A parametric Boltzmann equation analysis of CO_2 dissociation in cold plasmas and afterglows.

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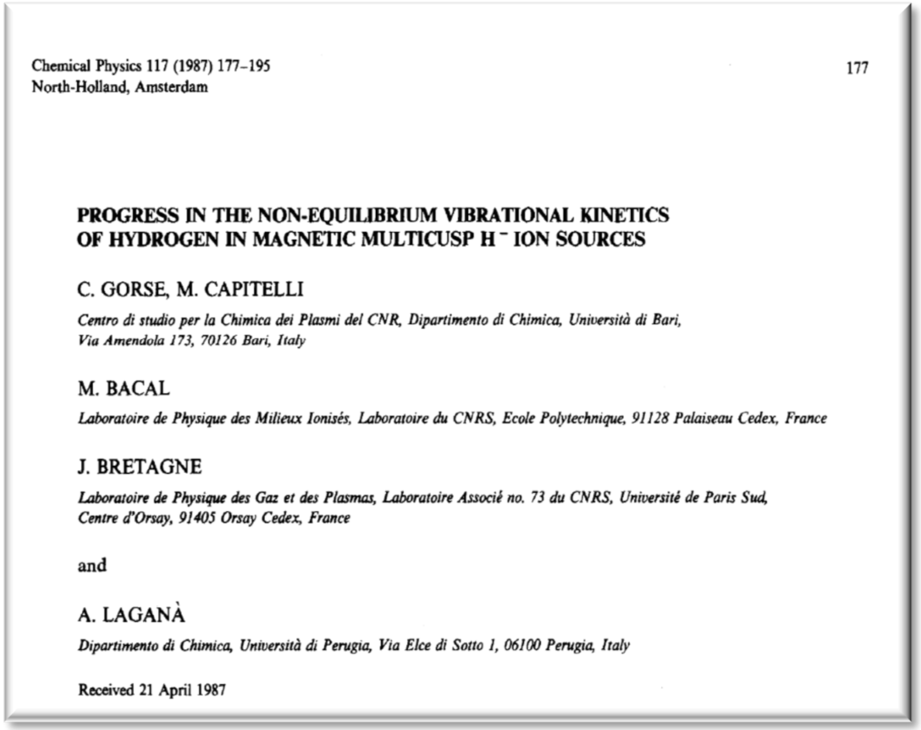

Chemical Physics 117 (1987) 177–195
North-Holland, Amsterdam
177

PROGRESS IN THE NON-EQUILIBRIUM VIBRATIONAL KINETICS OF HYDROGEN IN MAGNETIC MULTICUSP H^- ION SOURCES

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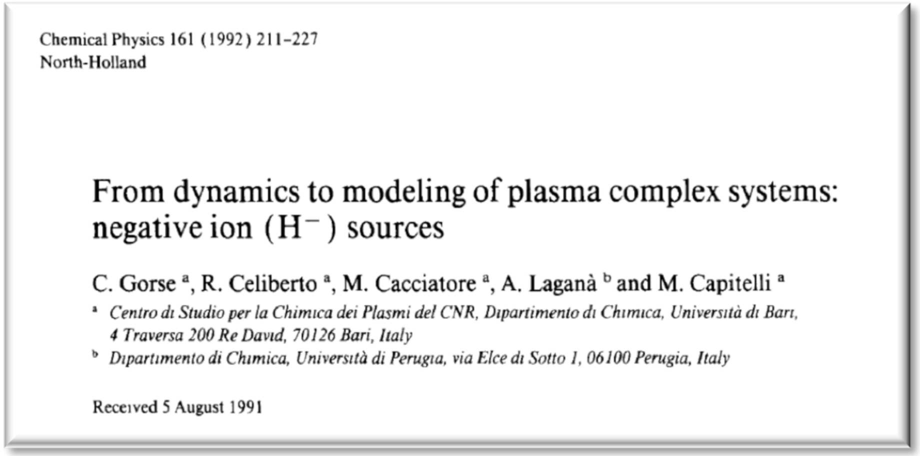

Chemical Physics 161 (1992) 211–227
North-Holland

From dynamics to modeling of plasma complex systems: negative ion (H^-) sources

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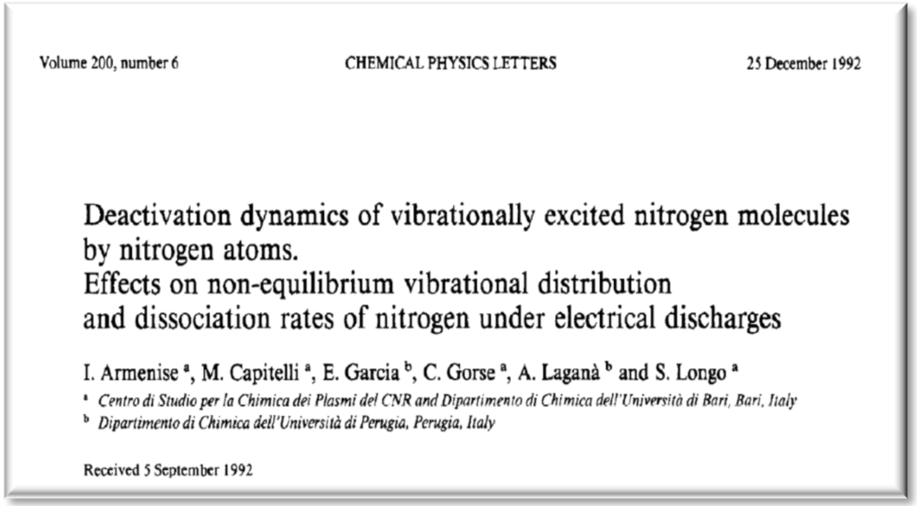

Volume 200, number 6 CHEMICAL PHYSICS LETTERS 25 December 1992

Deactivation dynamics of vibrationally excited nitrogen molecules by nitrogen atoms.
Effects on non-equilibrium vibrational distribution and dissociation rates of nitrogen under electrical discharges

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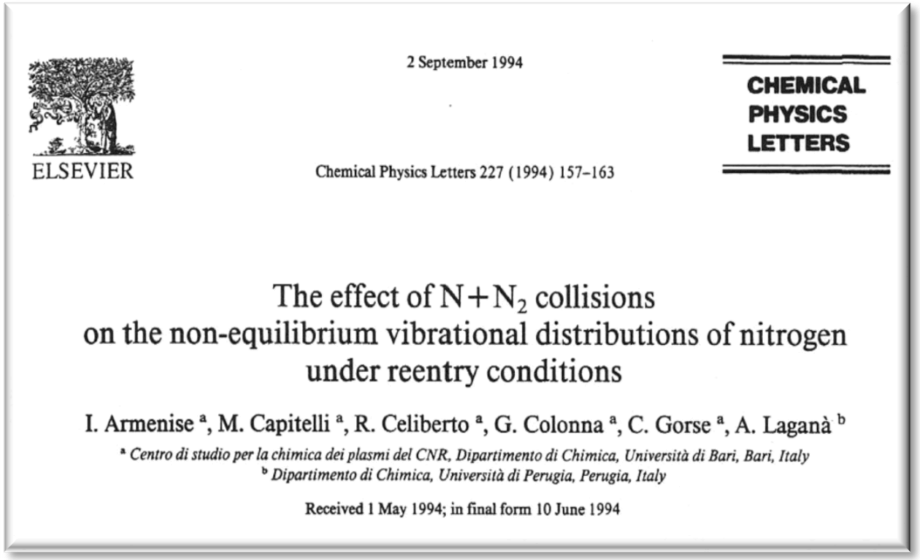

ELSEVIER
2 September 1994
CHEMICAL PHYSICS LETTERS
Chemical Physics Letters 227 (1994) 157–163

The effect of $N+N_2$ collisions on the non-equilibrium vibrational distributions of nitrogen under reentry conditions

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Outline

- Main idea: role of CO_2 vibrational excitation in dissociation
- Dissociation by Pure Vibrational Mechanisms (PVM)
- Dissociation by Direct Electron Impact (DEI)
- Electron Boltzmann equation
- Continuous Discharges
- Post-discharge conditions
- Conclusions

Main idea:

Increase the dissociation of CO_2 by using the vibrational energy introduced by electron molecule collisions followed by vibrational climbing up to the dissociation limit.

The necessary power is that one to excite the vibrational levels of the CO_2 molecule much lower than that one requested for thermal dissociation of CO_2 as well as for electron impact dissociation.

