ for $t > 10\ ns$







BOLTZMANN plot



SAHA-BOLTZMANN plot