Vibrational Kinetics of Electronically Excited States in H_2

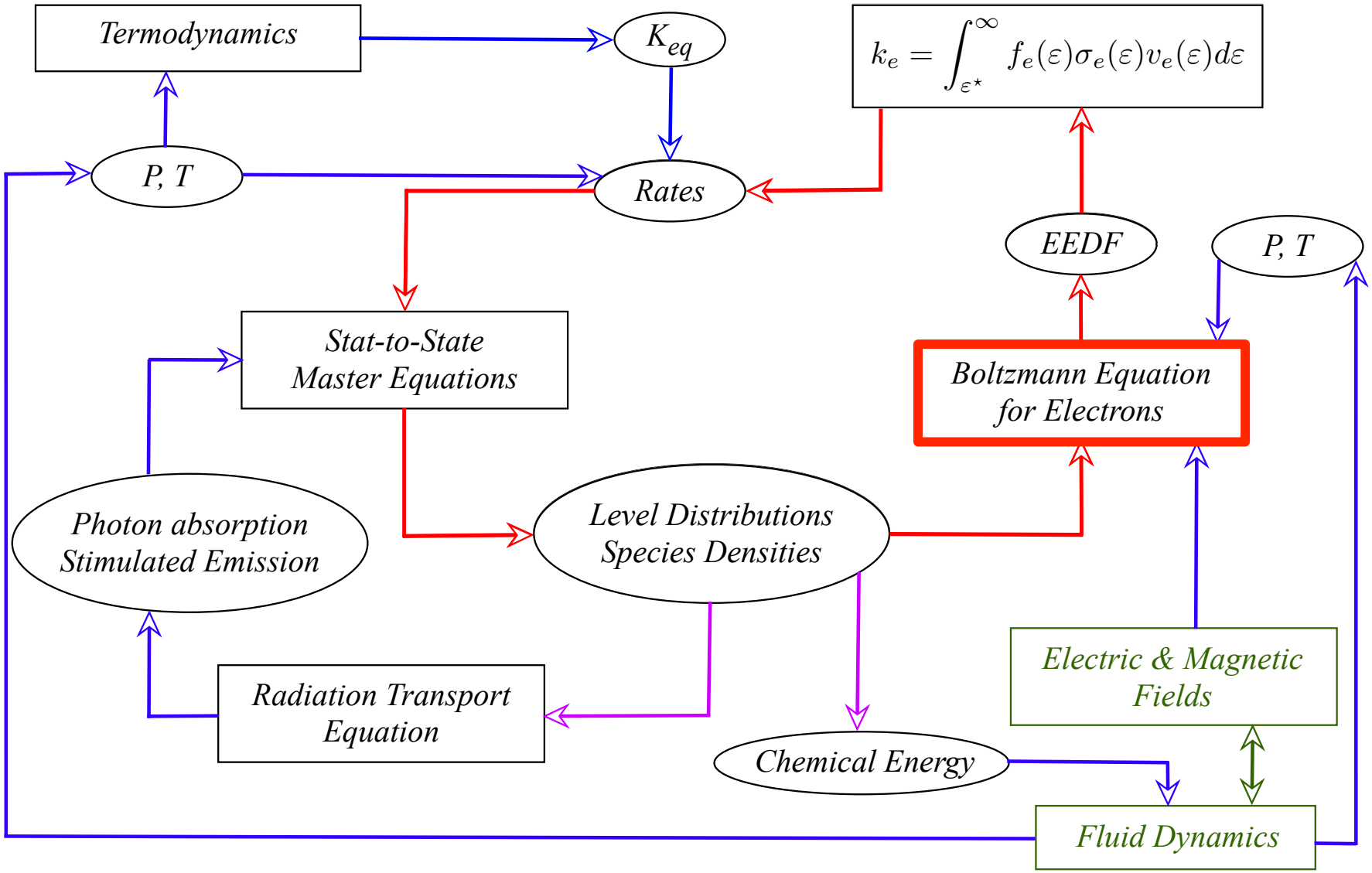
Gianpiero Colonna

CNR-PLASMI-lab, Bari

Lucia Daniela Pietanza
Giuliano D'Ammando
Roberto Celiberto
Mario Capitelli
Annarita Laricchiuta

OVERVIEW

- Self-consistent chemical kinetics
- Electron Kinetics: Boltzmann equation
- Discharge Modeling
- Hydrogen plasma kinetics
- Vibrational kinetics of singlets and improved ion model
- Results


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
Electric & Magnetic
Fields
Radiation Transport
Equation
Chemical Energy
Fluid Dynamics

ELECTRON KINETICS 1

BOLTZMANN EQUATION

$$\frac{\partial f}{\partial t} + \vec{v}\cdot\vec{\nabla}_r f + \vec{A}\cdot\vec{\nabla}_v f + \vec{v}\wedge\vec{R}\cdot\vec{\nabla}_v f = \left(\frac{\delta f}{\delta t}\right)_c$$

$$\vec{A} = -\frac{e}{m_e}\vec{E} \qquad \vec{R} = -\frac{e}{m_e}\vec{B}$$

Electric and Magnetic accelleration

ELECTRON VELOCITY DISTRIBUTION

$f = f(\vec{r},\vec{v},t)$ **in phase space**

$\int_v f d^3v = N_e$ **electron density**

$\frac{1}{N_e}\int_v \vec{v} f d^3v = \vec{V}_d$ **electron mean velocity**

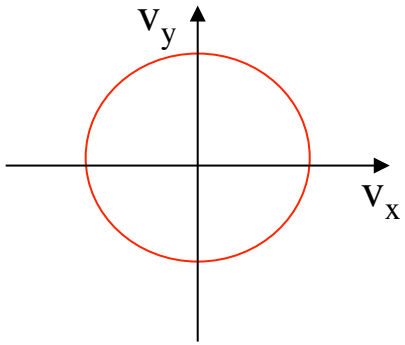
ELECTRON KINETICS

Two-term approximation

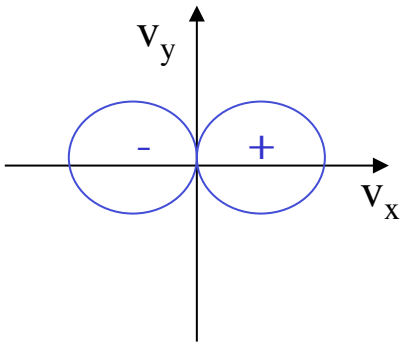
QUASI ISOTROPIC DISTRIBUTION

$$f(\vec{r},\vec{v},t) = f_0(\vec{r},v,t) + \frac{\vec{v}}{v}\cdot\vec{f}_1(\vec{r},v,t)$$

isotropic



anisotropic



$$\frac{\partial f_0}{\partial t} = -\frac{\partial J_f}{\partial \varepsilon} - \frac{\partial J_{el}}{\partial \varepsilon} - \frac{\partial J_{ee}}{\partial \varepsilon} + S_{in} + S_{sup}$$