A. Fridman et al. (1977)[1,2]
E. Molinari et al. (1976)[3,4]

A. Bogaerts et al. (2014)[5,6]
T. Silva et al. (2014)[7]
R. Van de Sanden et al. (2014)[8]

[1] A. Fridman, *Plasma Chemistry*, Cambrigde University Press, New York (2008)
[2] V. A. Legasov, V. K. Givotov, E. G. Krashennikov, V. D. Rusanov, A. Fridman, *Sov. Phys. Doklady* **238**, 66 (1977)
[3] P. Capezzuto, F. Cramarossa, R. D'Agostino and E. Molinari, *J. Phys. Chem*. 80, 882 (1976)
[4] M. Capitelli and E. Molinari, *Topics in Current Chemistry* **90**, 59 (1980)
[5] T. Kozak and A. Bogaerts, *Plasma Sources Sci. and Technol.* **23**, 045004 (2014)
[6] T. Kozak and A. Bogaerts, *Plasma Sources Sci. and Technol.* **24**, 015024 (2015)
[7] T. Silva, N. Britun, T. Godfroid and R. Snyders., *Plasma Sources Sci. and Technol.* **23**, 025009 (2014)
[8] A. Goede et al., XARMAE Workshop, Barcelona (2014)

Dissociation by Pure Vibrational Mechanism (PVM)

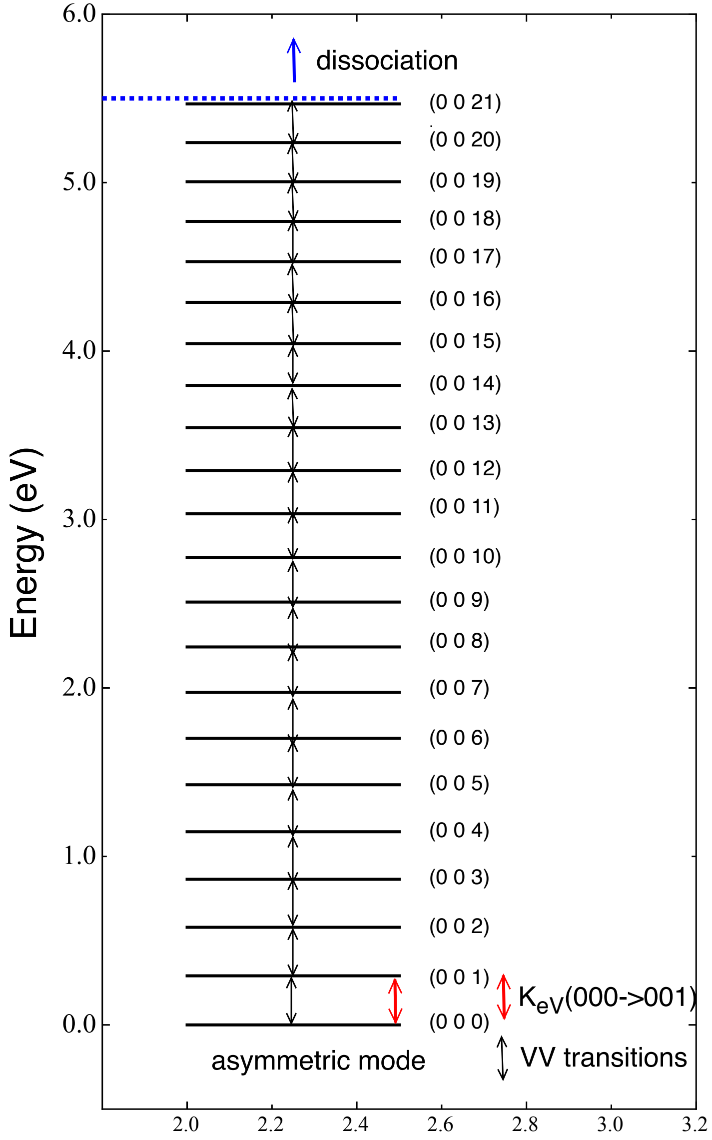
- **eV** (**electron vibration**) energy exchange processes;
- **VV** (**vibration vibration**) and **VT** (**vibrational translation**) energy exchange processes;
- **Dissociation** linking the last vibrational level and the continuum.

PVM Upper Limit dissociation rates

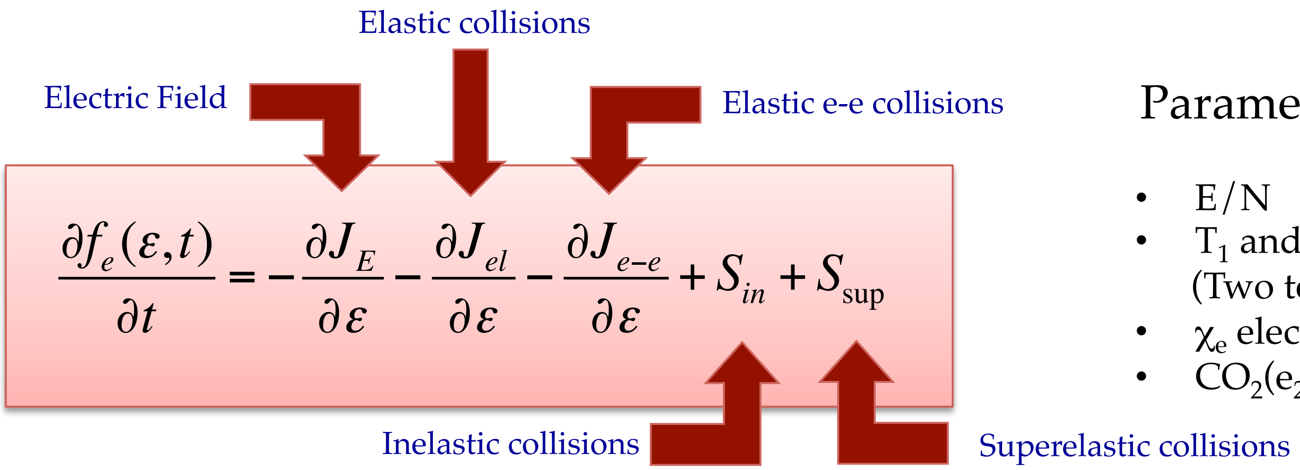
$$K_d^{(ulPVM)} = \frac{1}{v_{\max}} k_{eV}\left(000 \rightarrow 001\right)$$

including the effect of excited vibrational levels

$$K_d^{(ulPVM)}\left(all\right) = \frac{1}{v_{\max}} \sum_n \frac{\varepsilon_{v_n}}{\varepsilon_{v_8}} k_{eV}(v_0 \rightarrow v_n)$$



Electron Boltzmann Equation (BE)



Elastic collisions

Electric Field

Elastic e-e collisions

$$\frac{\partial f_e(\varepsilon,t)}{\partial t} = -\frac{\partial J_E}{\partial \varepsilon} - \frac{\partial J_{el}}{\partial \varepsilon} - \frac{\partial J_{e-e}}{\partial \varepsilon} + S_{in} + S_{\sup}$$

Inelastic collisions

Superelastic collisions

Parametric solution of the BE

- E/N
- T_1 and T_2 vibrational temperatures (Two temperature Boltzmann distrib.)
- χ_e electron molar fraction
- $CO_2(e_2)$ electr. excited state population

Phelphs database

$CO_2(v_0)$	(000)	0.00
$CO_2(v_1)$	(010)	0.083
$CO_2(v_2)$	(020)+(100)	0.167
$CO_2(v_3)$	(030)+(110)	0.252
$CO_2(v_4)$	(0n0)+(n00)	0.339
$CO_2(v_5)$	(0n0)+(n00)	0.442
$CO_2(v_6)$	(0n0)+(n00)	0.505
$CO_2(v_7)$	(0n0)+(n00)	2.5
$CO_2(v_8)$	(001)	0.291
$CO_2(e_1)$		7.0
$CO_2(e_2)$		10.5
CO_2^+		13.3

Vibrational Excitation/De-excitation

$$e^- + CO_2(v_0) \leftrightarrow e^- + CO_2(v_i) \quad \text{with} \quad 1 \le i \le 8$$

Electronic Excitation/De-excitation (10.5 eV)

$$e^- + CO_2(v_0) \leftrightarrow e^- + CO_2(e_2)$$

Dissociative Excitation (7.0 eV)

$$e^- + CO_2(v_0) \rightarrow e^- + CO + O$$

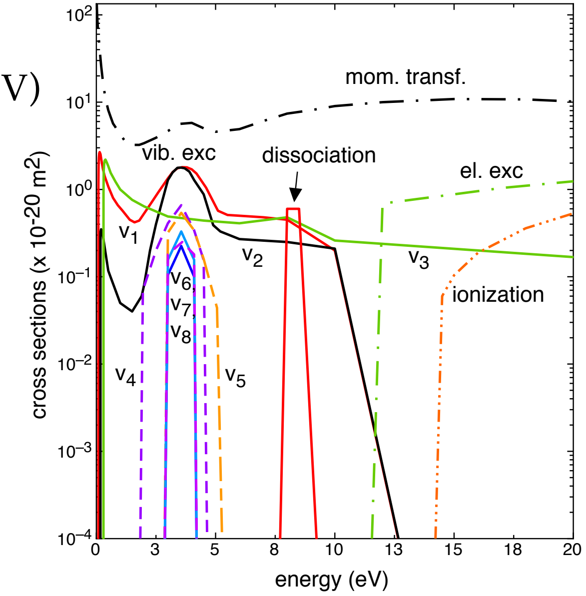
Ionization

$$e^- + CO_2(v_0) \rightarrow e^- + e^- + CO_2^+$$

Momentum transfer

$$e^- + CO_2 \leftrightarrow e^- + CO_2$$

E-impact cross sections



* A. V. Phelphs Database: http://www.lxcat.laplace.univ-tlse.fr

Direct electron impact dissociation

$$k_d(000) = \int_{E_{thr}} f(\varepsilon)\sigma(\varepsilon)v(\varepsilon)d\varepsilon$$

