State-to-state self-consistent kinetic modelling of hydrogen plasmas

A Laricchiuta, R Celiberto⋆, L D Pietanza, M Capitelli and G Colonna

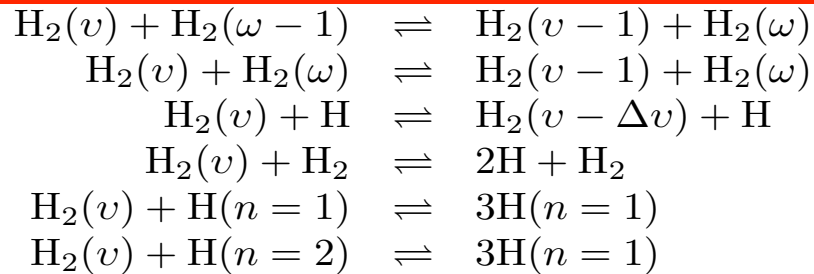CNR ISTP Bari, Italy
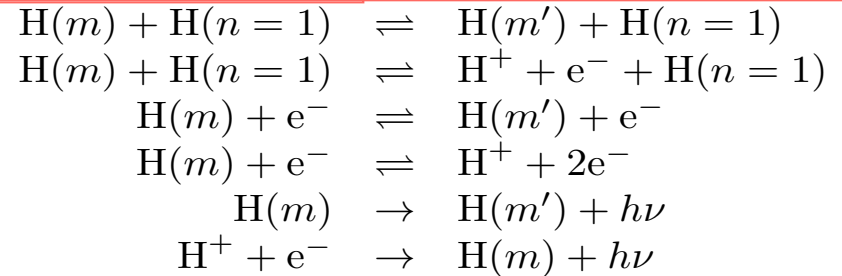⋆ DICATECh Polytechnic of Bari & CNR ISTP Bari, Italy

Plasma Kinetics & Processes

H$_2$/H STATE-TO-STATE KINETICS

Ground state vibrational kinetics

Ground state vibrational kinetics

$$
\begin{aligned}
H_2(v) + H_2(\omega - 1) &\rightleftharpoons H_2(v-1) + H_2(\omega) \\
H_2(v) + H_2(\omega) &\rightleftharpoons H_2(v-1) + H_2(\omega) \\
H_2(v) + H &\rightleftharpoons H_2(v - \Delta v) + H \\
H_2(v) + H_2 &\rightleftharpoons 2H + H_2 \\
H_2(v) + H(n=1) &\rightleftharpoons 3H(n=1) \\
H_2(v) + H(n=2) &\rightleftharpoons 3H(n=1)
\end{aligned}
$$

Atomic level kinetics

$$
\begin{aligned}
H(m) + H(n=1) &\rightleftharpoons H(m') + H(n=1) \\
H(m) + H(n=1) &\rightleftharpoons H^+ + e^- + H(n=1) \\
H(m) + e^- &\rightleftharpoons H(m') + e^- \\
H(m) + e^- &\rightleftharpoons H^+ + 2e^- \\
H(m) &\rightarrow H(m') + h\nu \\
H^+ + e^- &\rightarrow H(m) + h\nu
\end{aligned}
$$

Electron impact induced processes

$$
\begin{aligned}
H_2(v) + e^- &\rightleftharpoons H_2(\omega) + e^- \\
H_2(v) + e^- &\rightleftharpoons H_2^+ + 2e^- \\
H_2(v) + e^- &\rightleftharpoons H^+ + H(n=1) + 2e^- \\
H_2(v) + e^- &\rightleftharpoons H_2(b, e^3\Sigma_u^+) + e^- \rightleftharpoons H(n=1) + H(n=1) + e^- \\
H_2(v) + e^- &\rightleftharpoons H_2(^1Y^\star) + e^- \rightleftharpoons H(n=1) + H(n=2,3,4) + e^-
\end{aligned}
$$

Molecular ion kinetics

$$
\begin{aligned}
e^- + H_2^+ &\rightleftharpoons H(m') + H(n=1) \\
e^- + H_2^+ &\rightleftharpoons H^+ + H(n=1) + e^- \\
e^- + H_2^+ &\rightleftharpoons 2H^+ + 2e^- \\
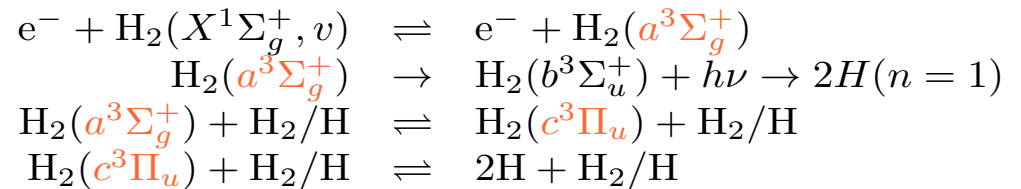H^+ + H_2(v'') &\rightleftharpoons H + H_2^+
\end{aligned}
$$
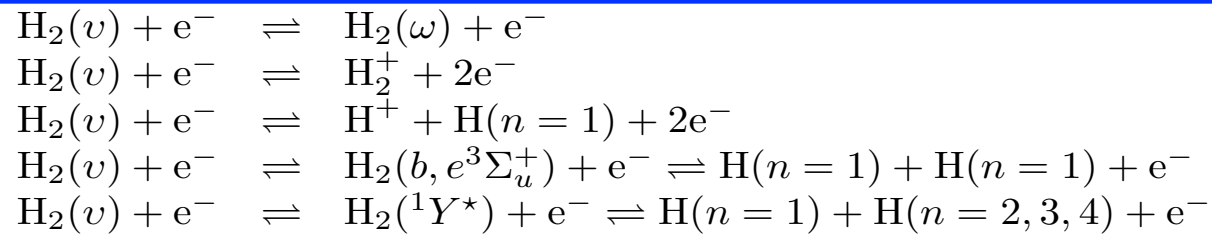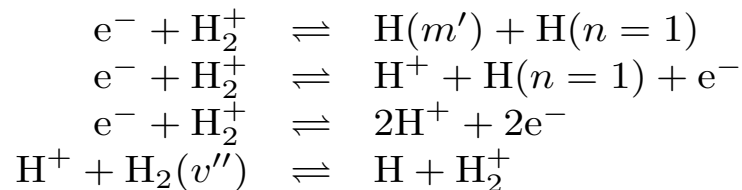
H$_2$/H STATE-TO-STATE KINETICS

Updated model

Singlets vibrational kinetics

$$\begin{aligned}
\mathrm{H}_2(X^1\Sigma_g^+, v'') + \mathrm{e}^- &\rightleftharpoons \mathrm{H}_2(^1Y^\star, v') + \mathrm{e}^- \\
\mathrm{H}_2(^1Y^\star, v') &\rightarrow \mathrm{H}_2(X^1\Sigma_g^+, v'') + h\nu \\
\mathrm{H}_2(^1Y^\star, v') &\rightarrow \mathrm{H}_2(X^1\Sigma_g^+, \varepsilon) + h\nu \rightarrow 2\mathrm{H}(n=1) \\
\mathrm{H}_2(^1Y^\star, v') + \mathrm{H}_2/\mathrm{H} &\rightarrow 2\mathrm{H}(n=1) + \mathrm{H}_2/\mathrm{H}
\end{aligned}$$

Triplets kinetics

$$\begin{aligned}
\mathrm{e}^- + \mathrm{H}_2(X^1\Sigma_g^+, v) &\rightleftharpoons \mathrm{e}^- + \mathrm{H}_2(a^3\Sigma_g^+) \\
\mathrm{H}_2(a^3\Sigma_g^+) &\rightarrow \mathrm{H}_2(b^3\Sigma_u^+) + h\nu \rightarrow 2H(n=1) \\
\mathrm{H}_2(a^3\Sigma_g^+) + \mathrm{H}_2/\mathrm{H} &\rightleftharpoons \mathrm{H}_2(c^3\Pi_u) + \mathrm{H}_2/\mathrm{H} \\
\mathrm{H}_2(c^3\Pi_u) + \mathrm{H}_2/\mathrm{H} &\rightleftharpoons 2\mathrm{H} + \mathrm{H}_2/\mathrm{H}
\end{aligned}$$

Negative Ions kinetics

$$\begin{aligned}
\mathrm{e}^- + \mathrm{H}_2(X^1\Sigma_g^+, v'') &\rightleftharpoons \mathrm{H}^- + \mathrm{H} \\
\mathrm{e}^- + \mathrm{H}_2^+ &\rightleftharpoons \mathrm{H}^- + \mathrm{H}^+ \\
\mathrm{H}^- + \mathrm{H}^+ &\rightleftharpoons \mathrm{H}(n=1) + \mathrm{H}(n>1) \\
\mathrm{H}^- + \mathrm{H}_2^+ &\rightleftharpoons \mathrm{H}_2(v''=0) + \mathrm{H}(n=1) \\
\mathrm{H}^- + \mathrm{H}_3^+ &\rightleftharpoons \mathrm{H}_2(v''=0) + \mathrm{H}_2(v''=0)
\end{aligned}$$
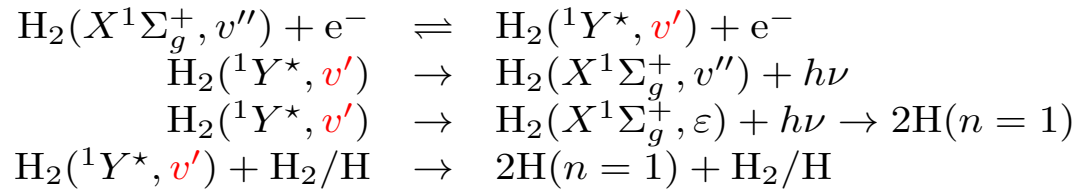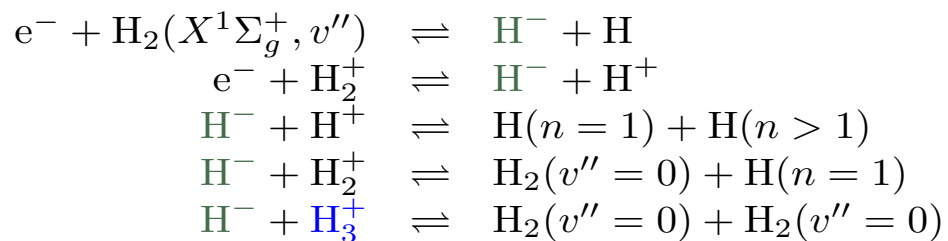
Trihydrogen cation kinetics