$\vec{E}$ & $\vec{B}$

$$e(\varepsilon) + N_2(v) \rightarrow e(\varepsilon - d\varepsilon) + N_2(v)$$

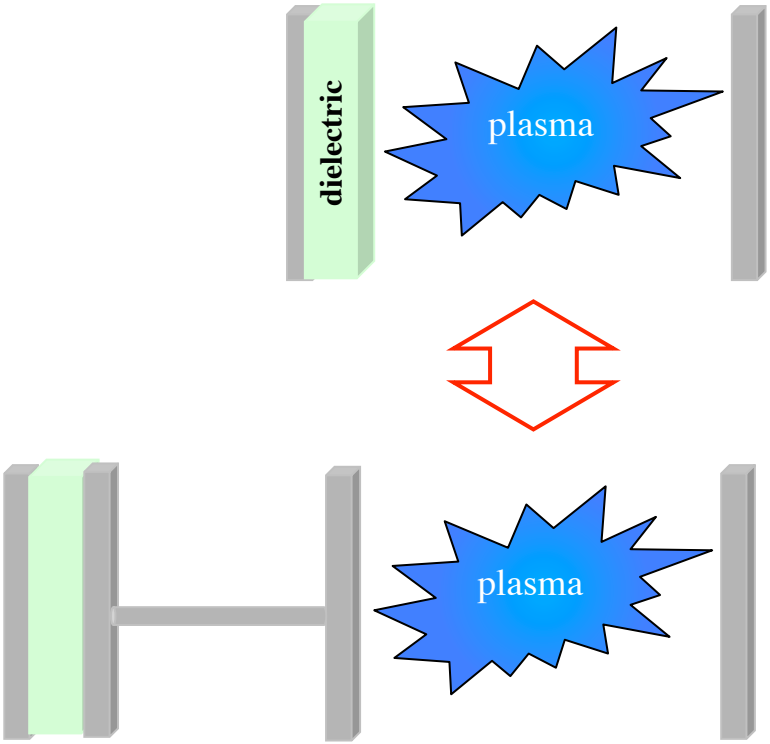
$$e(\varepsilon_a) + e(\varepsilon_b) \rightarrow e(\varepsilon_a + d\varepsilon) + e(\varepsilon_b - d\varepsilon)$$

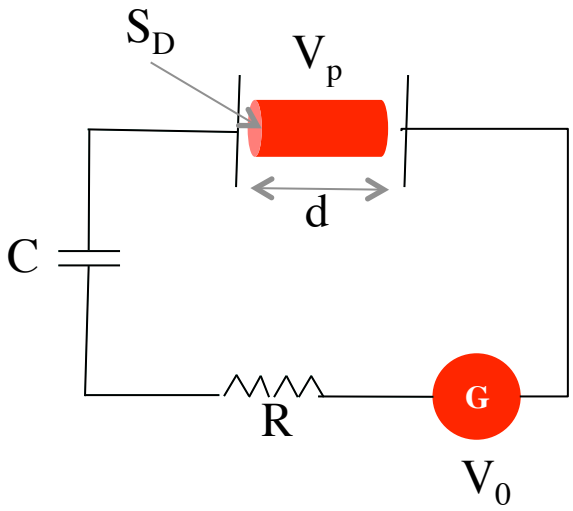
$$e(\varepsilon) + N_2(v) \rightarrow e(\varepsilon - \varepsilon^\star) + N_2(v_f > v)$$

$$e(\varepsilon) + N_2(v) \rightarrow e(\varepsilon + \varepsilon^\star) + N_2(v_f < v)$$

$$K_{v\rightarrow v_f} = \int_0^\infty f_0(\varepsilon)\varepsilon\sigma_{v\rightarrow v_f}(\varepsilon)d\varepsilon$$

Model for DBD & RPD-ns





$$V_p(t) = V_0(t) - RI(t) - \frac{1}{C}\int_0^t I(\tau)d\tau$$

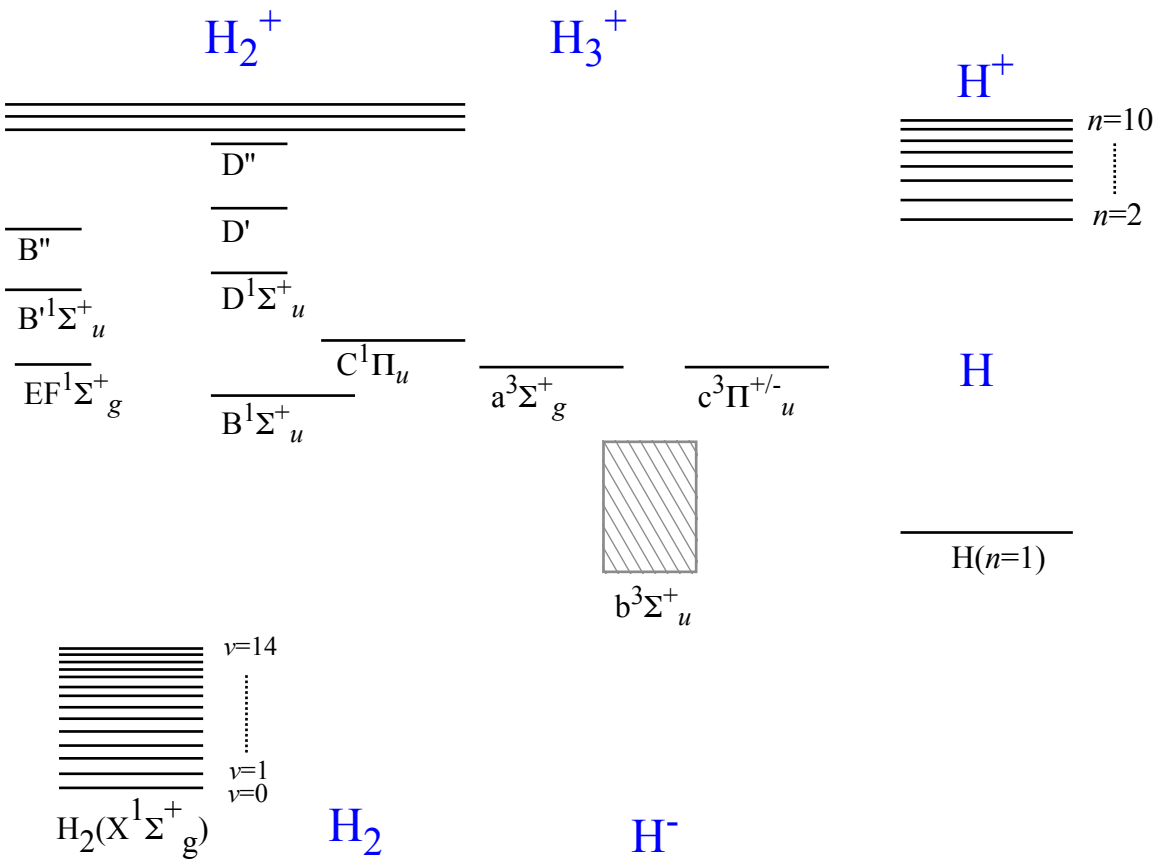
$$I(t) = E_p \mu_e(t) N_e(t) S_D$$

$$E_p = \frac{V_p}{d}$$

$$E_p(t) = E_0(t) - \tilde{R}\mu_e(t)N_e(t)E_p(t) - \frac{1}{\tilde{C}}\int_0^t \mu_e(\tau)N_e(\tau)E_p(t)d\tau$$

$$E_0 = \frac{V_0}{d} \qquad \tilde{R} = R\,\frac{S_D}{d} \qquad \tilde{C} = C\,\frac{d}{S_D}$$