Including the effect of excited vibrational levels

Assumptions

- Shift of cross section thresholds (-> $\exp(1/T_e)$)
- Boltzmann population for the excited states at T_v

$$K_d(all) = \sum_{v}^{v_{\max}} \exp\left[\frac{\varepsilon_{00v}}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right] k_d(000)$$

For $T_e = T_v$ $\quad K_d(all) = v_{\max} k_d(000)$

CO_2 Continuous Discharge: **Stationary EEDF**

E/N=15-30-50-80 Td

T_1 symmetric, bending levels

T_2 first asymmetric level (001), $CO_2(e_2)$

no e-e

Cold case

$$T_1 = 0, T_2 = 0$$

inelastic collisions

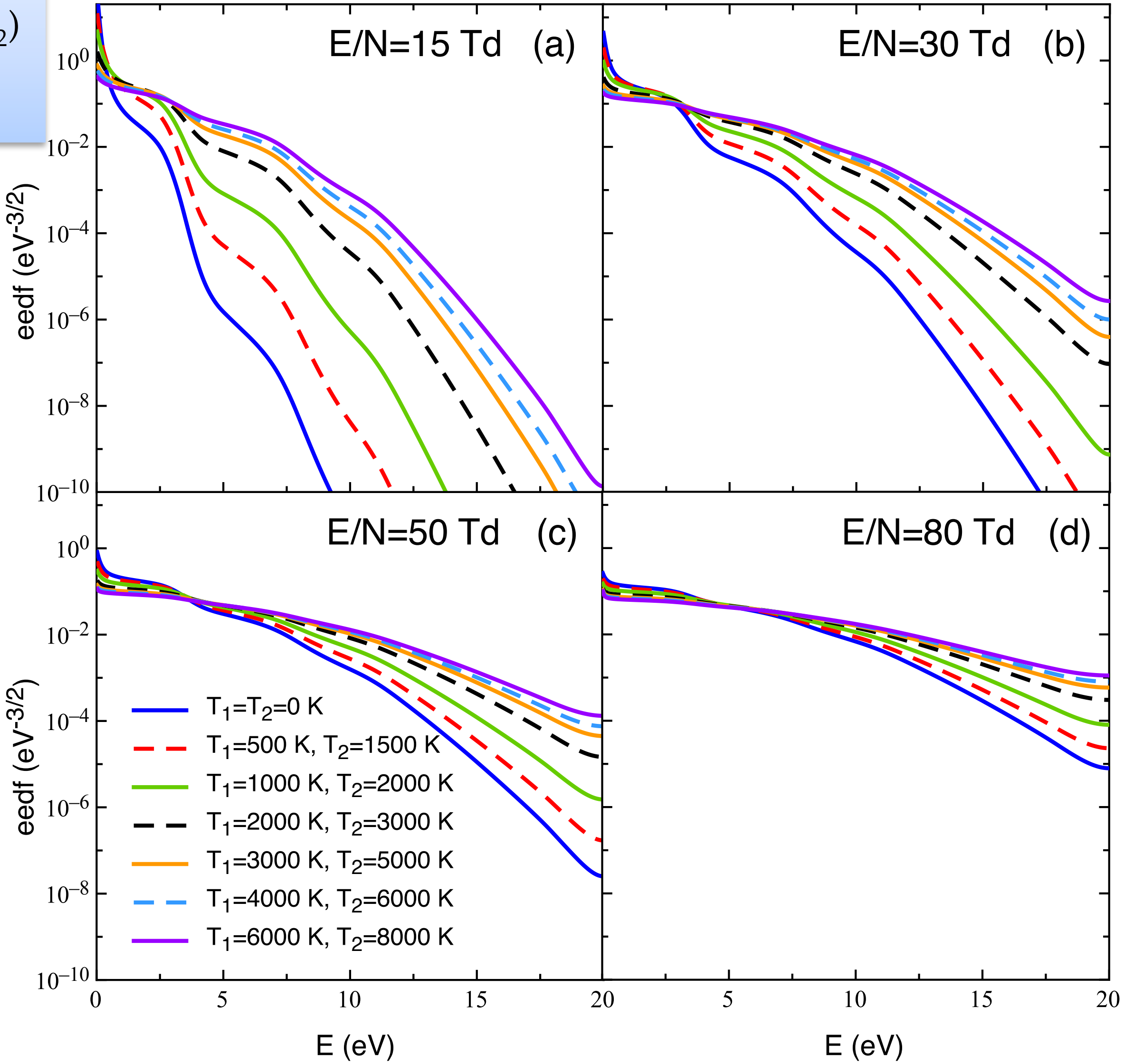
$$e^-(\varepsilon) + CO_2(v_0) \rightarrow e^-(\varepsilon - E_{thr}) + CO_2(v_i)$$

$$T_1 \neq 0, T_2 \neq 0$$

superelastic vibr. and electr. collisions

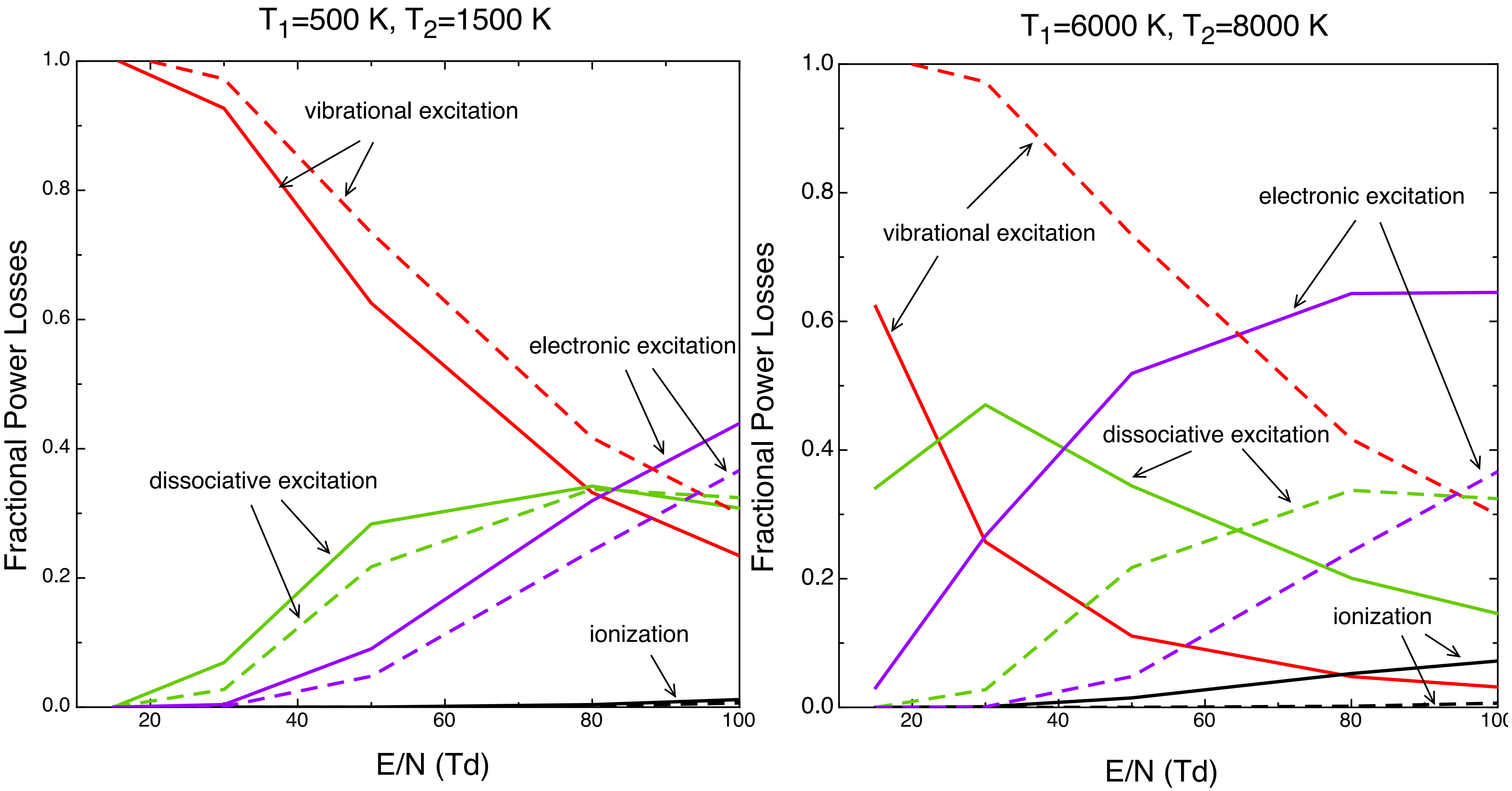
$$e^-(\varepsilon) + CO_2(v_i) \rightarrow e^-(\varepsilon + E_{thr}) + CO_2(v_0)$$