$$\begin{aligned}
\mathrm{H}^+ + 2\mathrm{H}_2(v''=0) &\rightleftharpoons \mathrm{H}_3^+ + \mathrm{H}_2(v''=0) \\
\mathrm{H}_2^+ + \mathrm{H}_2(v''=0) &\rightleftharpoons \mathrm{H}_3^+ + \mathrm{H}(n=1) \\
\mathrm{e}^- + \mathrm{H}_3^+ &\rightleftharpoons \mathrm{e}^- + \mathrm{H}^+ + 2\mathrm{H}(n=1) \\
\mathrm{e}^- + \mathrm{H}_3^+ &\rightarrow \mathrm{H}_2^+ + \mathrm{H}^- + h\nu \\
\mathrm{e}^- + \mathrm{H}_3^+ &\rightarrow \mathrm{H}_2(v=0) + \mathrm{H}(n=1) \\
\mathrm{e}^- + \mathrm{H}_3^+ &\rightarrow 3\mathrm{H}(n=1)
\end{aligned}$$
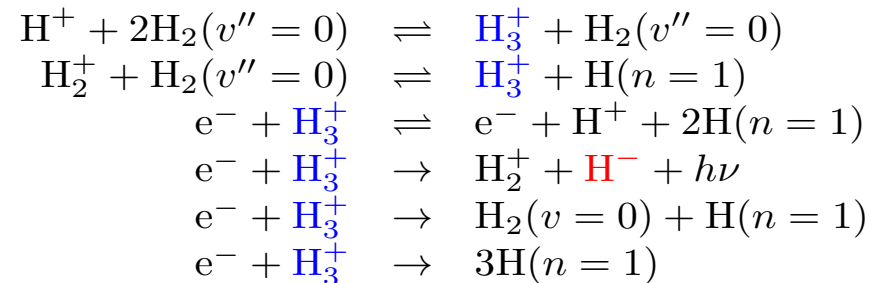
- ✔ state-to-state
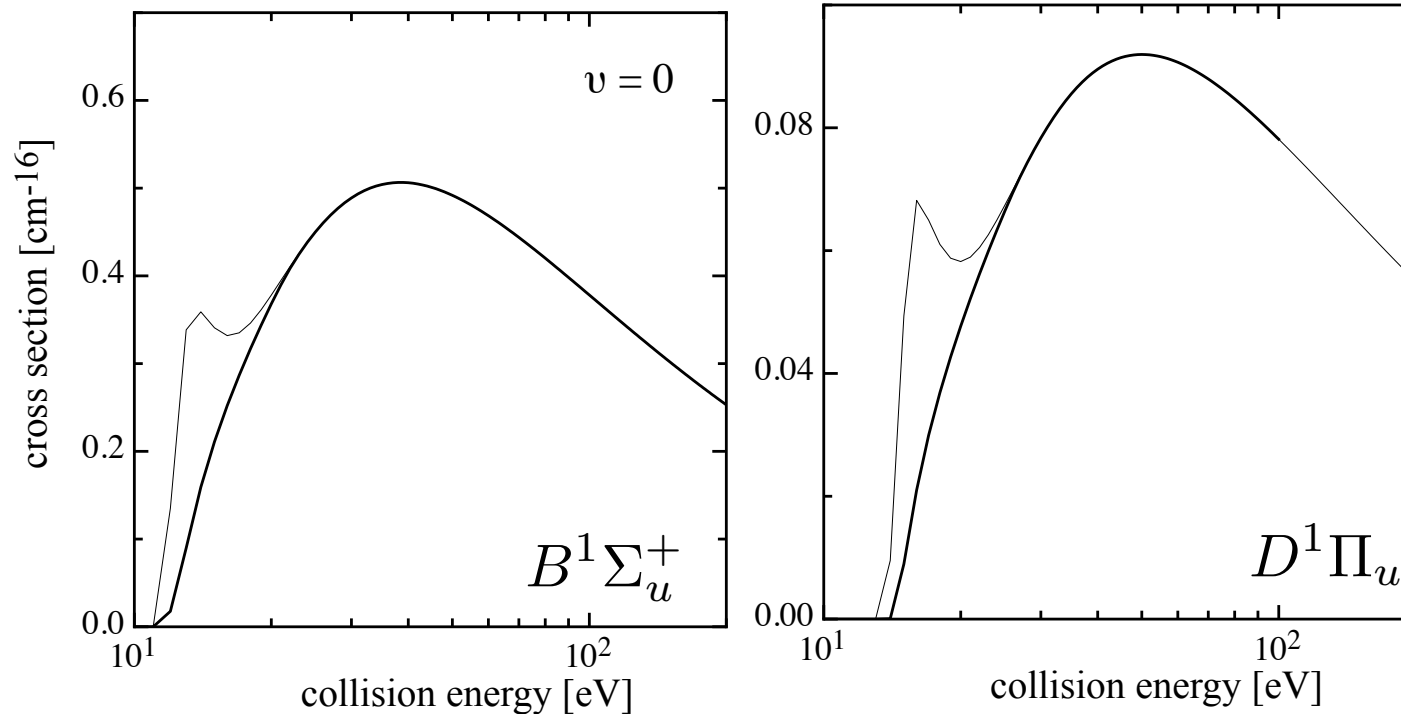- ✔ radiative processes
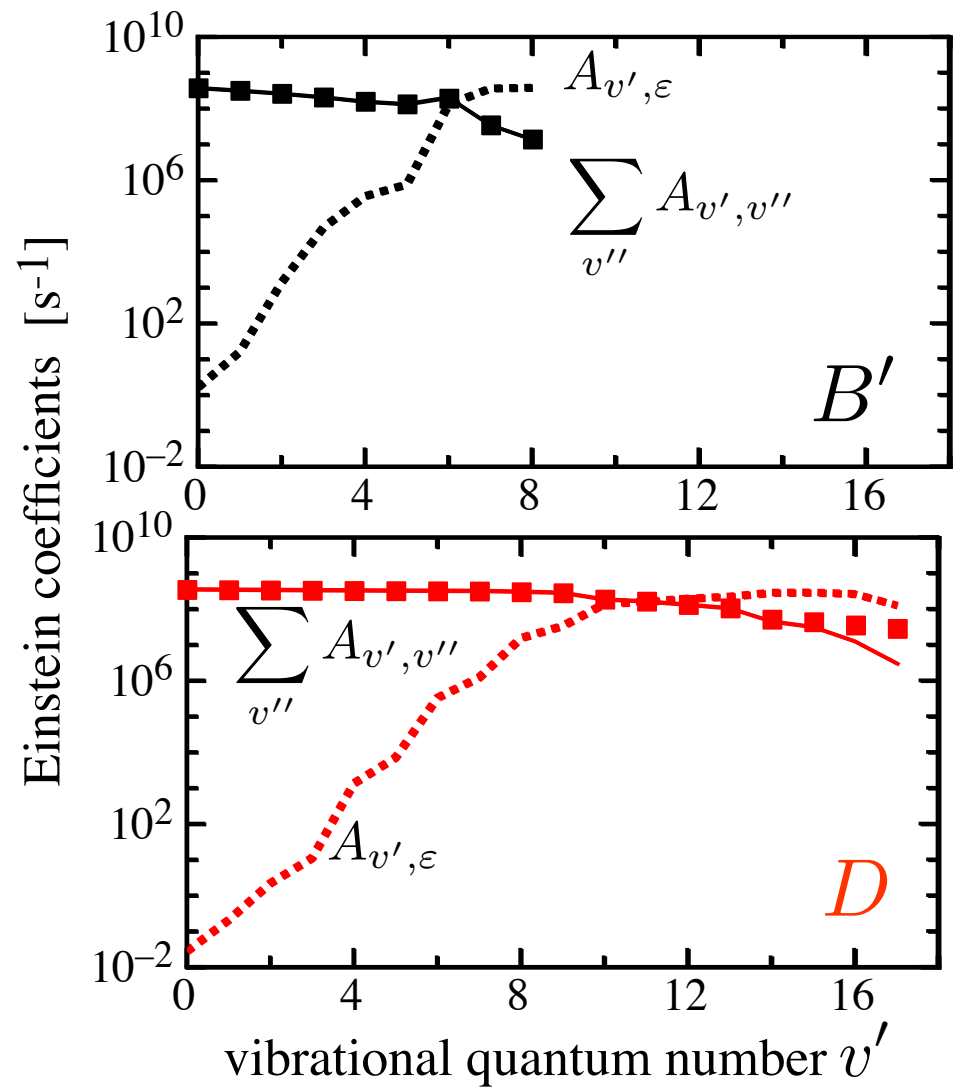
U. Fantz, D. Wünderlich, ADNDT (2006)