H_2/H LEVEL SYSTEM



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

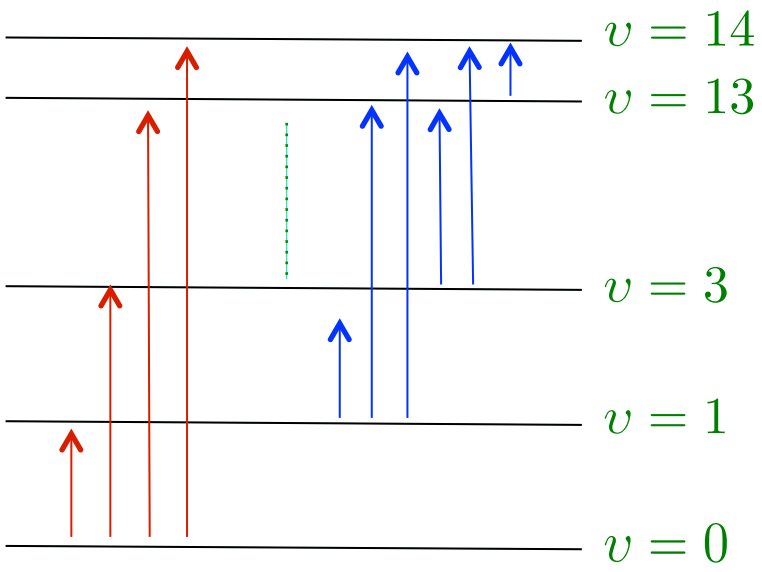
$$
\begin{aligned}
e^- + H_2^+ &\rightleftharpoons H(m') + H(n=1) \\
e^- + H_2^+ &\rightleftharpoons H^+ + H(n=1) + e^- \\
e^- + H_2^+ &\rightleftharpoons 2H^+ + 2e^- \\
H^+ + H_2(v'') &\rightleftharpoons H + H_2^+
\end{aligned}
$$

Fast discharges in hydrogen

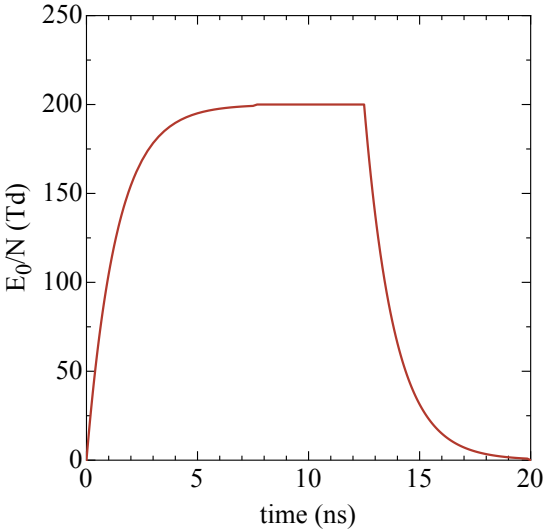
Investigating the role cross section set on the discharge behaviors:

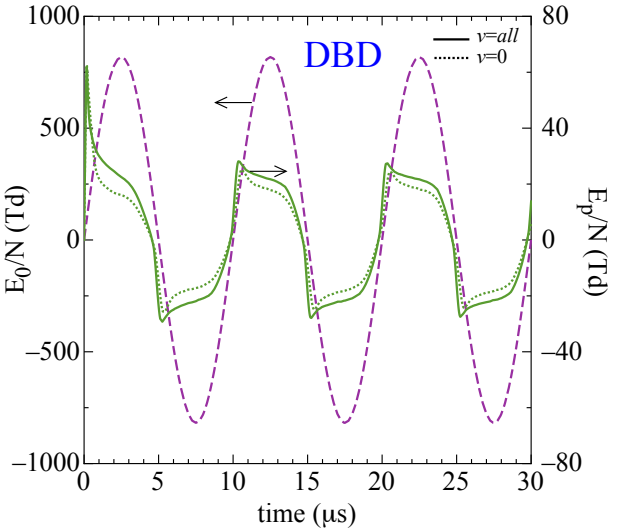
$v = 0 \quad e^- + H_2(v = 0) \rightleftharpoons e^- + H_2(v = w)$

$v = all \quad e^- + H_2(v) \rightleftharpoons e^- + H_2(w > v)$

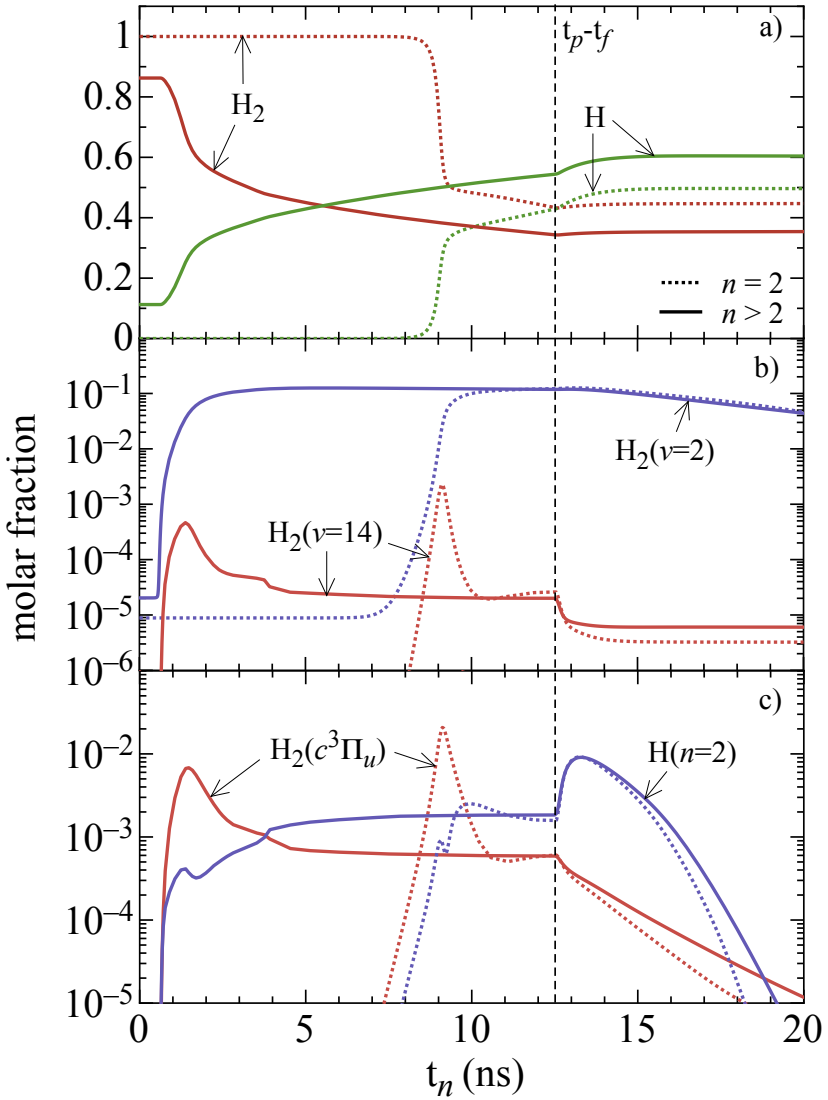


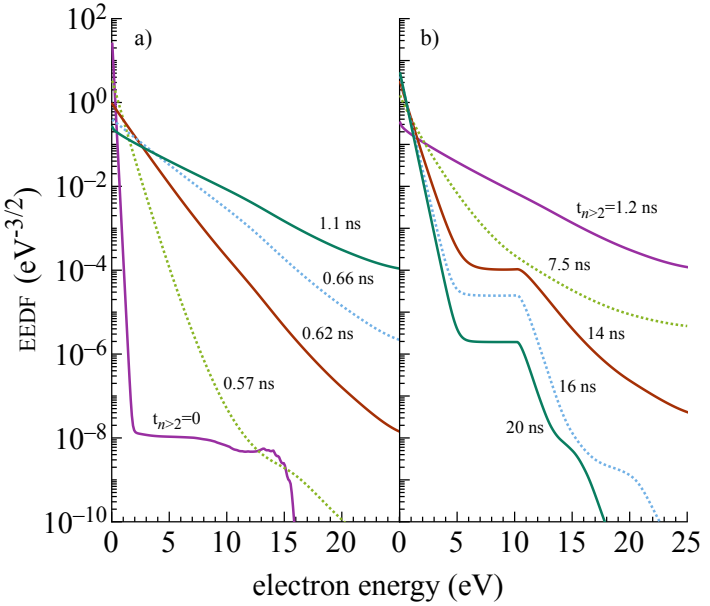
Ns repetitively pulsed discharge
Interpulse delay Δt=25μs