Electron Energy Distribution Function (eedf)



CO_2 Continuous Discharge: **Fractional Power Losses**

Cold gas approximation (dashed lines)
with (full lines) and without (dashed lines) **superelastic collisions**



CO_2 Continuous Discharge: **Dissociation Rates**

Direct electron impact

$$k_d(000) = \int_{E_{thr}} f(\varepsilon)\sigma(\varepsilon)v(\varepsilon)d\varepsilon$$

$$K_d(all) = \sum_{v}^{v_{\max}} \exp\left[\frac{\varepsilon_{00v}}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right] k_d(000)$$

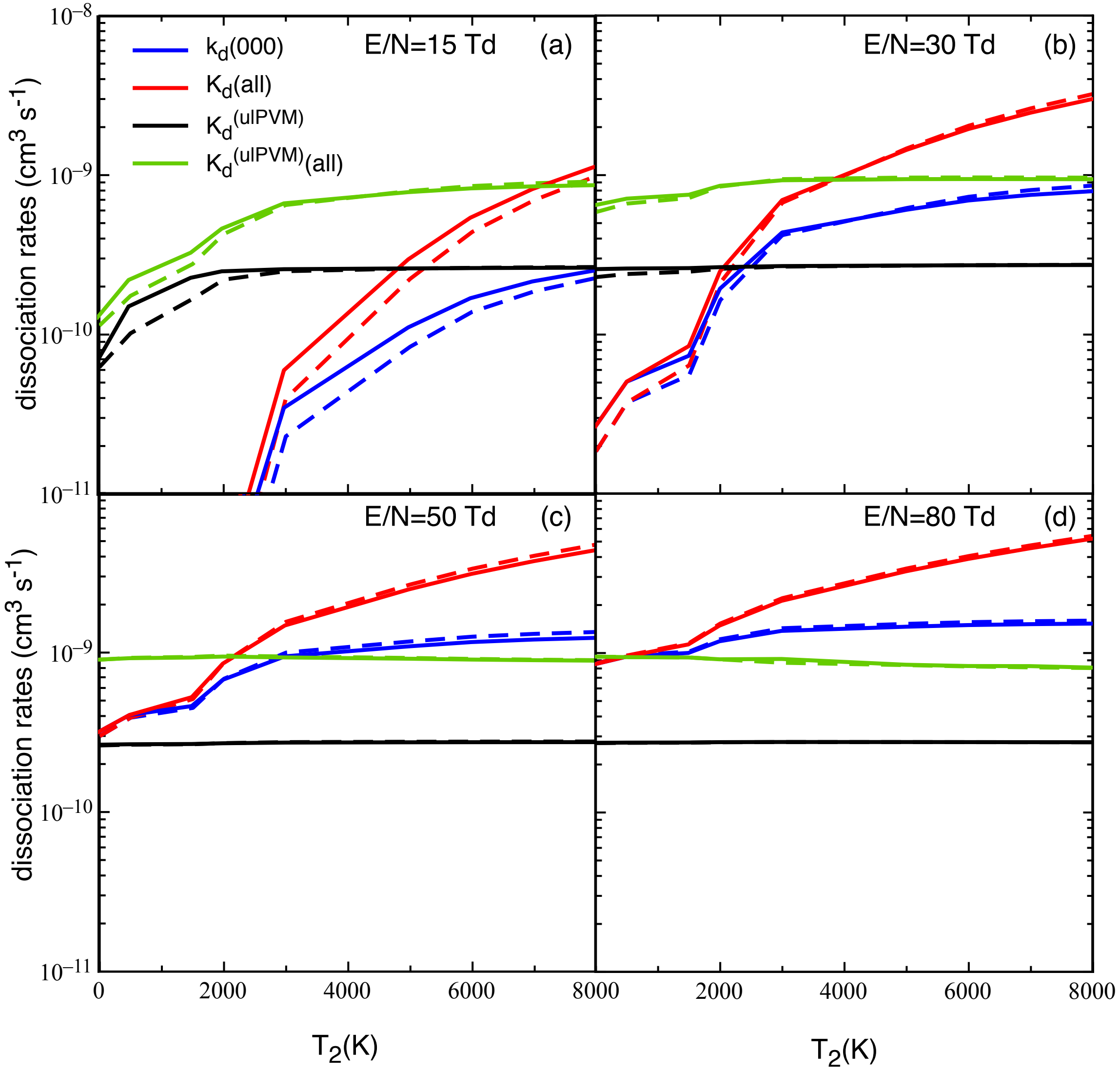
Pure Vibrational Mechanism

$$K_d^{up\_PVM}(001) = \frac{1}{v_{\max}} K_{eV}(000 \rightarrow 001)$$

$$K_d^{up\_PVM}(all) = \frac{1}{v_{\max}} \sum_{n=1}^{8} \frac{\varepsilon_{v_n}}{\varepsilon_{v_8}} K_{eV}(0 \rightarrow v)$$

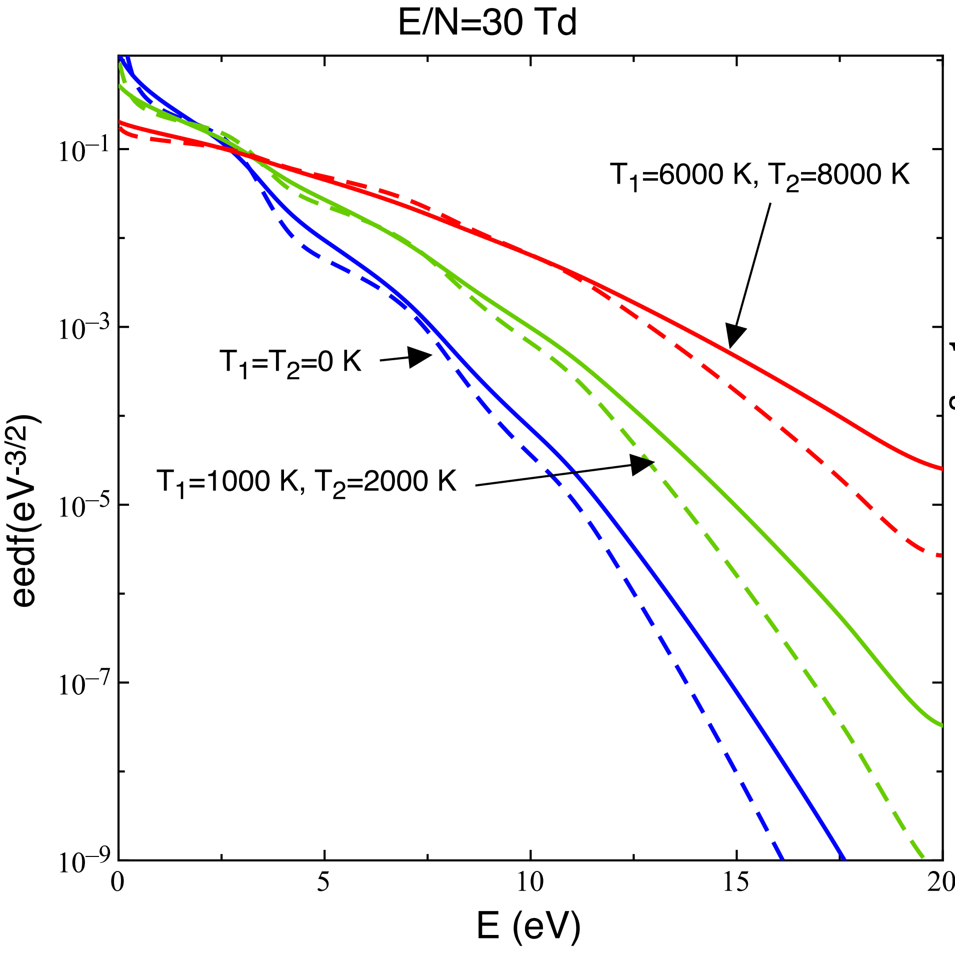
This results are important for guiding the different experiments expecially for the **MW sustained plasma**.