✓ state-to-state

✓ radiative processes
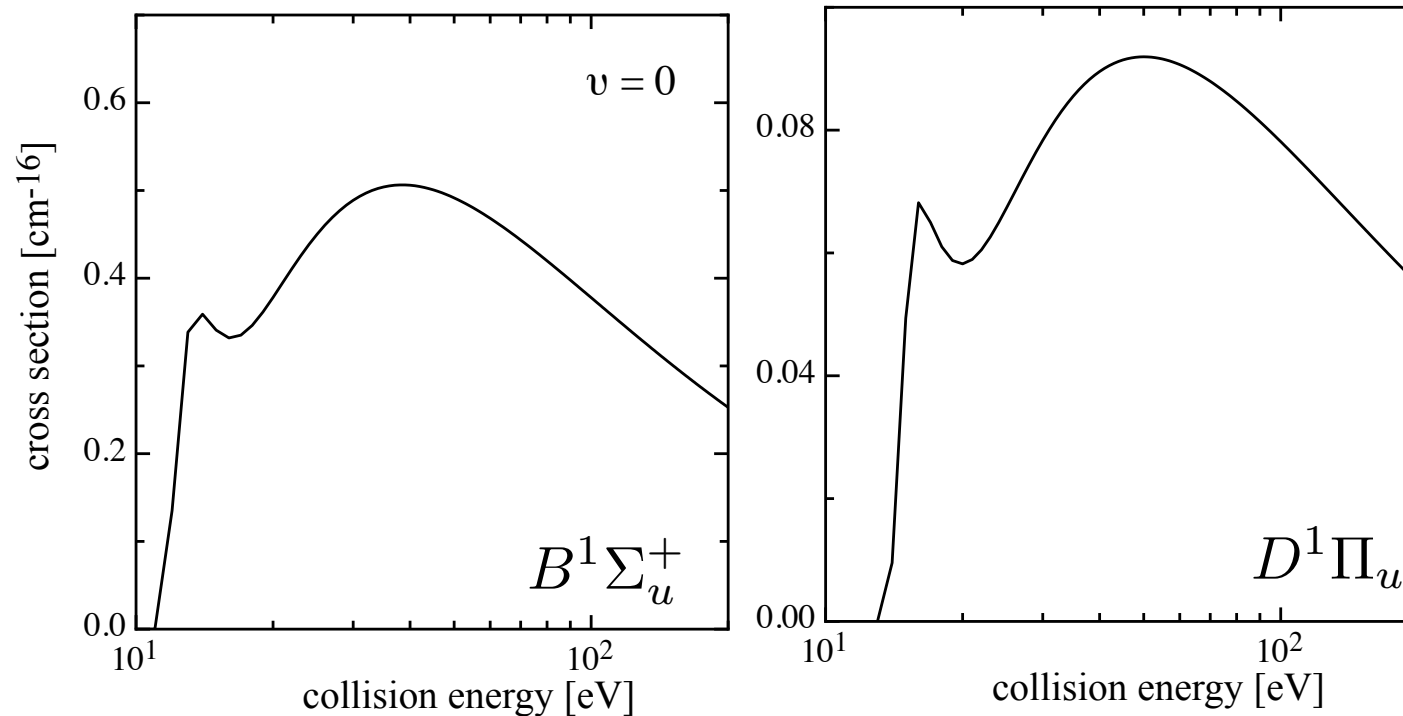
✓ energy profile smoothing

semiclassical IPM
R. Celiberto et al., ADNDT (2001)

✓ state-to-state

✓ radiative processes

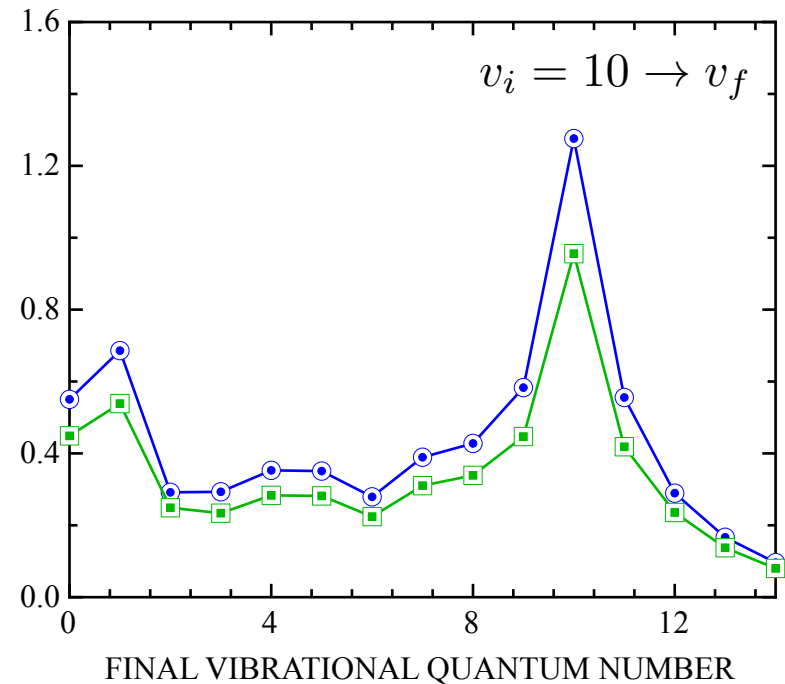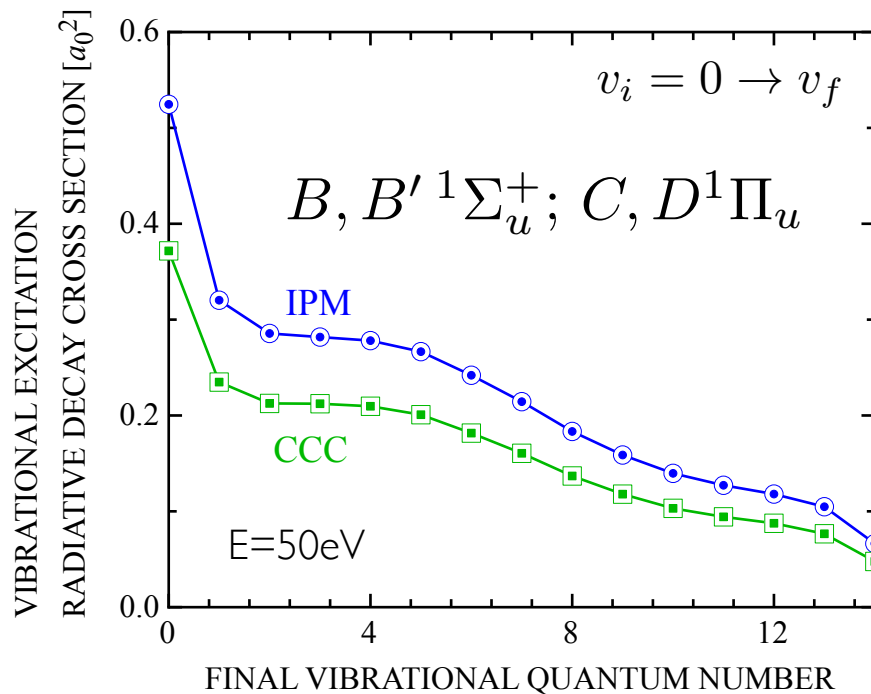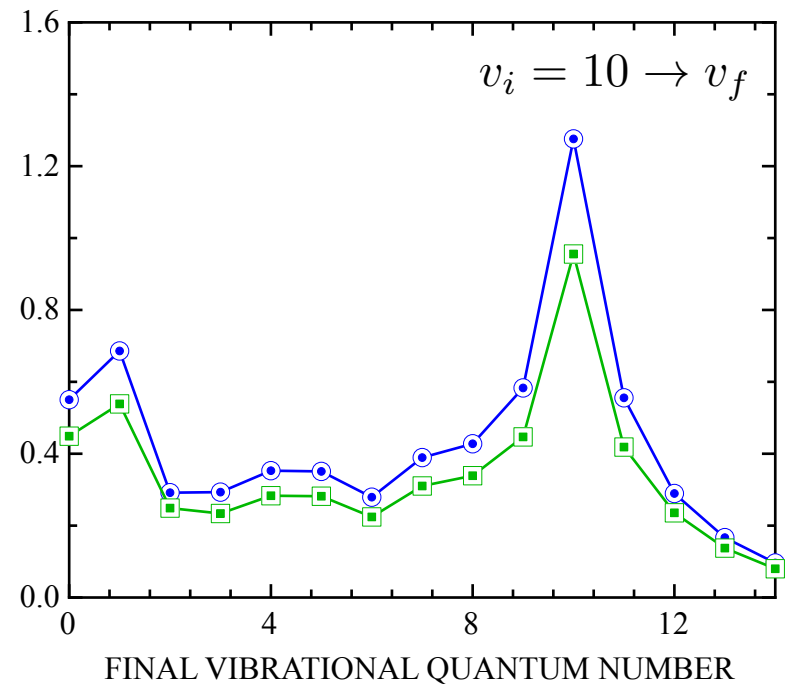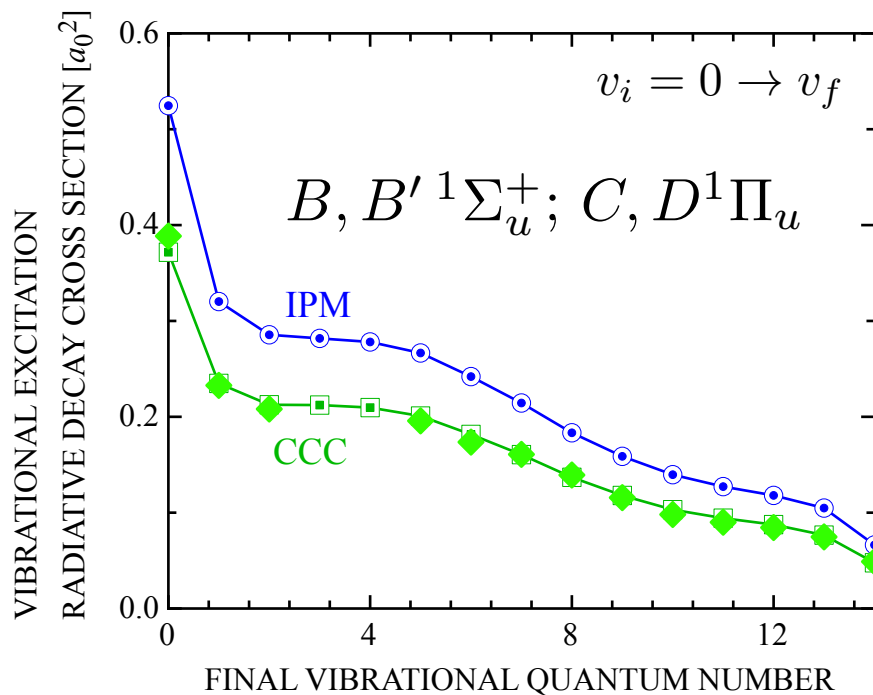✓ energy profile smoothing

$$\sigma(E) = a(\ln{(E/\Delta E)})^{0.6}$$

semiclassical IPM
R. Celiberto et al., ADNDT (2001)

✔ state-to-state

✔ radiative processes

✔ energy profile smoothing

✔ accuracy

semiclassical IPM
R. Celiberto et al, ADNDT (2001)

CCC
L H Scarlett et al, PSST (2019)

$v_i = 0 \to v_f$

$B, B'\,^1\Sigma_u^+;\ C, D^1\Pi_u$

IPM

CCC

E=50eV

$v_i = 10 \to v_f$

VIBRATIONAL EXCITATION RADIATIVE DECAY CROSS SECTION $[a_0^2]$

FINAL VIBRATIONAL QUANTUM NUMBER

FINAL VIBRATIONAL QUANTUM NUMBER

✔ state-to-state

✔ radiative processes

✔ energy profile smoothing

✔ accuracy

semiclassical IPM
R. Celiberto et al, ADNDT (2001)

CCC
L H Scarlett et al, PSST (2019)