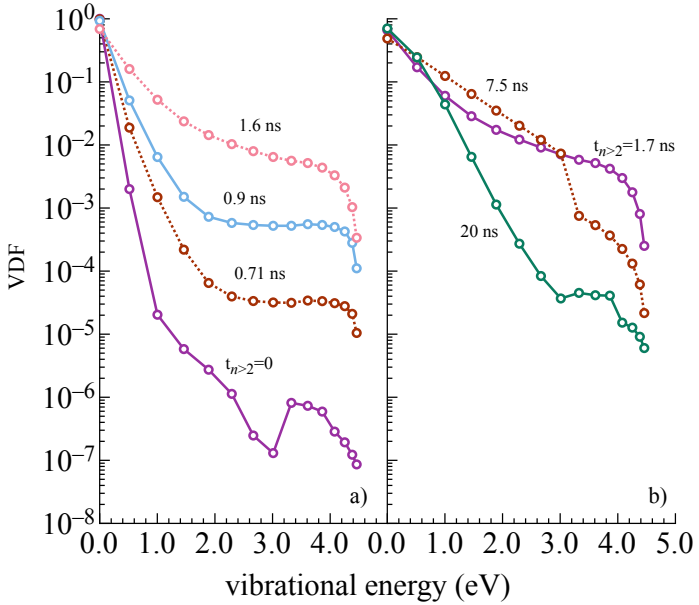




Fast discharges in hydrogen
Ns-RPD



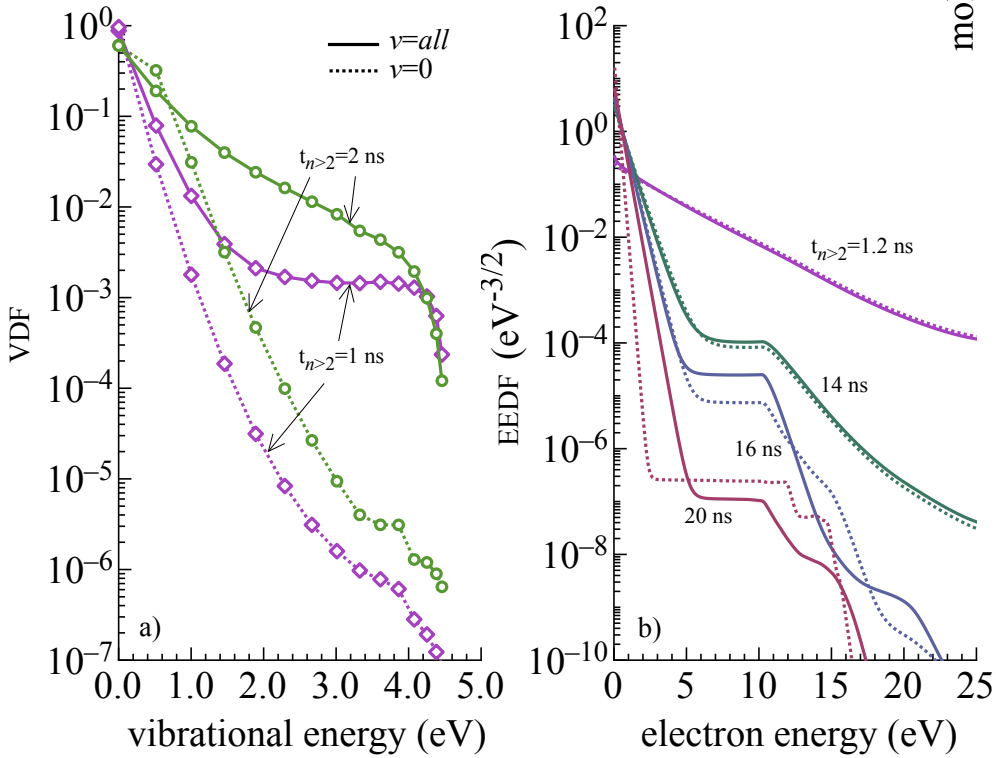


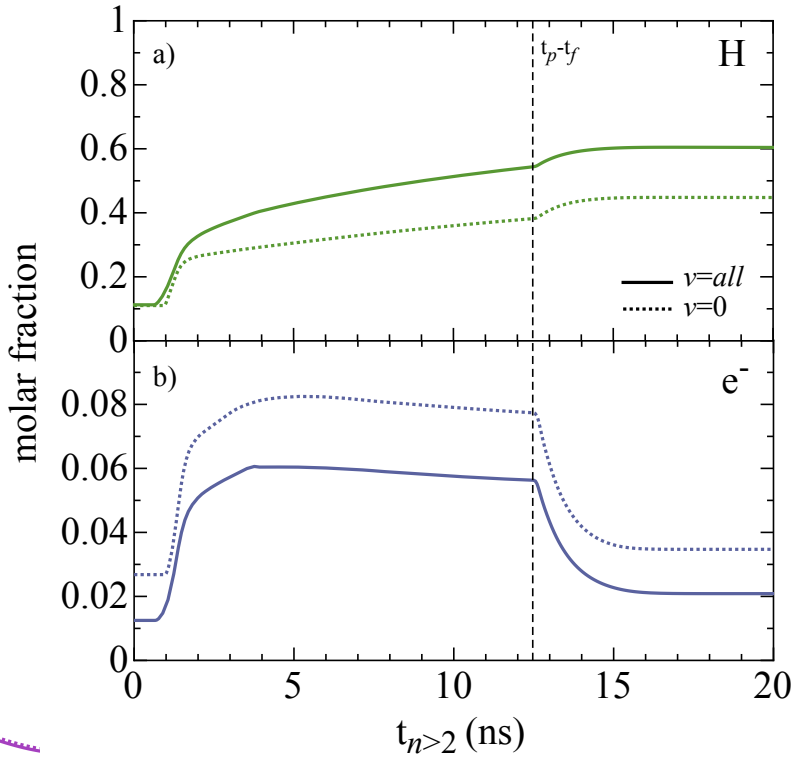


G. Colonna: *Vibrational kinetics of electronically excited states in* H_2
Ion Propulsion and Accelerator Industrial Applications (IPAIA2017)