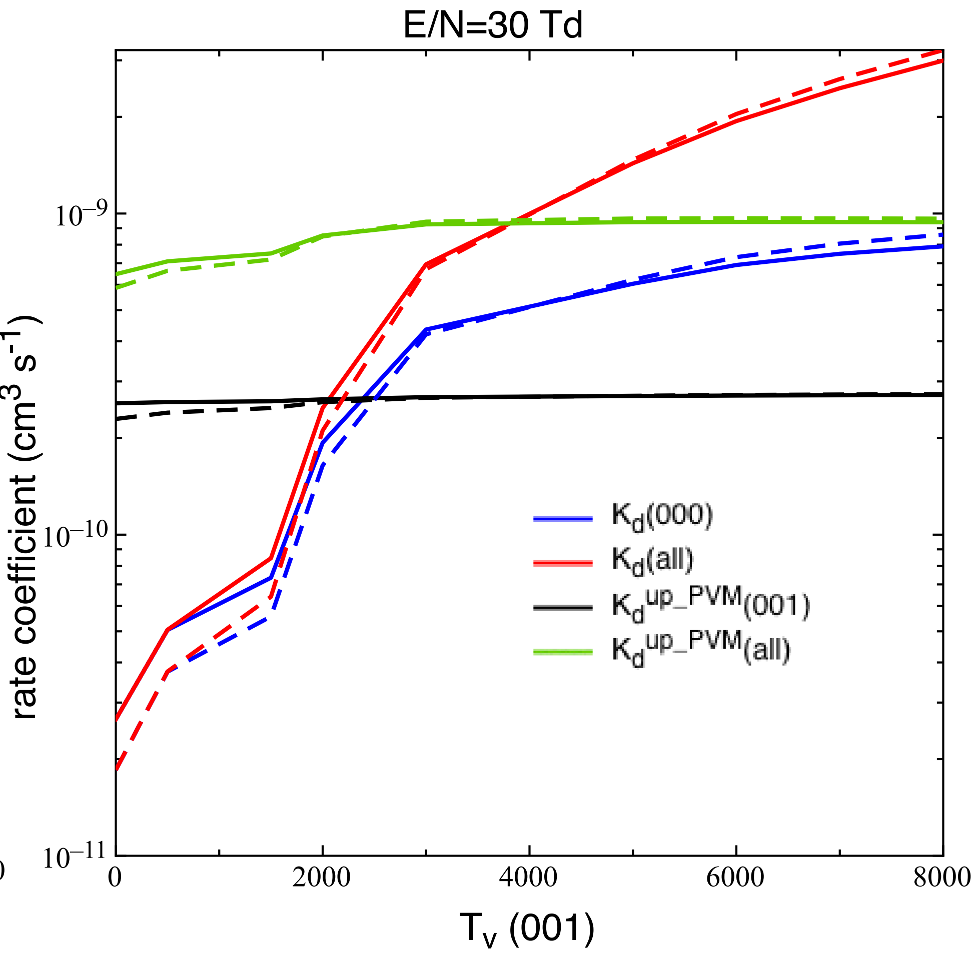
with (full lines) and without (dashed lines) **e-e collisions**



CO_2 Continuous Discharge: e-e collision effect

with (full lines) and without (dashed lines) **e-e collisions**

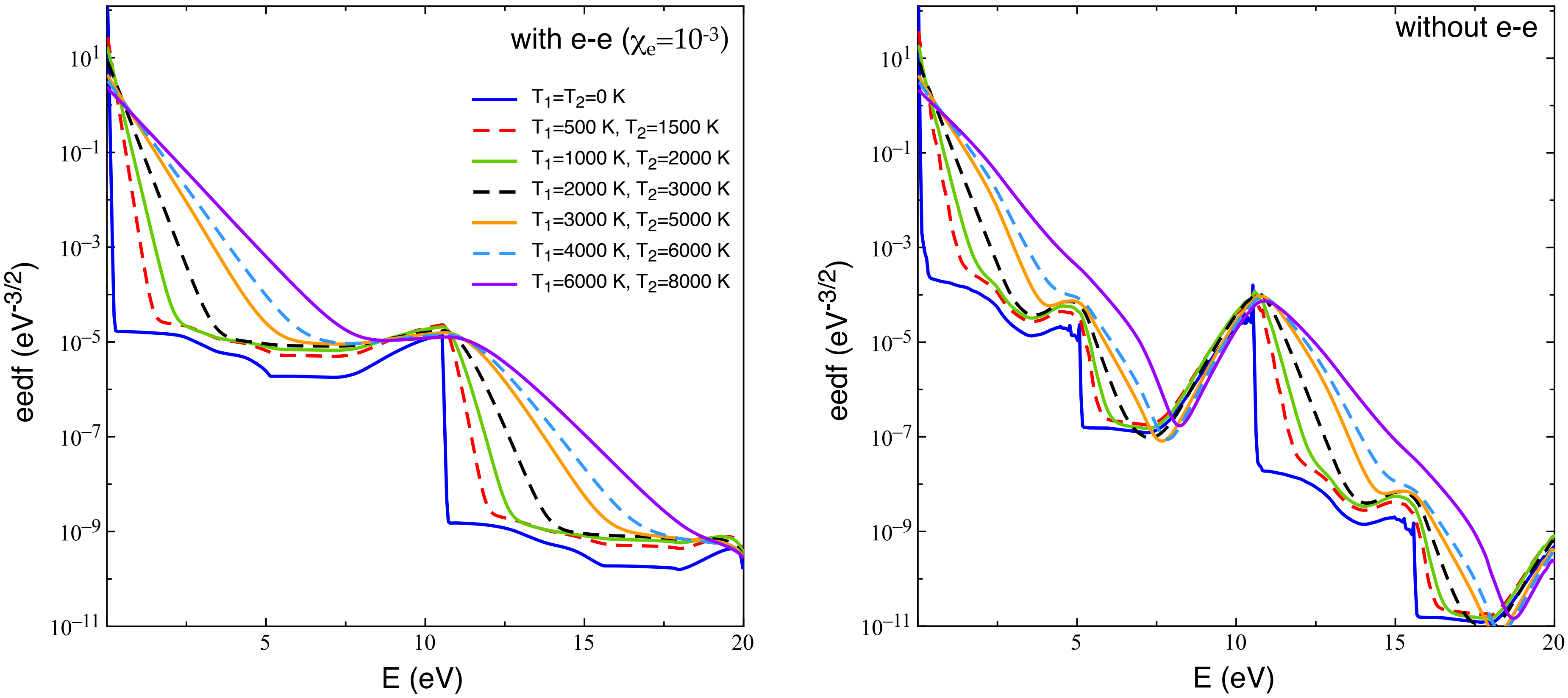




CO_2 Post Discharge: Stationary EEDF

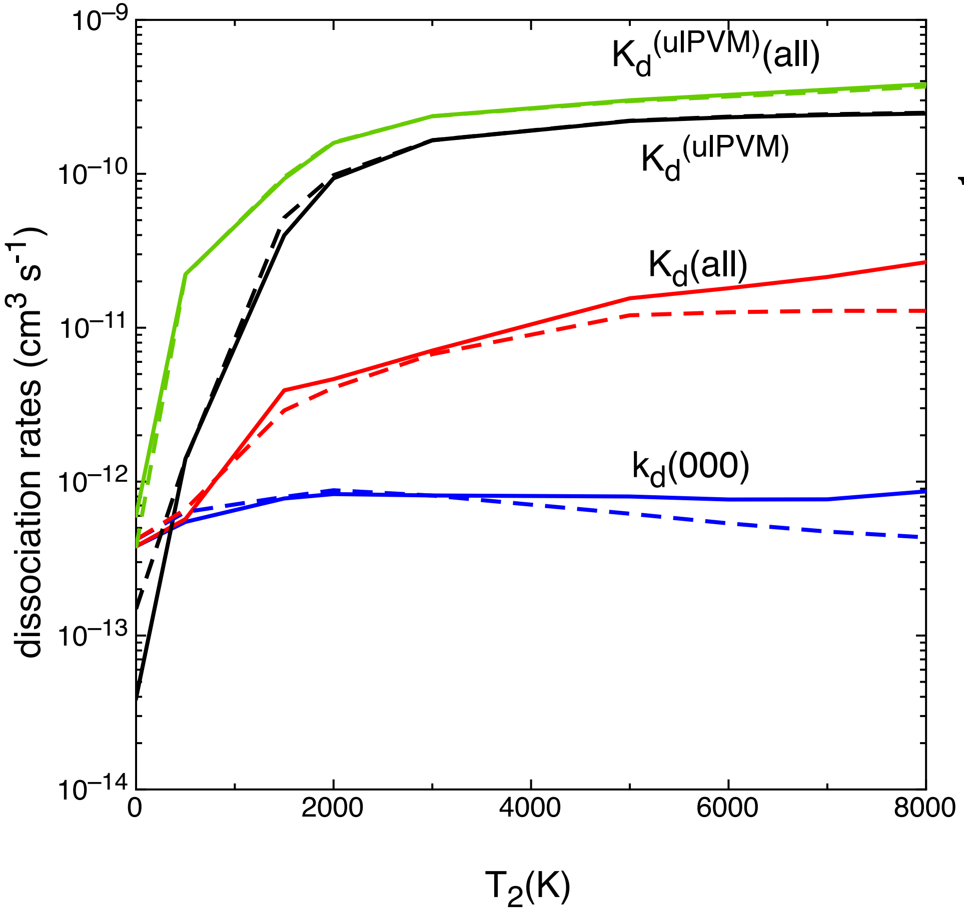
E/N=0 Td, $CO_2(e_2)=10^{-4}$
T_1 symmetric, bending levels
T_2 first asymmetric level (001)