Experiments
J. Hiskes, Journal of Applied Physics 70, 3409 (1991)

$v_i = 0 \to v_f$

$B, B'\,^1\Sigma_u^+;\ C, D\,^1\Pi_u$

IPM

CCC

VIBRATIONAL EXCITATION
RADIATIVE DECAY CROSS SECTION $[a_0^2]$

FINAL VIBRATIONAL QUANTUM NUMBER

$v_i = 10 \to v_f$

FINAL VIBRATIONAL QUANTUM NUMBER

A Laricchiuta (CNR ISTP Bari Italy) - Joint IAEA-FZJ Technical Meeting on the
C-R Properties of W and Hydrogen in Edge Plasma of Fusion Devices - VIRTUAL Meeting March 30, 2021

Electron-LiH state-specific CROSS SECTIONS

$$LiH(X^1\Sigma^+, v) + e \rightarrow LiH(A^1\Sigma^+, v'') + e \rightarrow LiH(X^1\Sigma^+, v') + e + h\nu$$

$v=0$

radiative decay
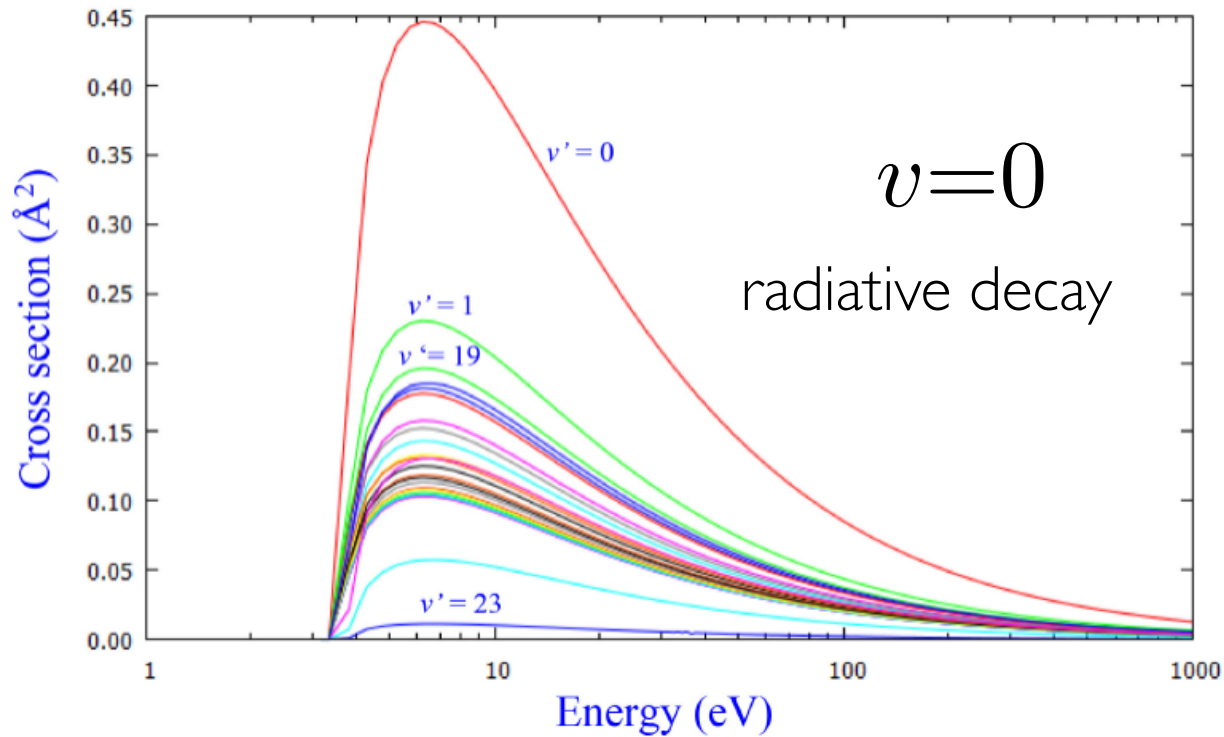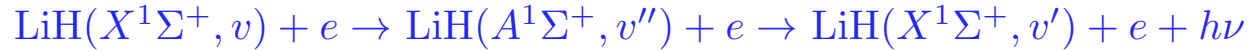
excitation cross section

R. Celiberto, RK Janev, A Laricchiuta PSST(2020)

R. Celiberto SPIG 2020 (VIRTUAL)
International Symposium on the Physics of Ionized Gases
Šabac, Serbia, August 24 – 28, 2020

A Laricchiuta (CNR ISTP Bari Italy) - Joint IAEA-FZJ Technical Meeting on the
C-R Properties of W and Hydrogen in Edge Plasma of Fusion Devices - VIRTUAL Meeting March 30, 2021

GPKIN COMPUTATIONAL TOOL

- In-house C code

- Self-consistent approach

- State-to-state & macroscopic kinetics

- Super-elastic collisions

- Electron-electron collisions

G. Colonna PSST 29 (2020) 065008

GPKIN COMPUTATIONAL TOOL

Termodynamics

K_{eq}

$$k_e = \int_{\varepsilon^\star}^{\infty} f_e(\varepsilon)\sigma_e(\varepsilon)v_e(\varepsilon)d\varepsilon$$

P, T

Rates

EEDF

P, T

Stat-to-State Master Equations

Boltzmann Equation for Electrons

Photon absorption Stimulated Emission

Level Distributions Species Densities

Radiation Transport Equation

Electric & Magnetic Fields

Chemical Energy

Fluid Dynamics

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H₂ plasma in ns RPD

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H₂ plasma in ns RPD

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Fast (ns-pulsed) discharges in hydrogen excited state concentration & singlets vibrational distributions

singlet VDF

$t_{rel} = 0 \div 5$ ns

$t_{rel} = 20$ ns

(f)

level energy (eV)

molar fractions

relative time (ns)

E$_0$/N (Td)

time (ns)

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H$_2$ plasma in ns RPD

Fast (ns-pulsed) discharges in hydrogen excited state concentration & singlets vibrational distributions

$t_{rel} = 0 \div 5$ ns

$t_{rel} = 20$ ns

(f)

$(f - q)$

molar fractions

singlet VDF

relative time (ns)

level energy (eV)

E_0/N (Td)

time (ns)

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H$_2$ plasma in ns RPD

Fast (ns-pulsed) discharges in hydrogen excited state concentration

& hydrogen negative ion
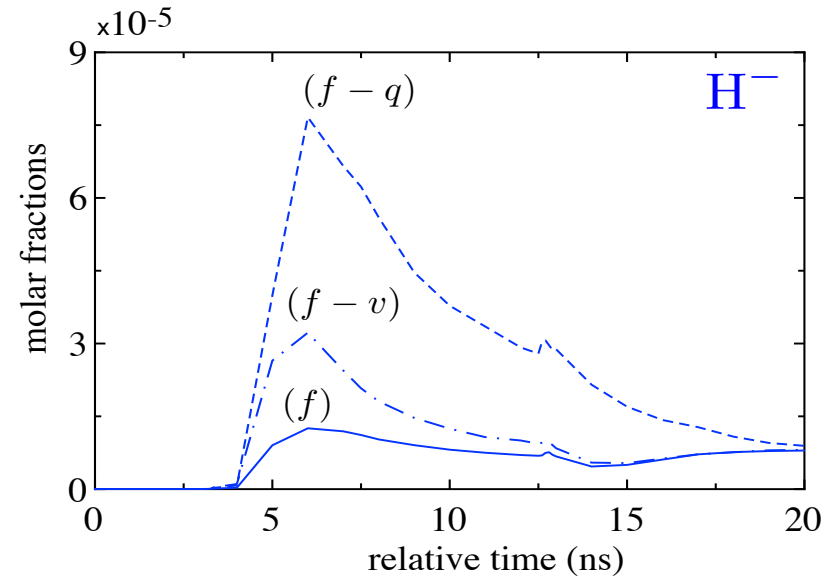
H₂ plasma in ns RPD

on ground state vibrational distributions
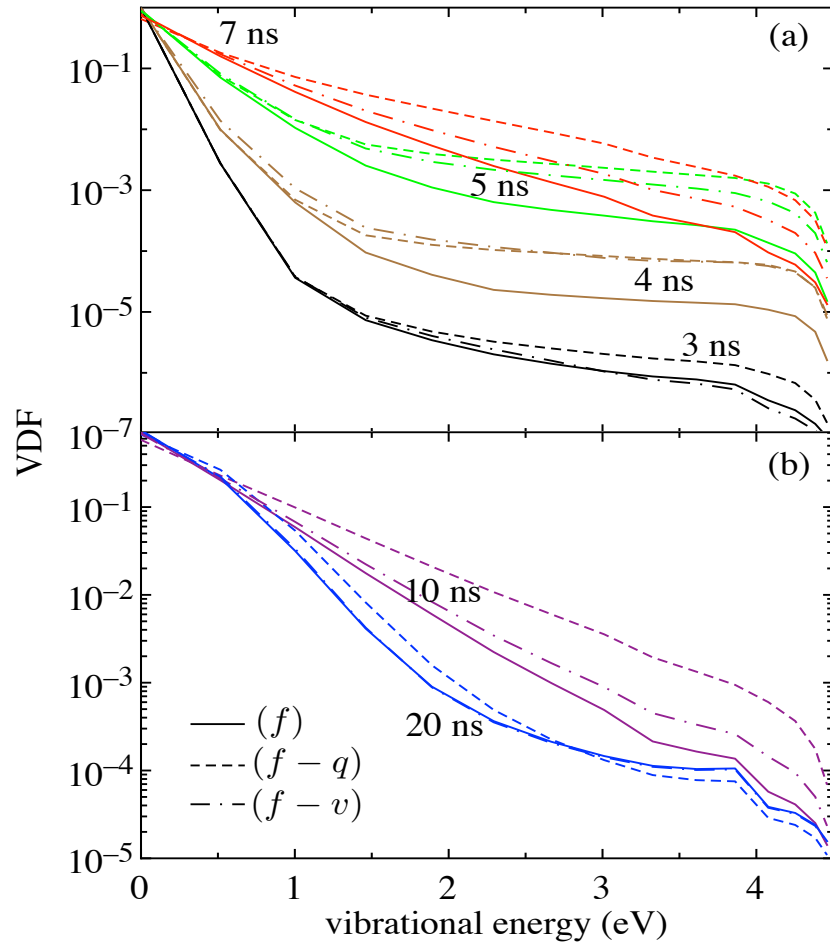
& on electron energy distribution
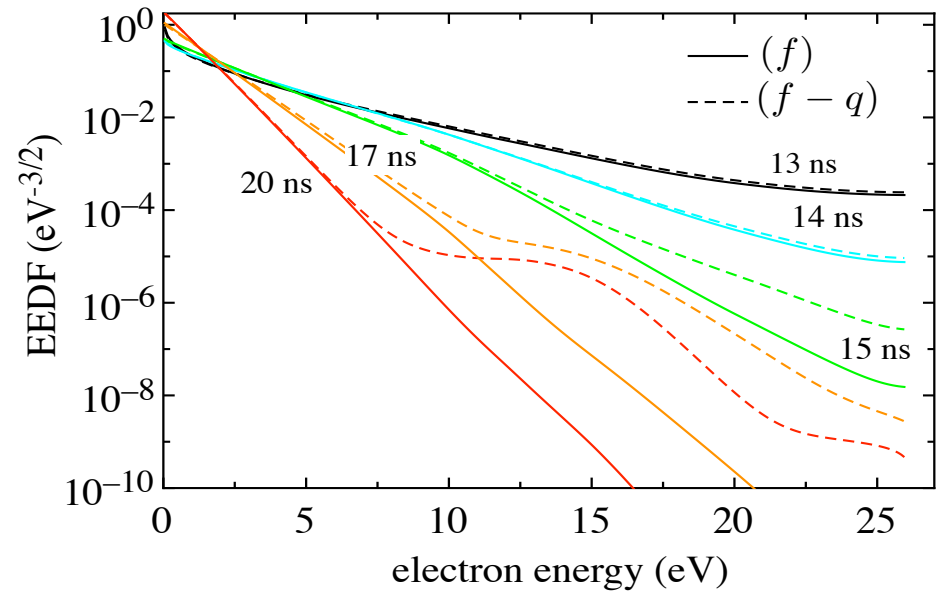
H$_2$-N$_2$ plasma in ns RPD : AMMONIA formation