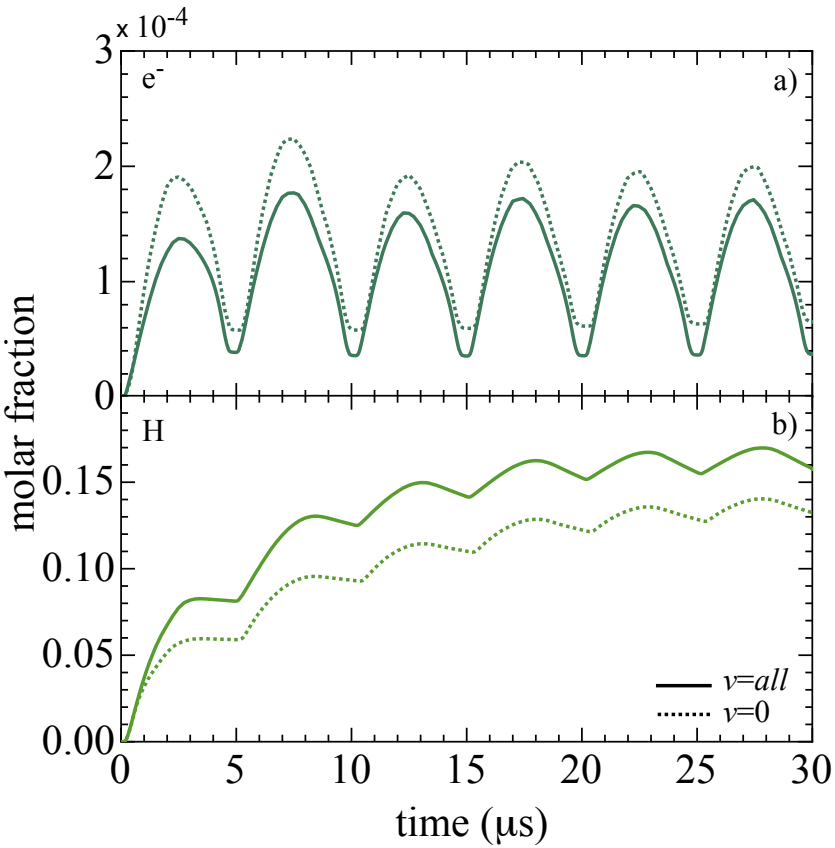
Bari, March 1nd-3rd2017

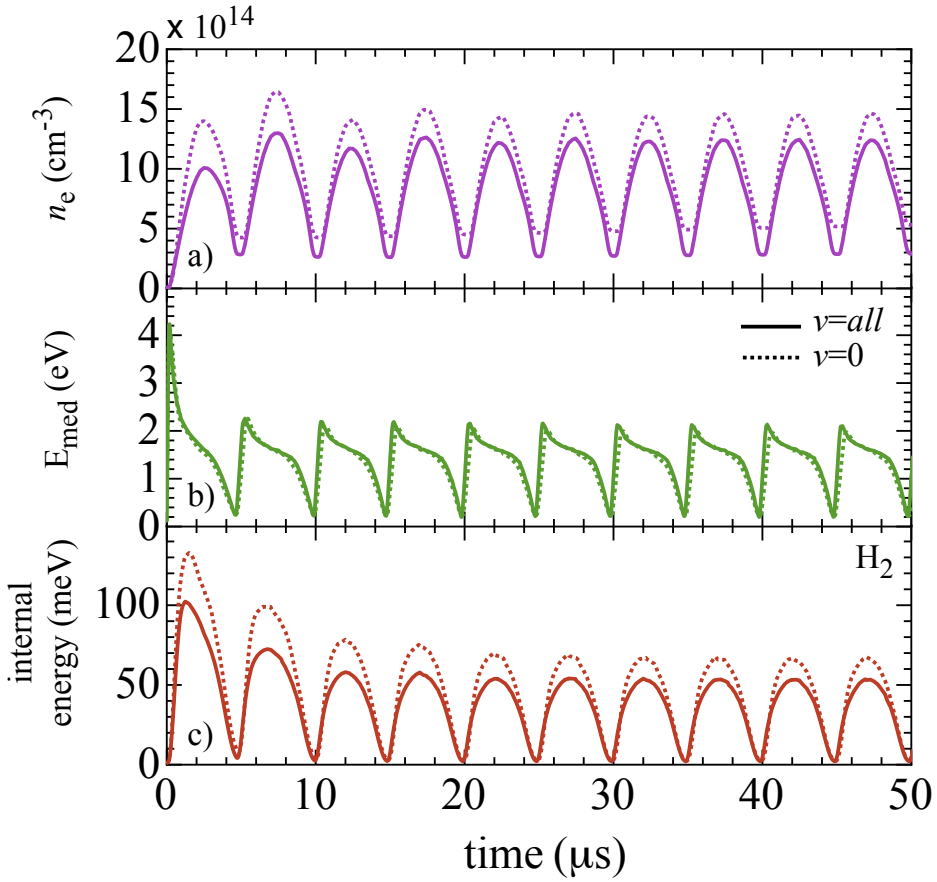
Fast discharges in hydrogen
Ns-RPD



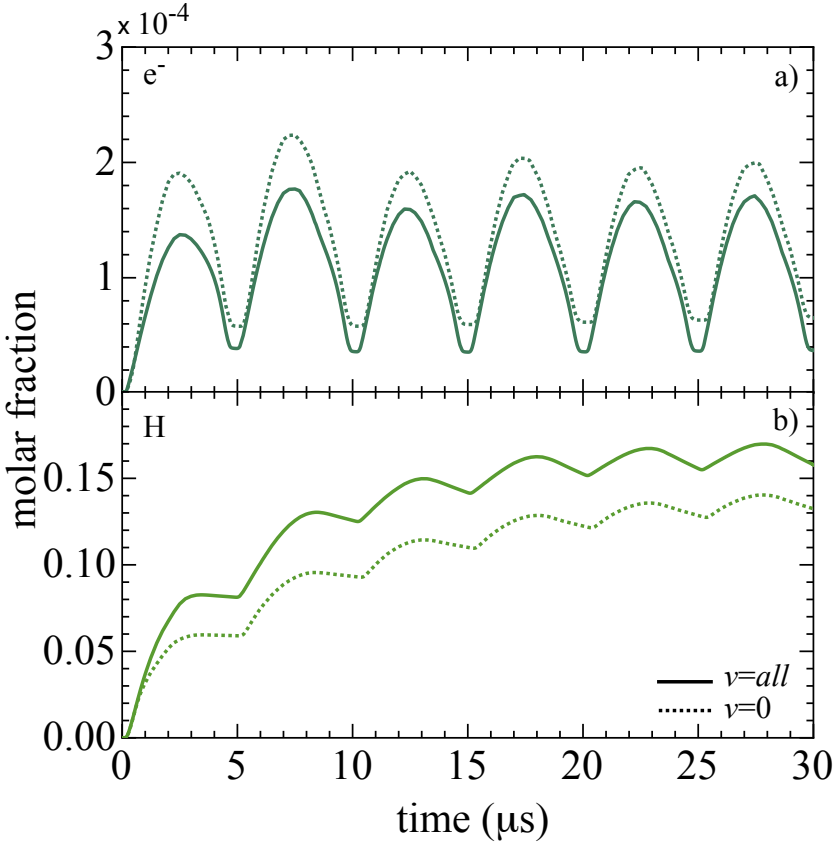


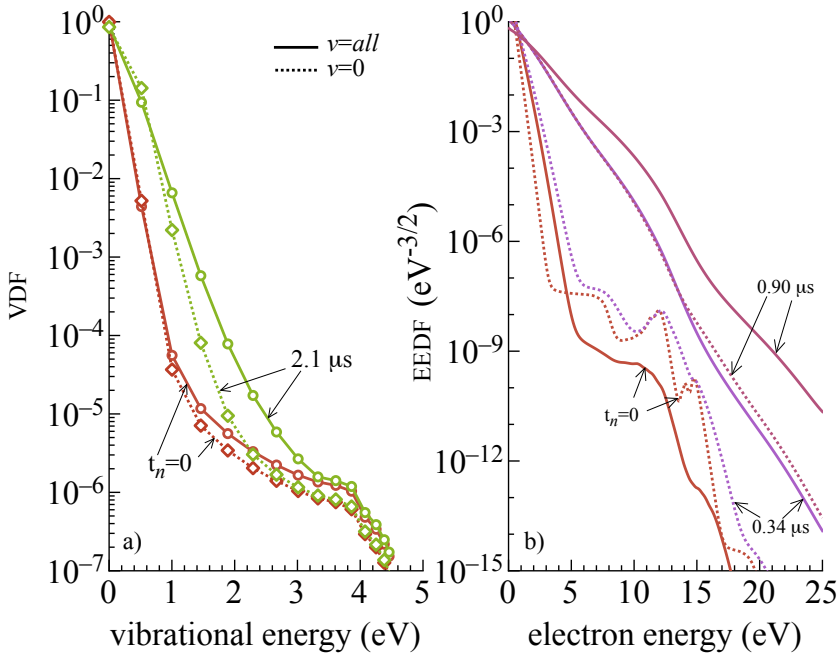
Fast discharges in hydrogen DBD



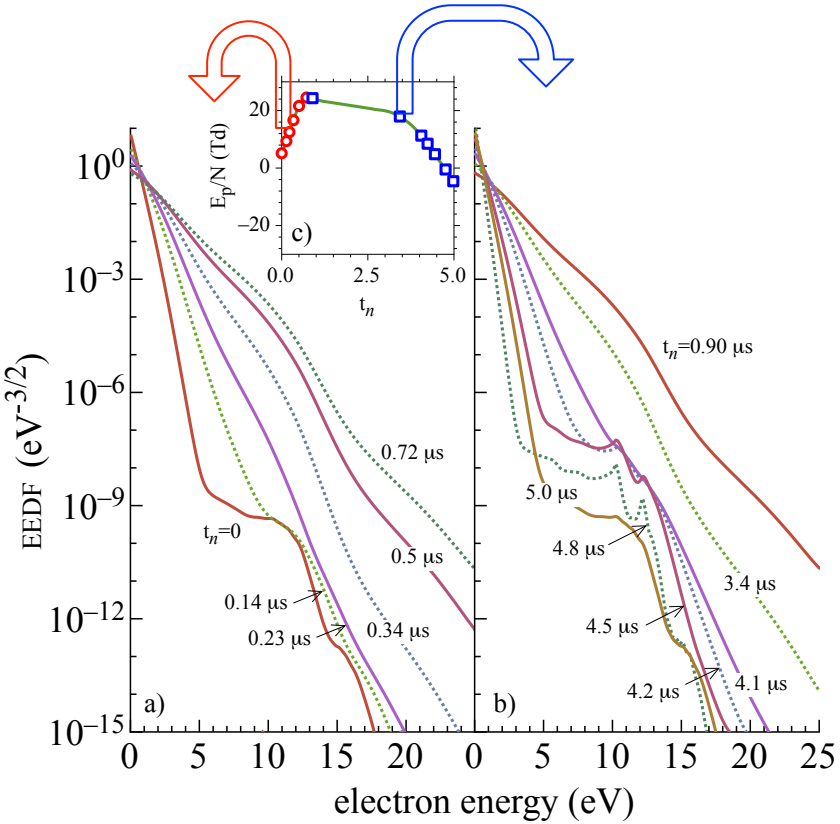


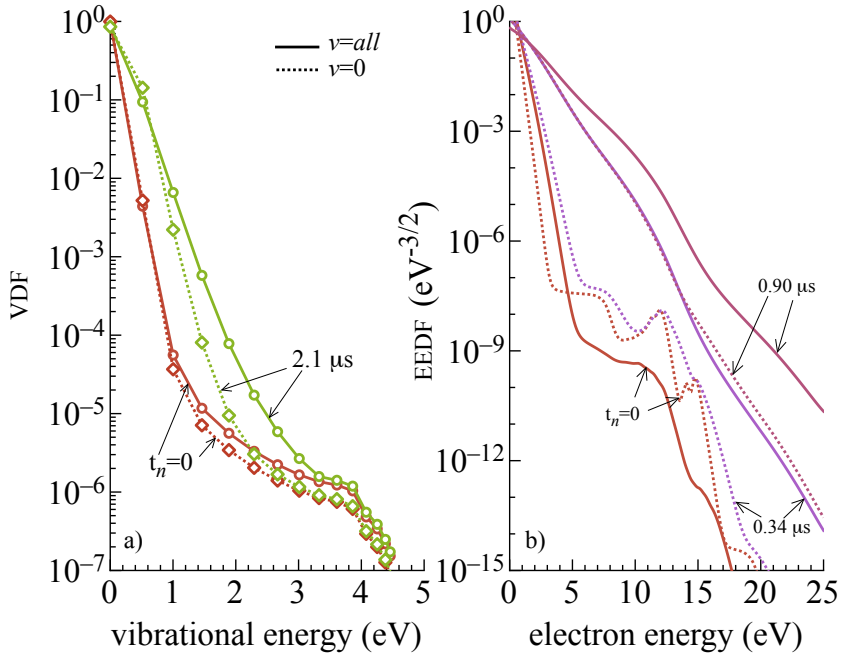
Fast discharges in hydrogen DBD





Fast discharges in hydrogen
DBD





H_2/H STATE-TO-STATE KINETICS

Updated model

Singlets vibrational kinetics

$$
\begin{aligned}
H_2(X^1\Sigma_g^+, v'') + e^- &\rightleftharpoons H_2(^1Y^\star, v') + e^- \\
H_2(^1Y^\star, v') &\rightarrow H_2(X^1\Sigma_g^+, v'') + h\nu \\
H_2(^1Y^\star, v') &\rightarrow H_2(X^1\Sigma_g^+, \varepsilon) + h\nu \rightarrow 2H(n=1) \\
H_2(^1Y^\star, v') + H_2/H &\rightarrow 2H(n=1) + H_2/H
\end{aligned}
$$