Electron Energy Distribution Function

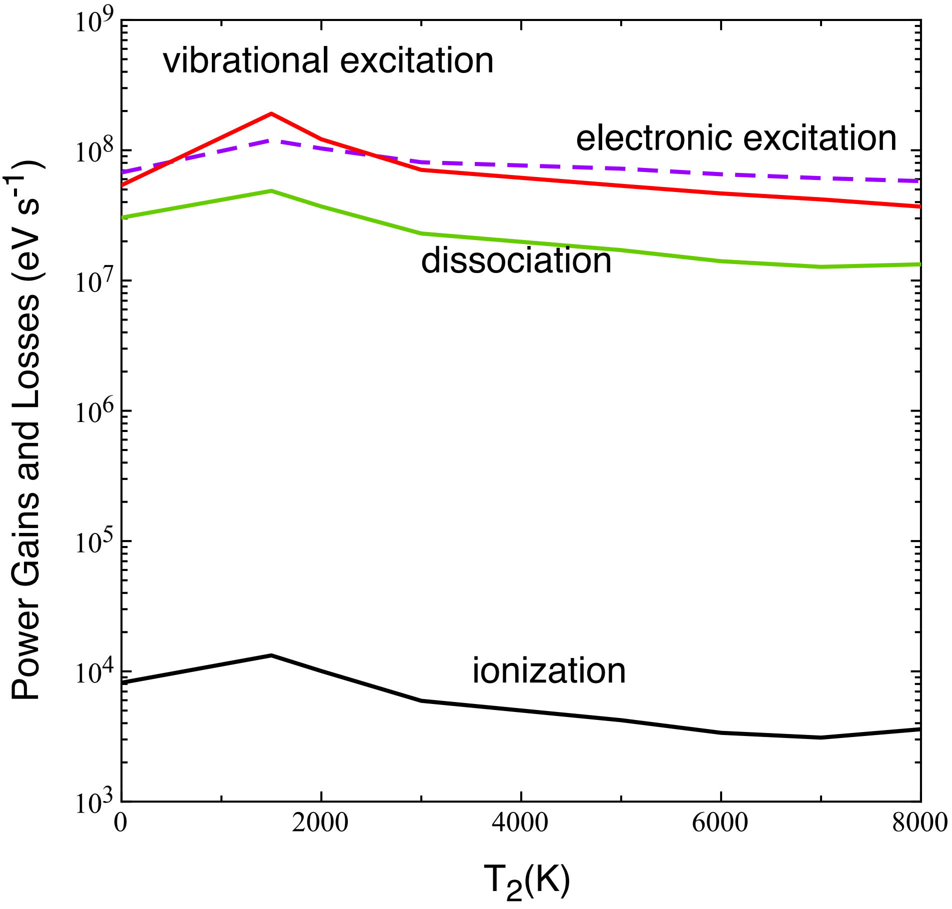


CO_2 Post Discharge

Dissociation rates

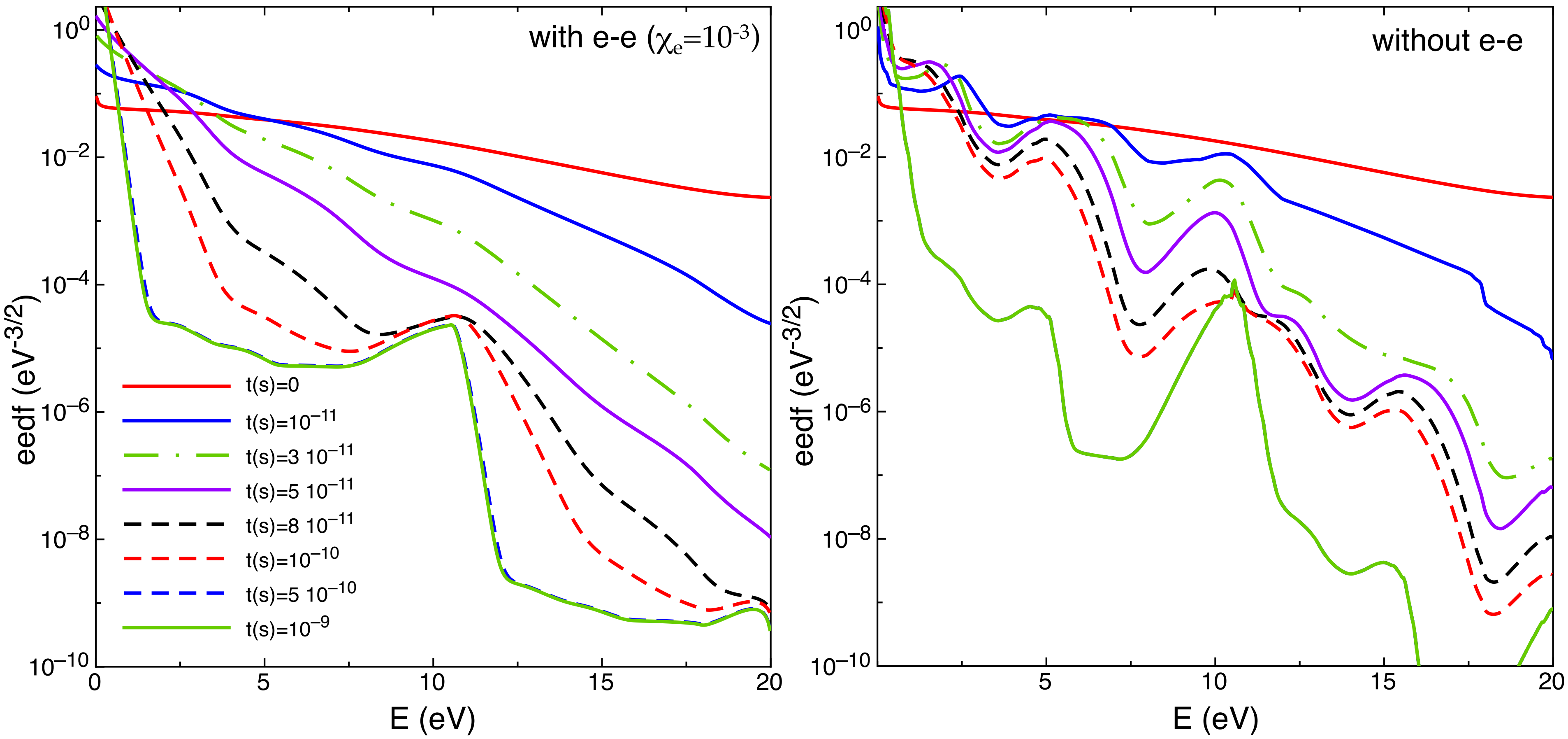


Energy channels



CO_2 Post Discharge: **Time-dependent EEDF**

T_1=500 K, T_2=1500 K



E-impact rates dependence on non equilibrium plasma conditions

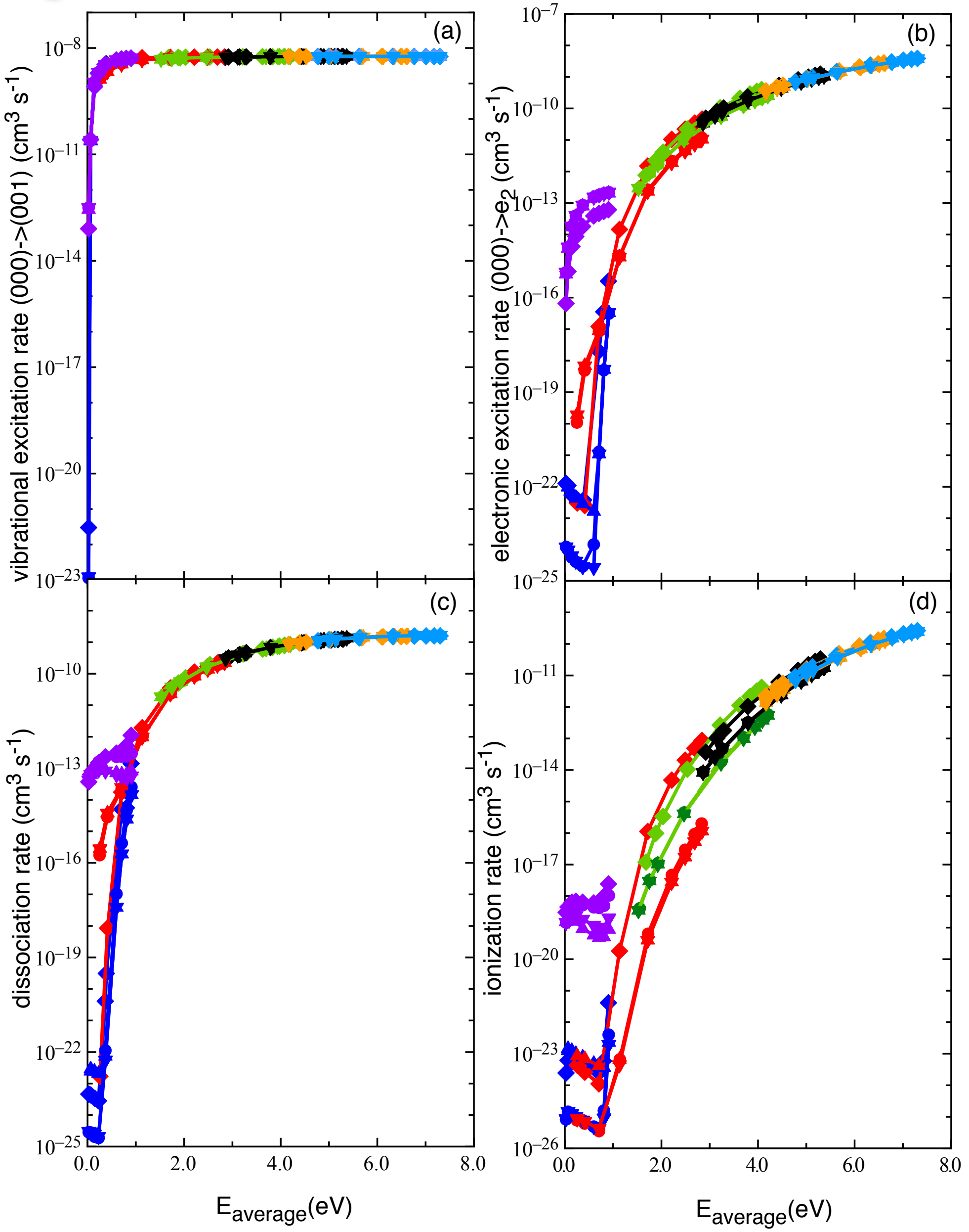
Global models

Macroscopic equation for T_e or $E_{average}$

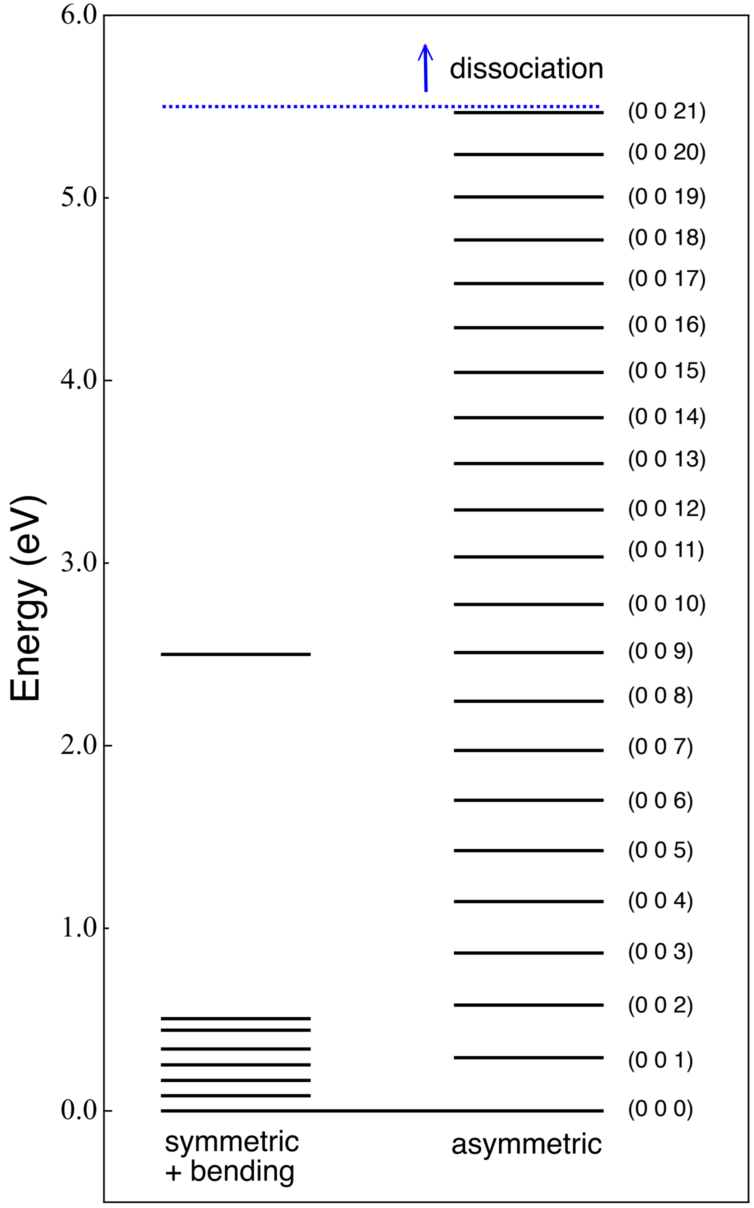
eM rates are calculated by using
- Maxwell distribution at T_e
- Boltzmann solver (rate vs E/N)

Data Collection

- E/N (0, 15, 30, 50, 80, 100 Td)
- Electron molar fraction 10^{-3}, 10^{-5}
- with and without e-e collisions