Chemical species

N_3^+ N_2H NH

N_4^+ N_2H_2 NH_2

NH^+ N_2H_3 NH_3

NH_2^+ N_2H_4

NH_3^+

NH_4^+

Selected processes

$$N_2(\upsilon)/N + H_2(\omega)/H$$

$$N_2^\star + X \to N_2(ground) + X$$

$$H_2^\star + X \to H_2(ground) + X$$

$$N(^4S,^2P,^2D) + H_2(\upsilon) \rightleftharpoons NH + H \quad *$$

Capitelli, M., Ferreira, C. M., Gordiets, B. F., and Osipov, A. I. Plasma kinetics in atmo- spheric gases, vol. 31. Springer, 2013.

Gordiets, B., Ferreira, C., Pinheiro, M., and Ricard, A. Self-consistent kinetic model of low- pressure-flowing discharges: I. volume processes. Plasma Sources Science and Technology 7, 3 (1998), 363.

* Fridman, A. Plasma chemistry. Cambridge university press, 2008.

* Macheret, S., Luo, H., and Alexeenko, A. Non-empirical analytical model of non-equilibrium dissociation in high-temperature air. In Hypersonic Metheoroid Entry Physics, G. Colonna, M. Capitelli, and A. Laricchiuta, Eds. IOP Publishing, 2019, ch. 17.

H_2-N_2 plasma in ns RPD : AMMONIA formation
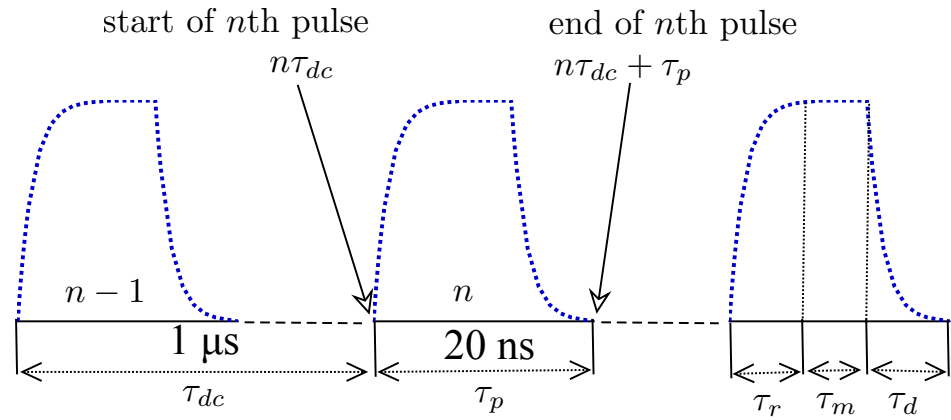
$$\frac{E_{max}}{N} = 100\ Td$$

5 pulses
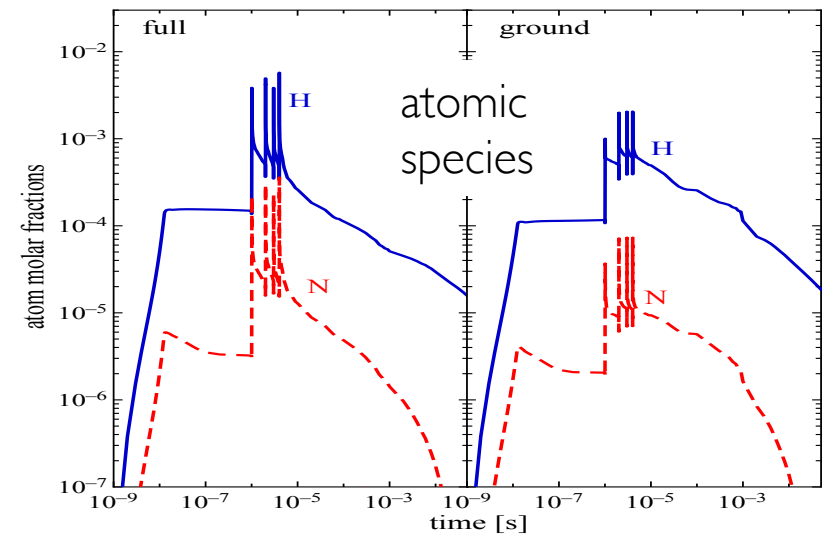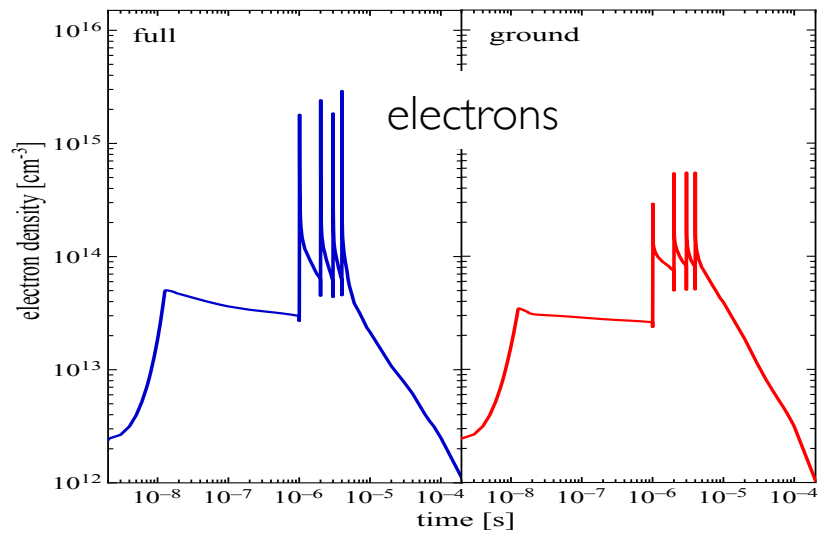
G Colonna, A. Laricchiuta, LD Pietanza,
Plasma Physics and Controlled Fusion (2020)