Triples kinetics

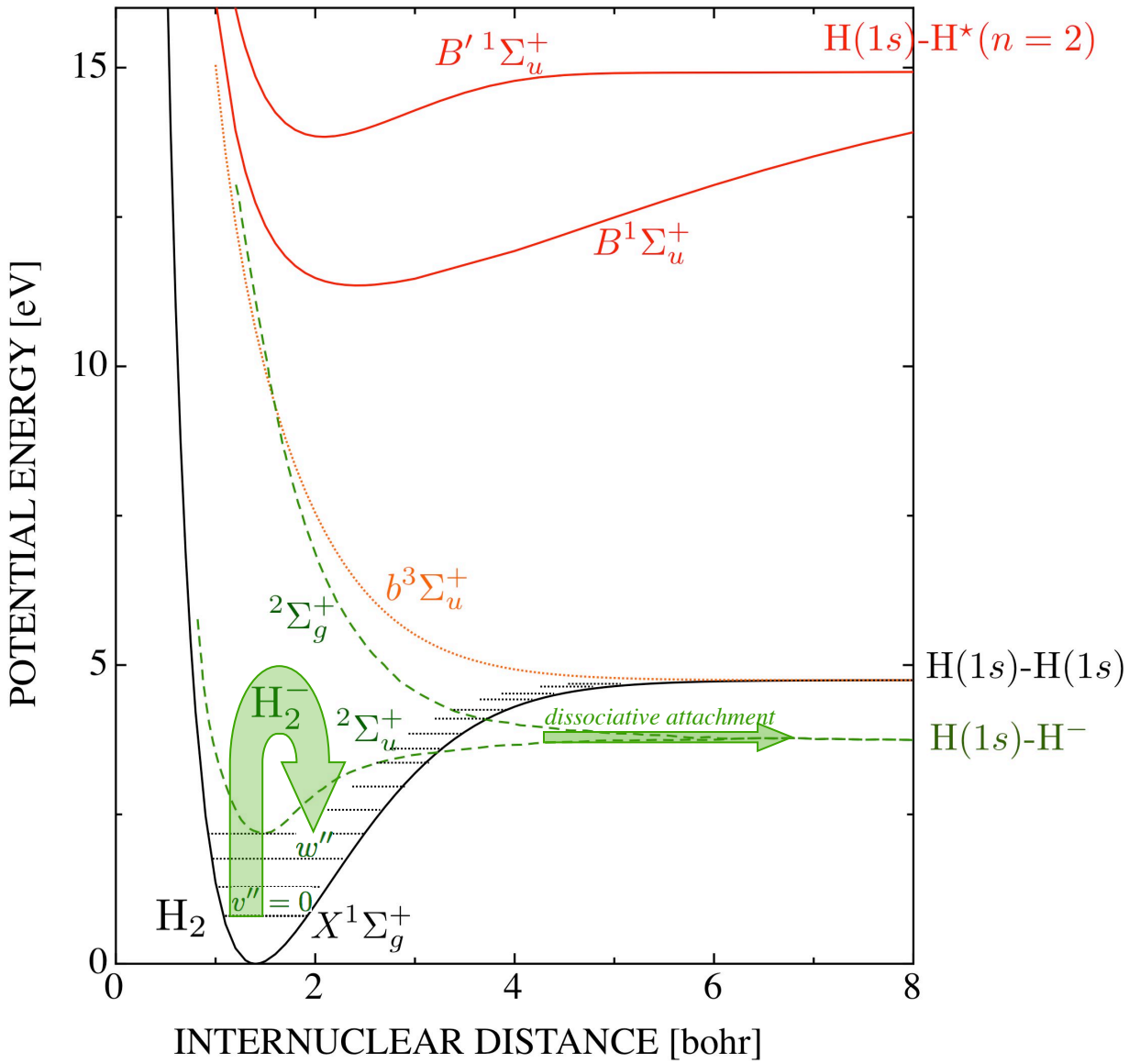
$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v) &\rightleftharpoons e^- + H_2(a^3\Sigma_g^+) \\
H_2(a^3\Sigma_g^+) &\rightarrow H_2(b^3\Sigma_u^+) + h\nu \rightarrow 2H(n=1) \\
H_2(a^3\Sigma_g^+) + H_2/H &\rightleftharpoons H_2(c^3\Pi_u) + H_2/H \\
H_2(c^3\Pi_u) + H_2/H &\rightleftharpoons 2H + H_2/H
\end{aligned}
$$