New set of eV cross sections



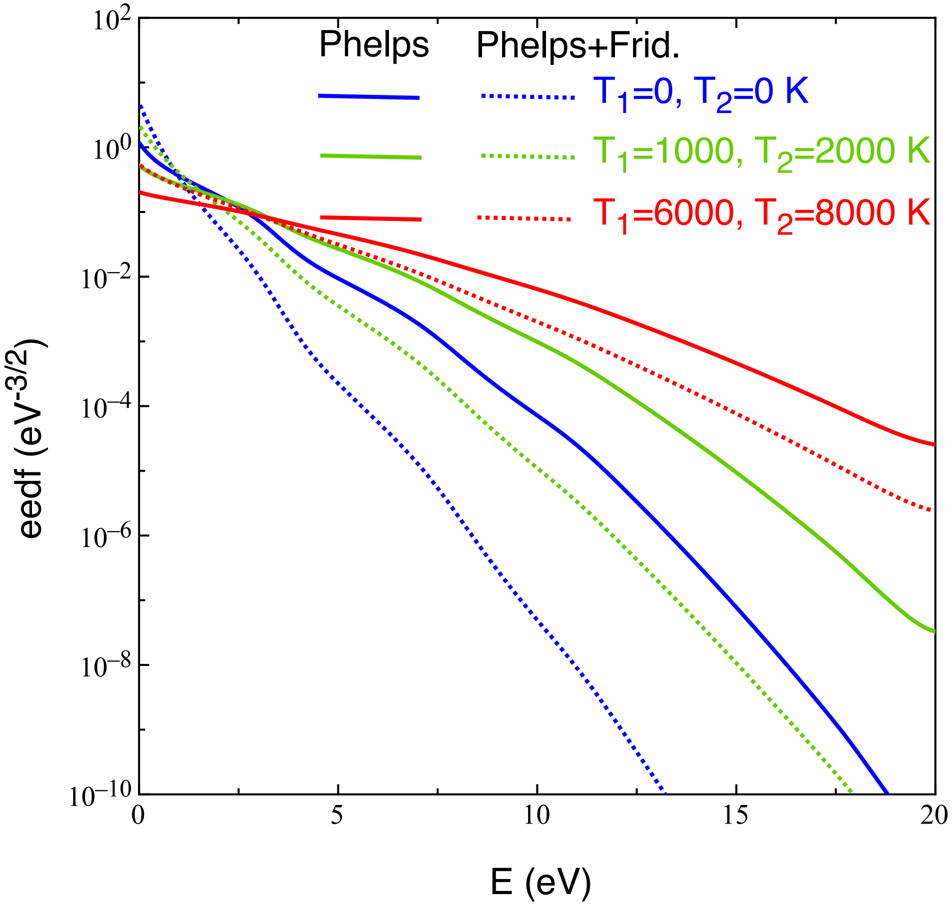
Phelps database

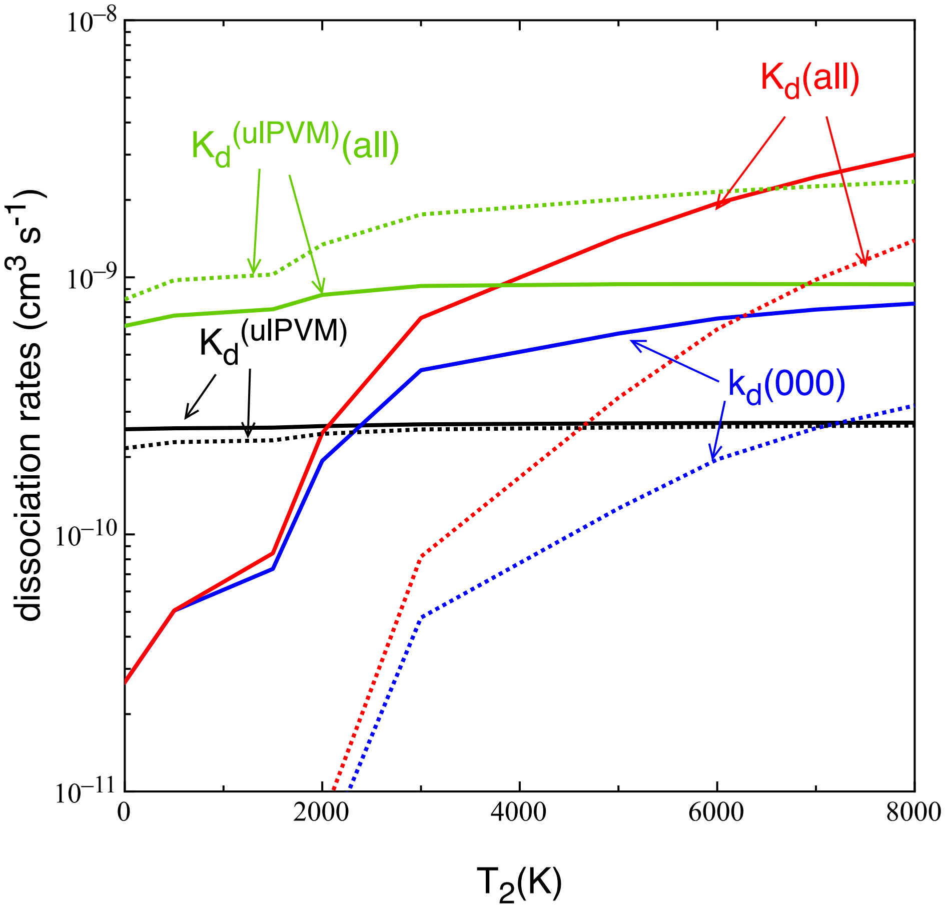
+

Fridman's semi empirical equation

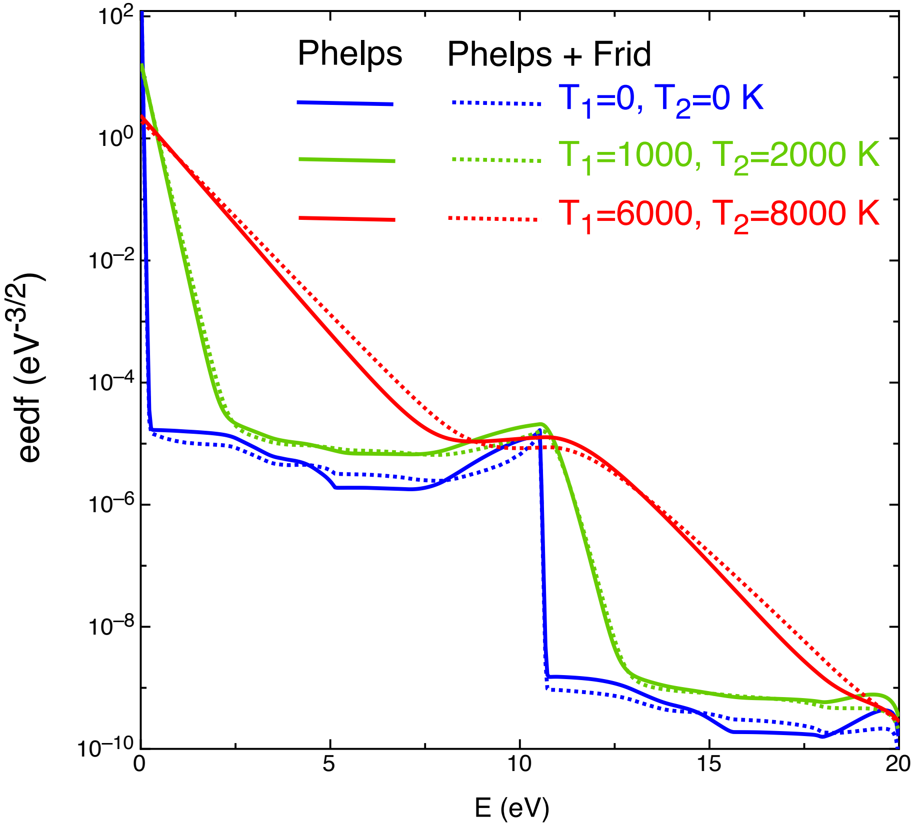
$$\sigma_{nm}(\varepsilon) = \frac{\exp(-\alpha(m-n-1))}{1+\beta n}\sigma_{01}\left(\varepsilon + E_{01} - E_{nm}\right)$$

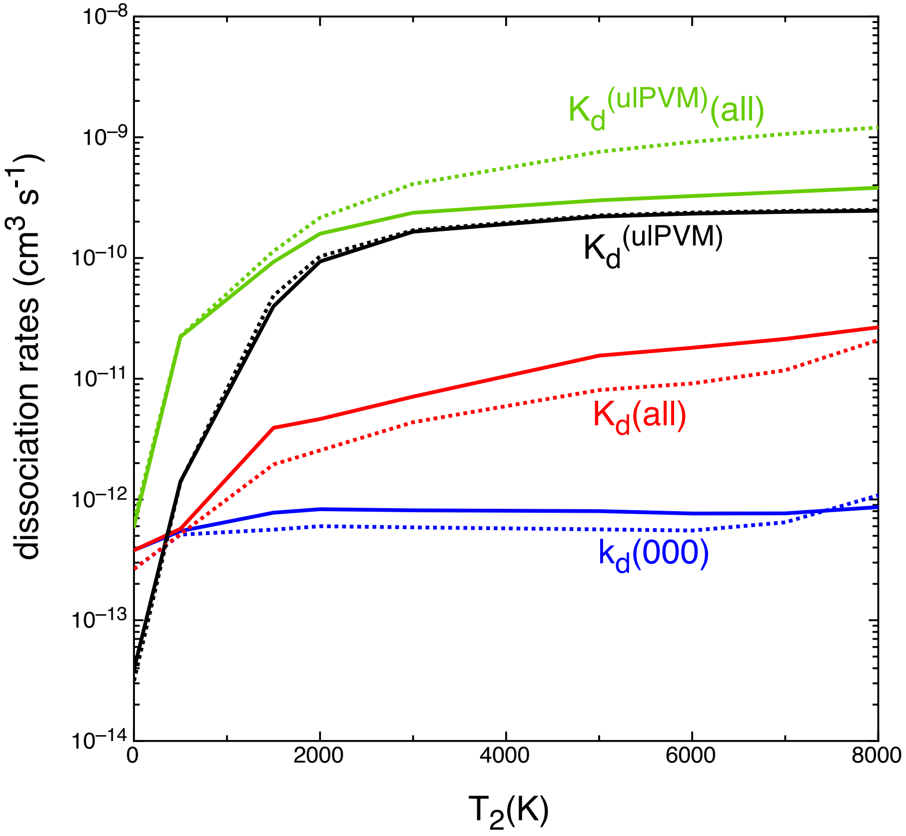
New set of eV cross sections: continuous discharge





New set of eV cross sections: post discharge



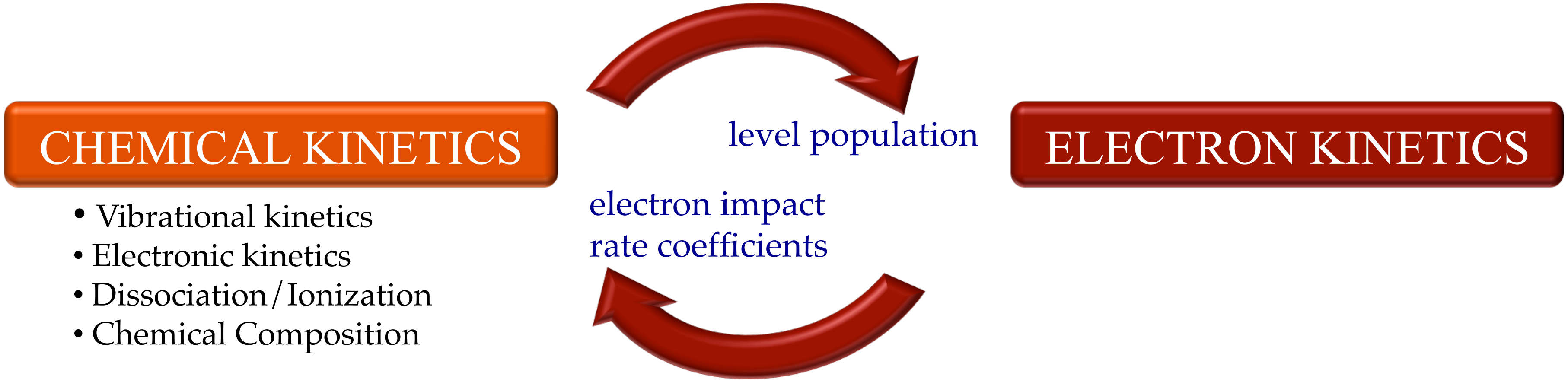


Conclusions

- A **parametric solution** of the **electron Boltzmann equation** (E/N, T_1/T_2, c_e, $CO_2(e_2)$) has been performed in CO_2 plasma in **continuous discharge** and **post-discharge** conditions.
- **Superelastic vibrational** and **electronic** collisions play an important role in affecting the **eedf, dissociation rates** and **electron fractional power losses.**
- **Electron power losses** depend also on **vibrational temperatures.**
- A comparison between **upper limit** dissociation rates of **Pure Vibrational Mechanism** and **electron impact dissociation rates** have been performed
- **Electron impact rates** depend on **non-equilibrium** plasma conditions
- The **accuracy** of the present results largely depends on the eV cross sections used in the Boltzmann solver.

Future improvements

- A more realistic CO_2 vibrational ladder (vibrational levels up to the dissociation limit).
- Complete set of VV and VT rates and eV cross sections for such levels.
- **Self consistent coupling** of **eedf** and **CO_2 vibrational level kinetics**.



CHEMICAL KINETICS

- Vibrational kinetics
- Electronic kinetics
- Dissociation/Ionization
- Chemical Composition

level population

electron impact
rate coefficients

ELECTRON KINETICS