ground state model

H₂-N₂ plasma in ns RPD : AMMONIA formation

full model
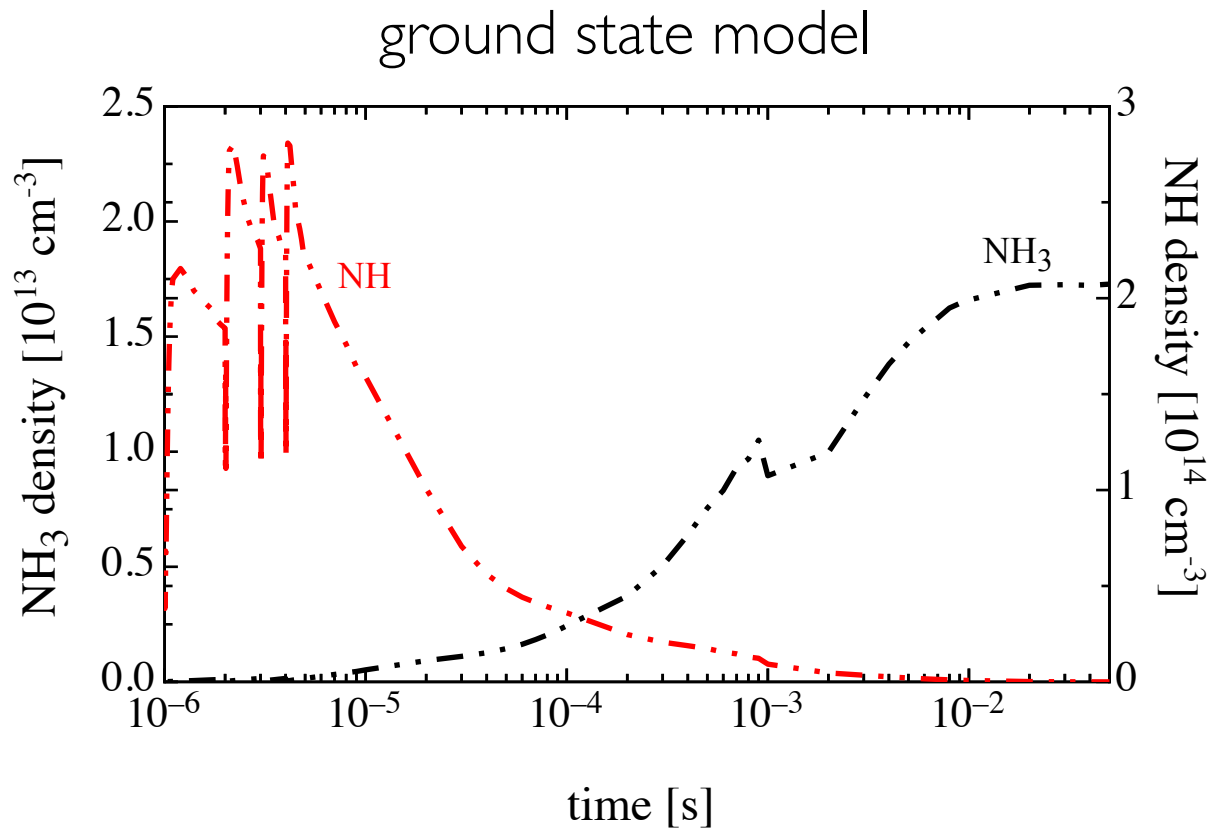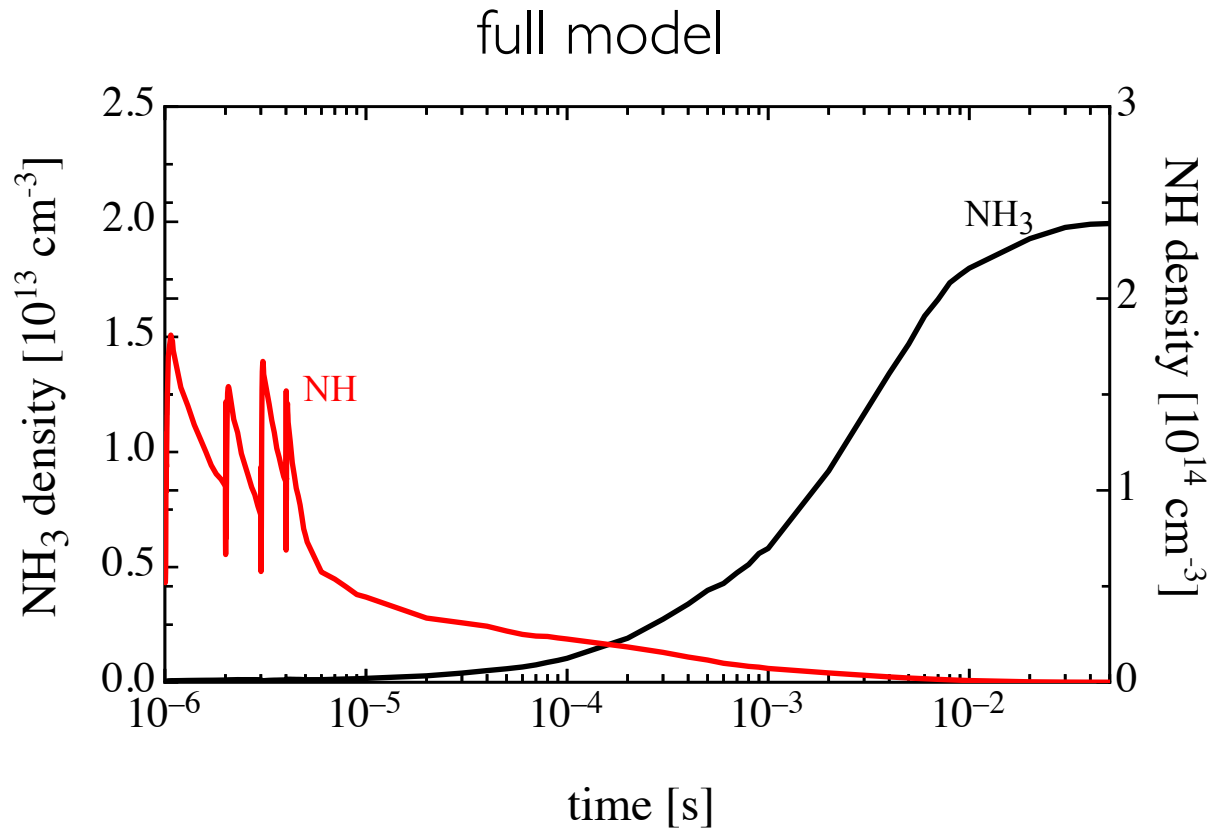
G Colonna, A. Laricchiuta, LD Pietanza,
Plasma Physics and Controlled Fusion (2020)

H$_2$-He plasma : entry conditions in giant planets

$P_0 = 0.2$ torr
$T_0 = 300$ K
$u_0 = 27$ km/s

B. A. Cruden,
Hydrogen-Helium shock Radiation tests for Saturn Entry Probes, 7th
International Workshop on Radiation of High Temperature Gases in
Atmospheric Entry
21-25 Nov. 2016; Stuttgart; Germany
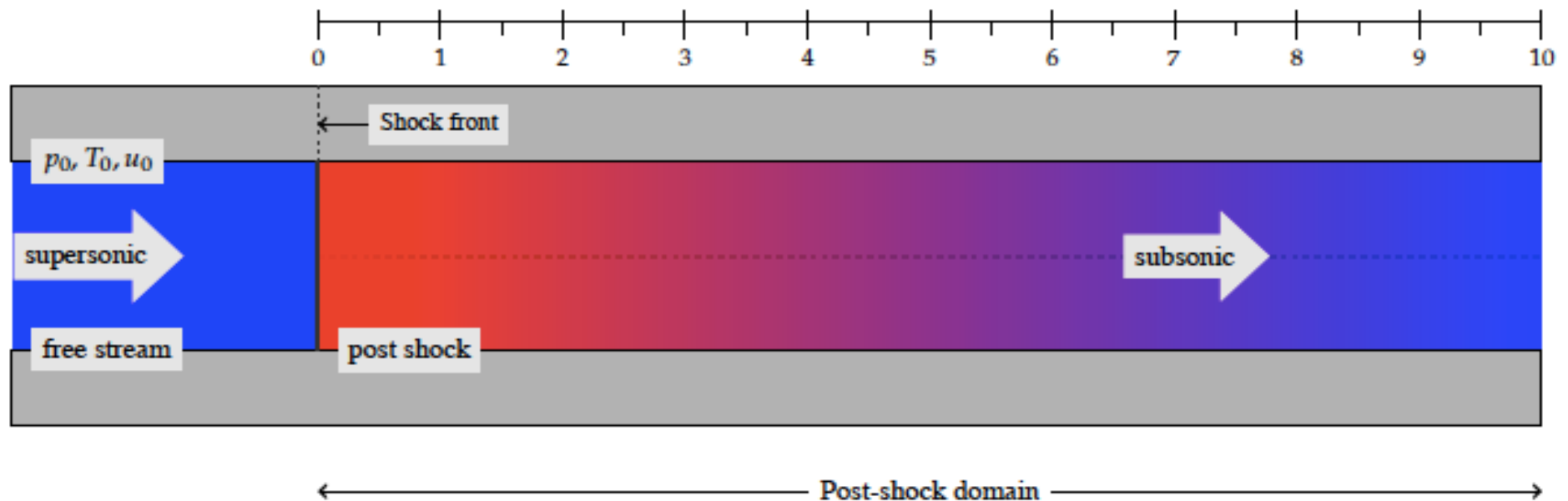
Shock front

p_0, T_0, u_0

supersonic

subsonic

free stream

post shock

Post-shock domain

$$H_2\text{-He plasma : entry conditions in giant planets}$$
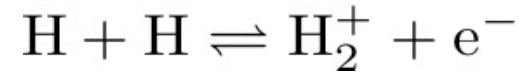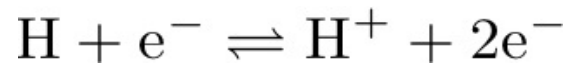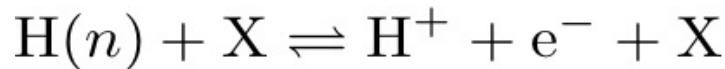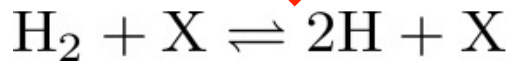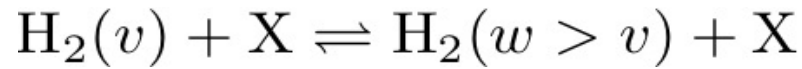
$$H_2(v) + X \rightleftharpoons H_2(w > v) + X$$

$$H_2 + X \rightleftharpoons 2H + X$$

Thermal ionization

$$H(n) + X \rightleftharpoons H(n' > n) + X$$

$$H(n) + X \rightleftharpoons H^+ + e^- + X$$

$$H(n) + e^- \rightleftharpoons H(n' > n) + e^-$$

$$H + e^- \rightleftharpoons H^+ + 2e^-$$

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H$_2$-He plasma : entry conditions in giant planets

$$H_2(v) + X \rightleftharpoons H_2(w > v) + X$$

$$H_2 + X \rightleftharpoons 2H + X$$

Thermal ionization

Chemi-ionization

$$H(n) + X \rightleftharpoons H(n' > n) + X$$
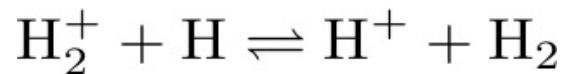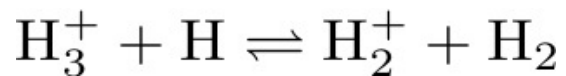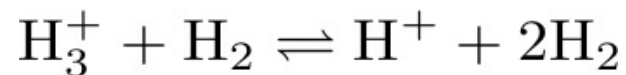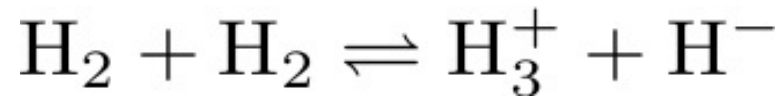
$$H + H \rightleftharpoons H_2^+ + e^-$$

$$H(n) + X \rightleftharpoons H^+ + e^- + X$$

$$H(n) + e^- \rightleftharpoons H(n' > n) + e^-$$

$$H + e^- \rightleftharpoons H^+ + 2e^-$$

$$H_2 + H_2 \rightleftharpoons H_3^+ + H^-$$

$$H_3^+ + H_2 \rightleftharpoons H^+ + 2H_2$$

$$H_3^+ + H \rightleftharpoons H_2^+ + H_2$$

$$H_2^+ + H \rightleftharpoons H^+ + H_2$$

$$H^+ \quad e^-$$

$$H_2 + H_2 \rightleftharpoons H_3^+ + H^-$$

$$H_3^+ + H_2 \rightleftharpoons H^+ + 2H_2 \qquad\qquad H^- + X \rightleftharpoons H + e^- + X$$

$$H_3^+ + H \rightleftharpoons H_2^+ + H_2 \qquad\qquad H^- + H \rightleftharpoons H_2 + e^-$$

$$H_2^+ + H \rightleftharpoons H^+ + H_2 \qquad\qquad H^- + H^+ \rightleftharpoons H^\star + H(n = 1)$$

$$H^+ \qquad e^-$$

H_2-He plasma : entry conditions in giant planets

G Colonna, LD Pietanza, A Laricchiuta
International Journal of Heat and Mass Transfer (2020)

H₂-He plasma : entry conditions in giant planets
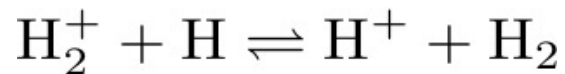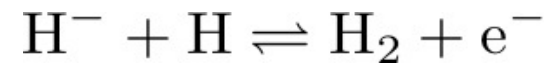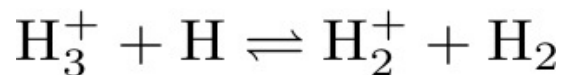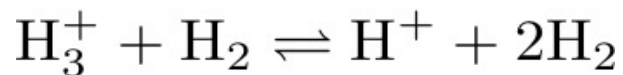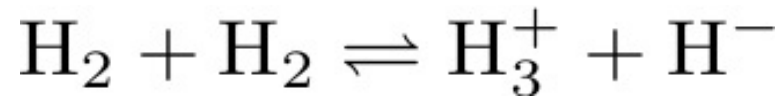
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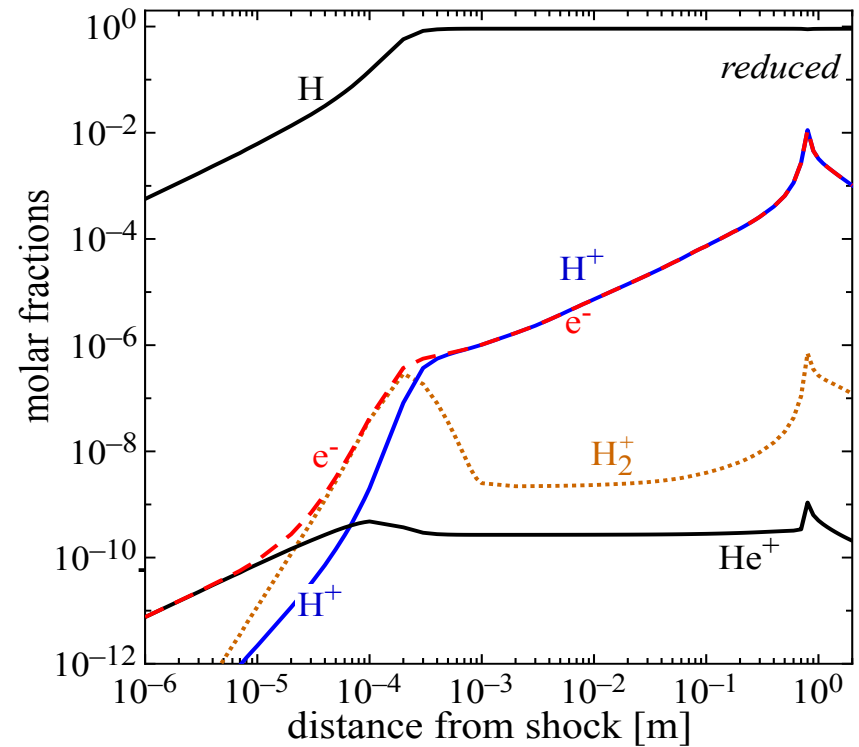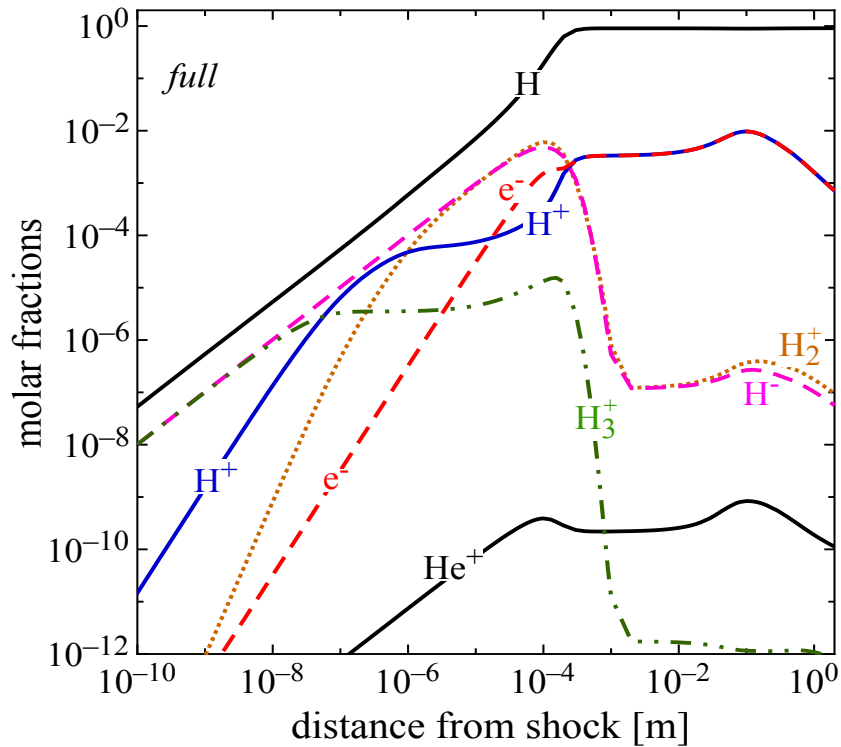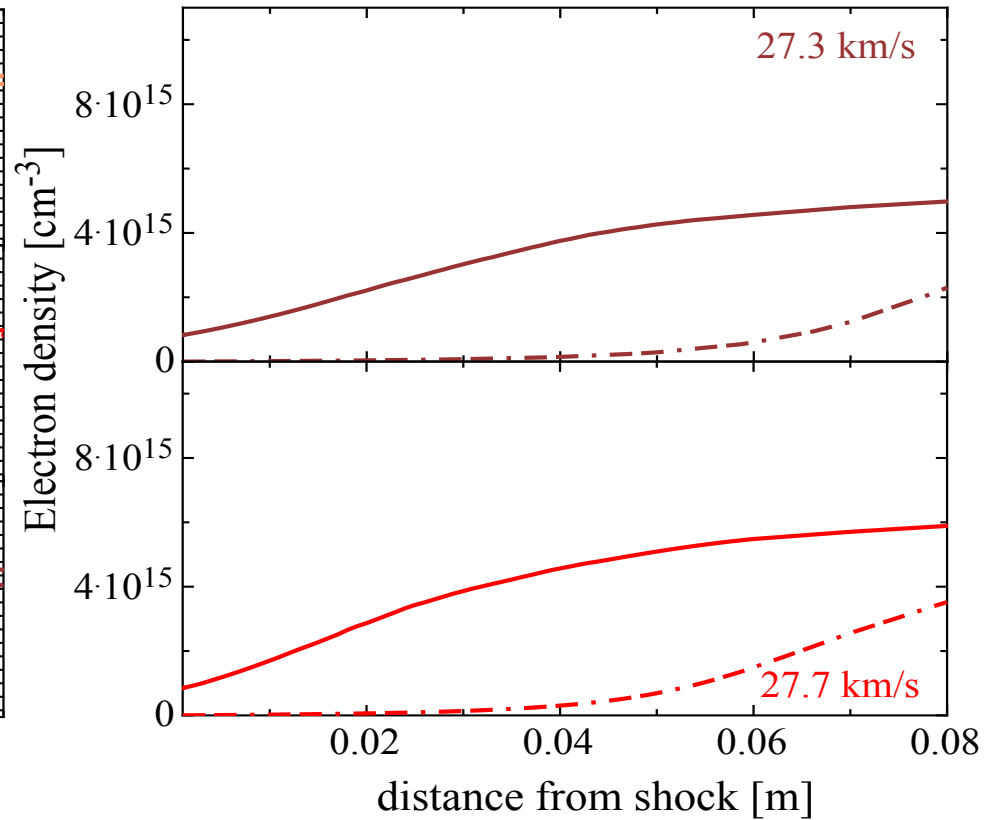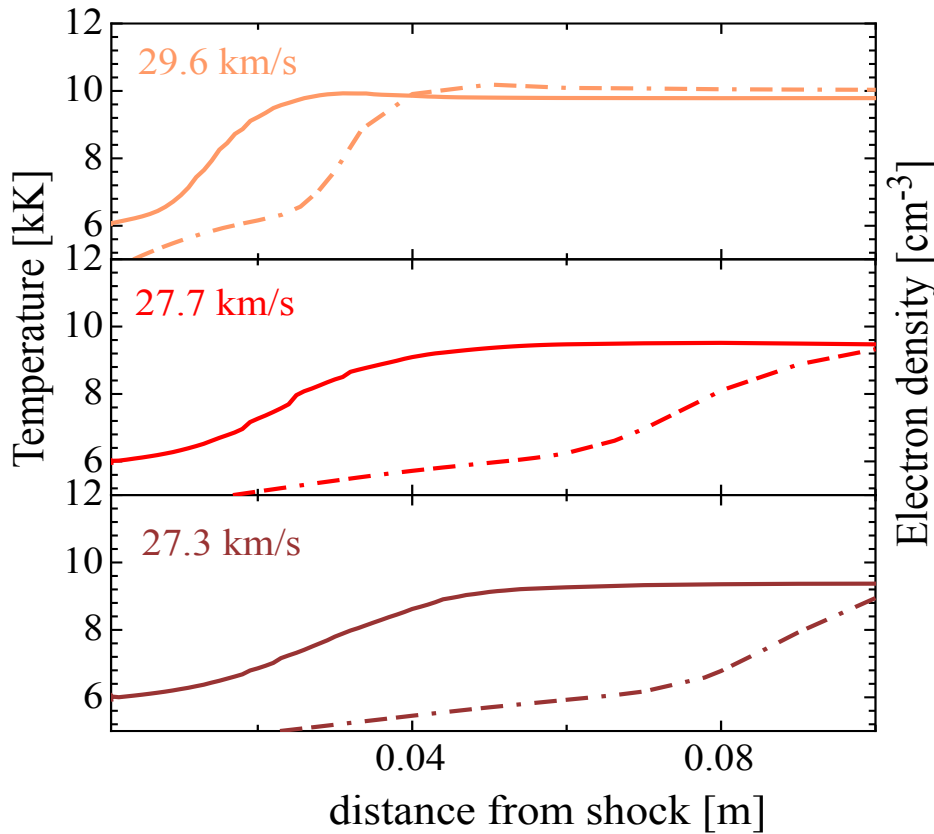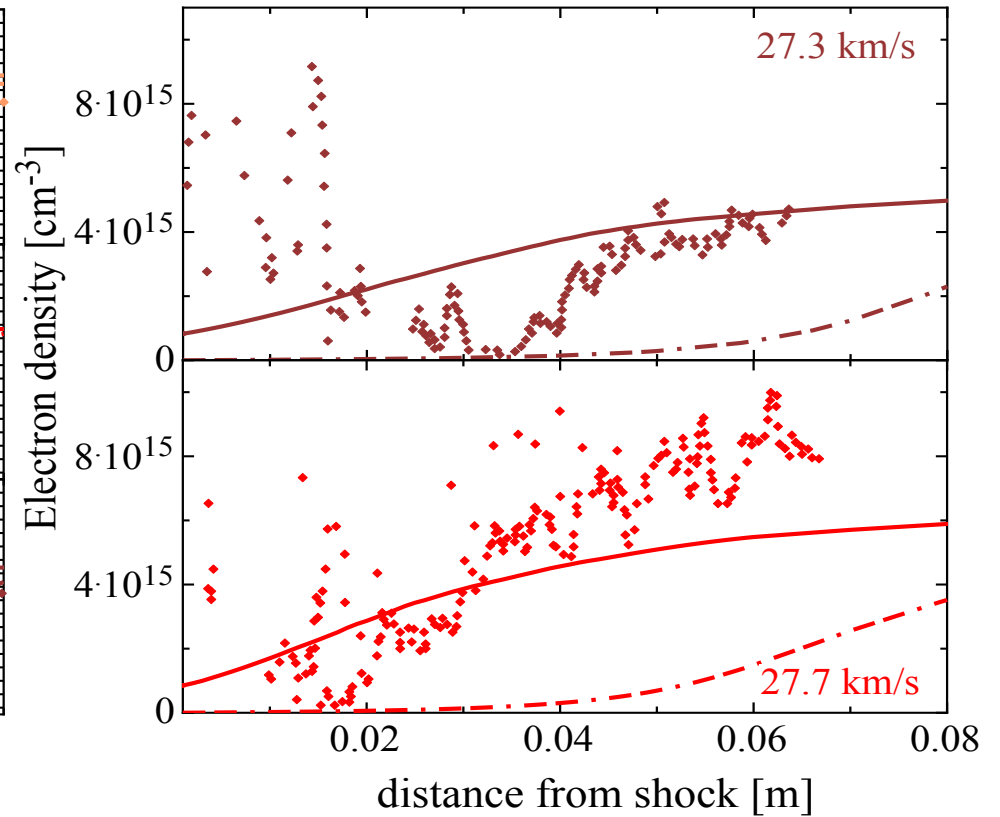
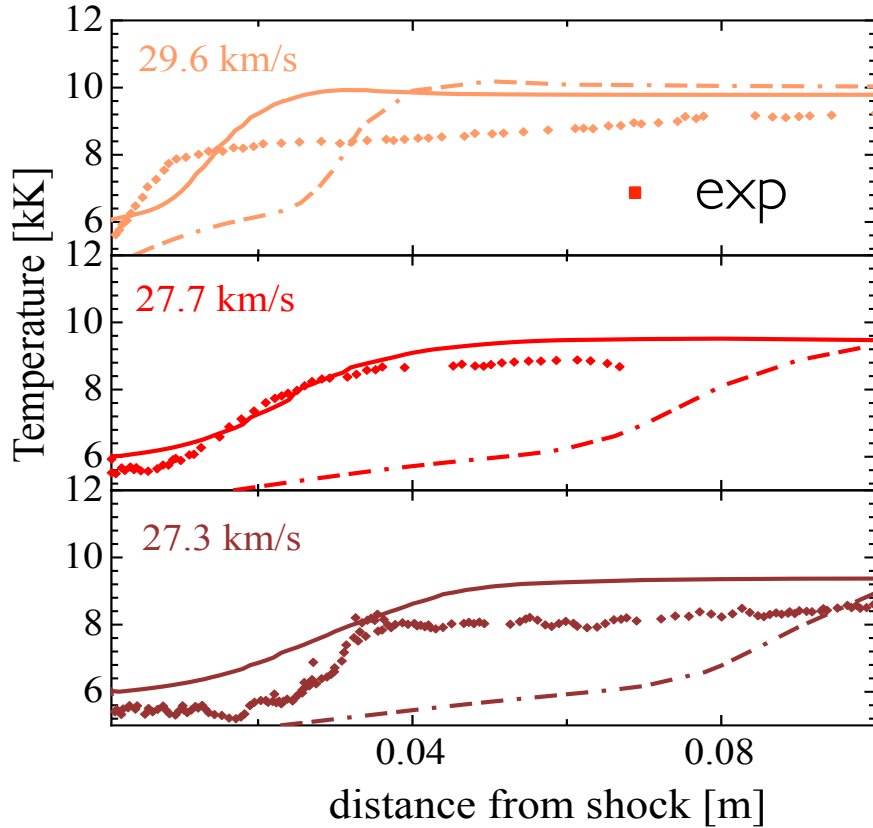H2-He plasma : entry conditions in giant planets

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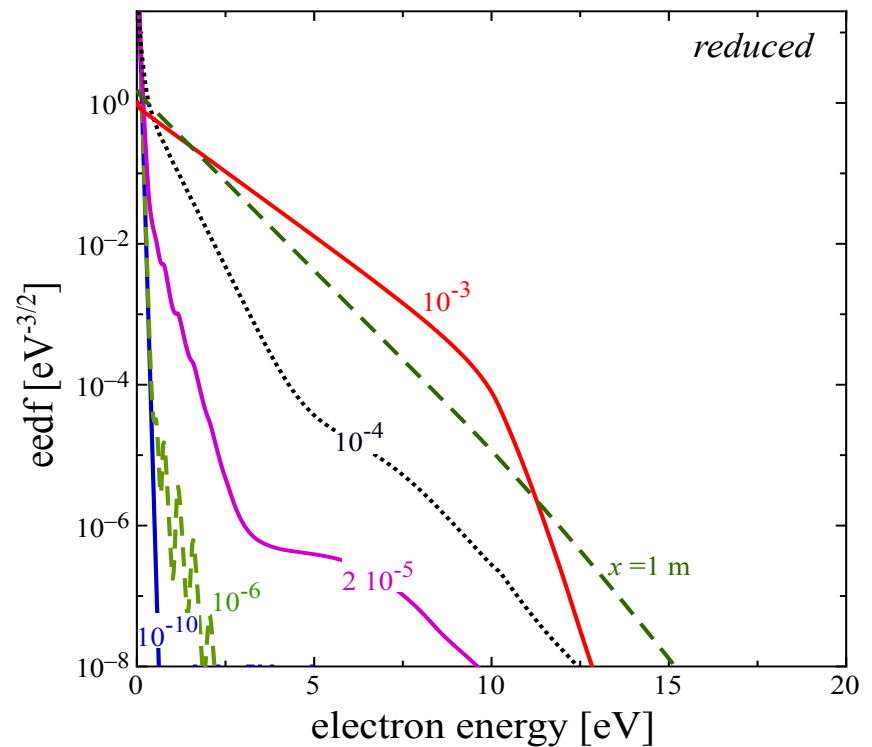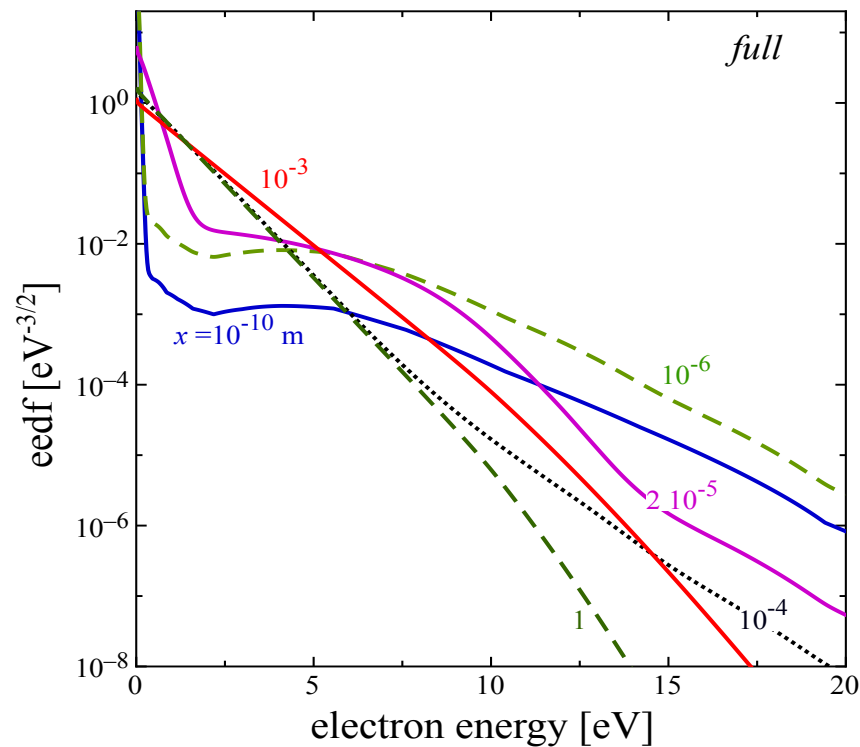
H$_2$-He plasma : entry conditions in giant planets

electron temperature
from Balmer-α lines

P$_0$=0.5 torr
thick plasma model

full
reduced

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ICAMDATA 2022
12th International Conference on Atomic and Molecular Data and Their Applications
Bari•Italy   September 2022

Considered the exceptional circumstances of the present time and the uncertainty that will characterize the next months due to the COVID-19 pandemic the International Program Committee and the Local Organizing Committee have made the decision to **further postpone the 12th International Conference on Atomic and Molecular Data and Their Applications (ICAMDATA) in Bari (Italy) to September 2022.**