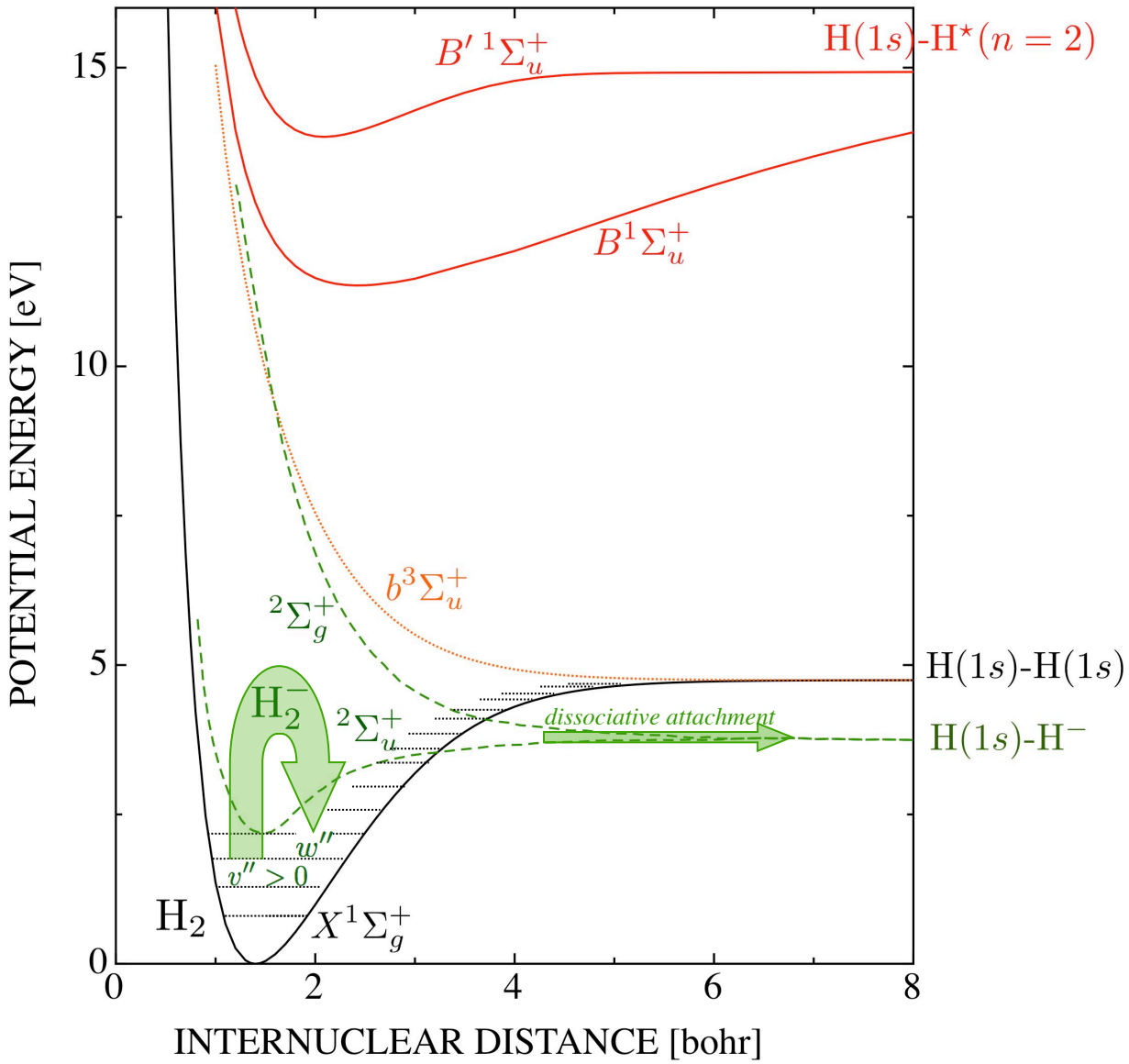
Negative Ions kinetics

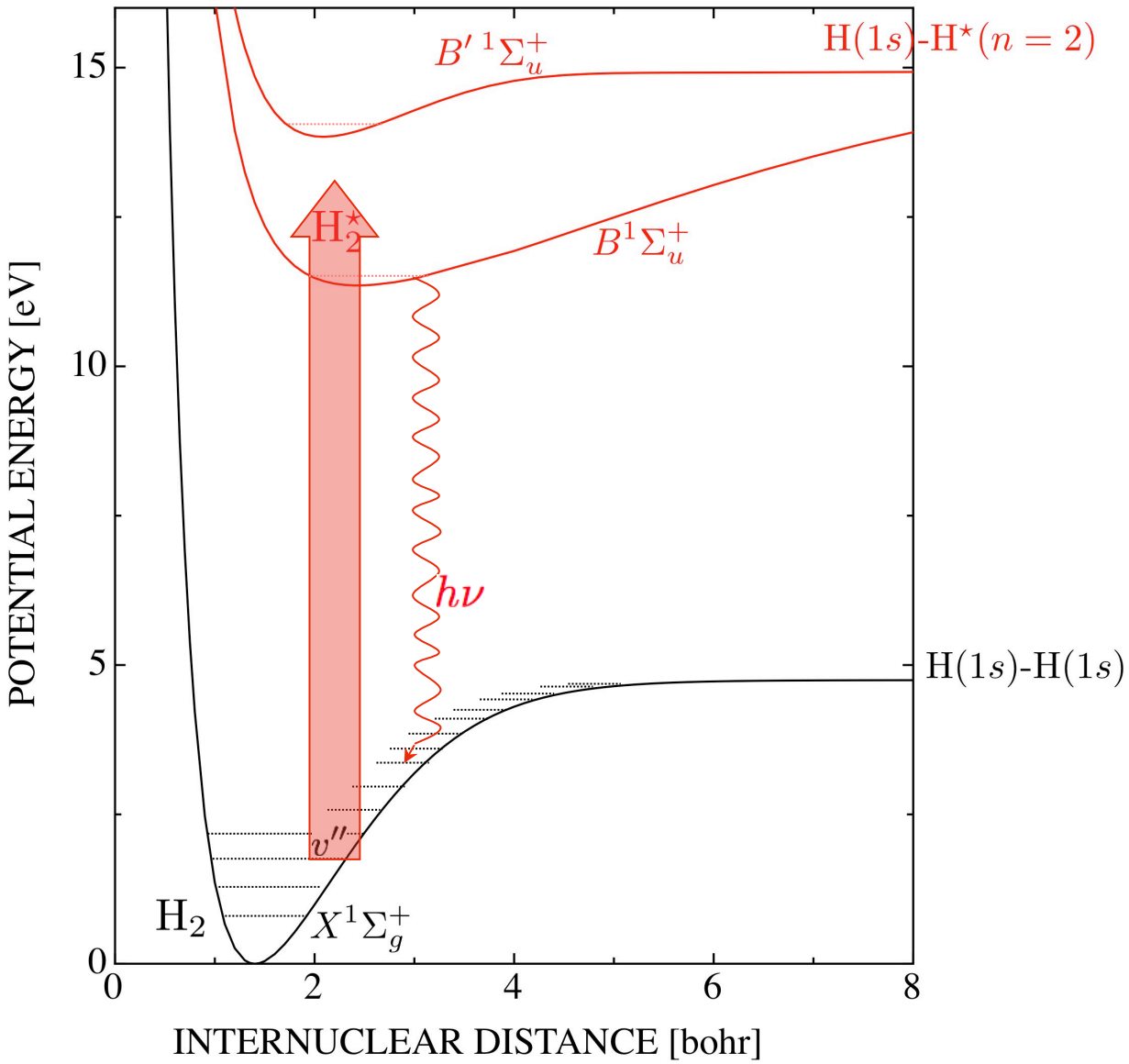
$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v'') &\rightleftharpoons H^- + H \\
e^- + H_2^+ &\rightleftharpoons H^- + H^+ \\
H^- + H^+ &\rightleftharpoons H(n=1) + H(n>1) \\
H^- + H_2^+ &\rightleftharpoons H_2(v''=0) + H(n=1) \\
H^- + H_3^+ &\rightleftharpoons H_2(v''=0) + H_2(v''=0)
\end{aligned}
$$

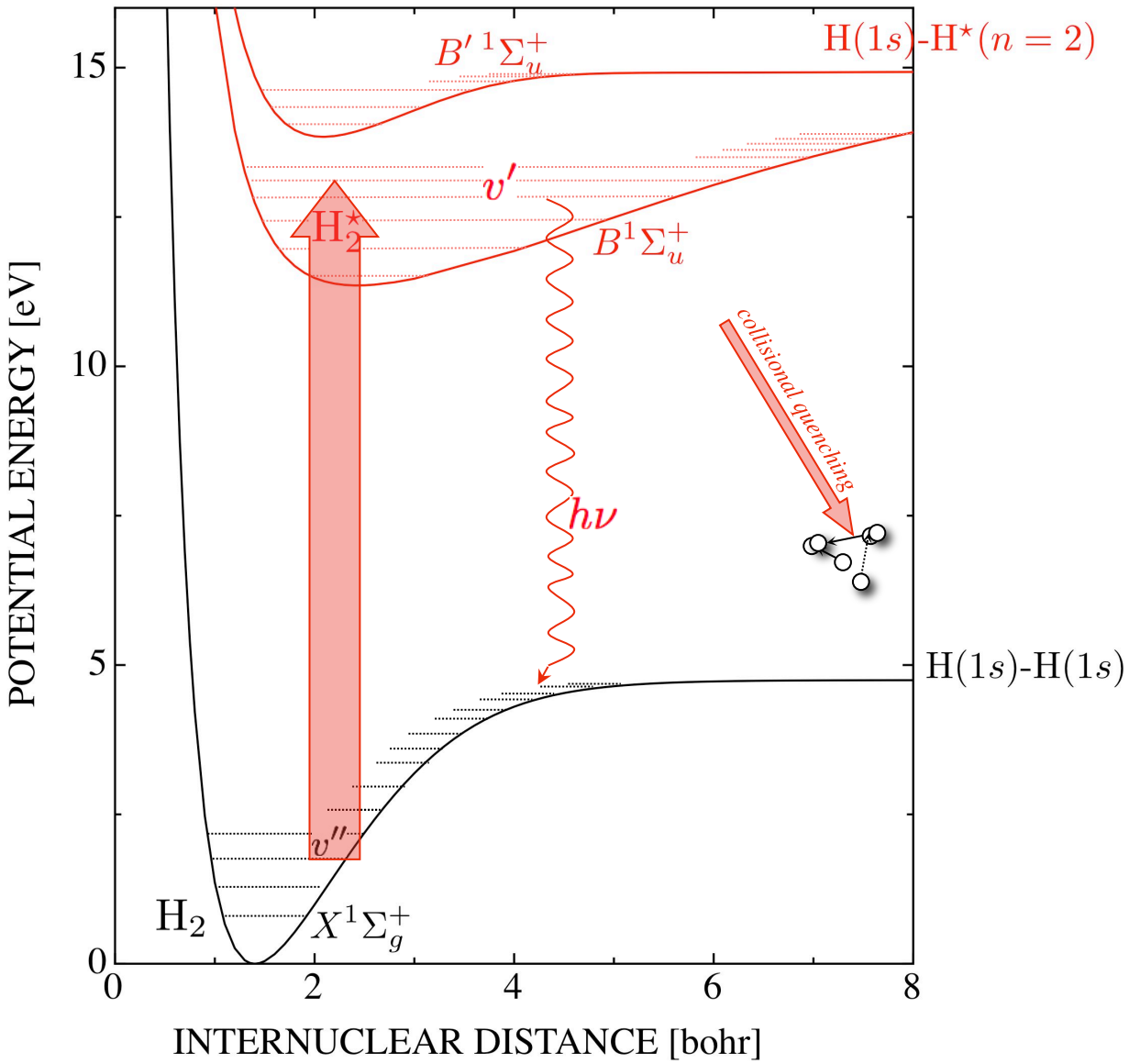
Trihydrogen cation kinetics

$$
\begin{aligned}
H^+ + 2H_2(v''=0) &\rightleftharpoons H_3^+ + H_2(v''=0) \\
H_2^+ + H_2(v''=0) &\rightleftharpoons H_3^+ + H(n=1) \\
e^- + H_3^+ &\rightleftharpoons e^- + H^+ + 2H(n=1) \\
e^- + H_3^+ &\rightarrow H_2^+ + H^- + h\nu \\
e^- + H_3^+ &\rightarrow H_2(v=0) + H(n=1) \\
e^- + H_3^+ &\rightarrow 3H(n=1)
\end{aligned}
$$


POTENTIAL ENERGY [eV]
INTERNUCLEAR DISTANCE [bohr]
0
5
10
15
0
2
4
6
8
$B'\,^1\Sigma_u^+$
H(1s)-H*(n = 2)
$B^1\Sigma_u^+$
$b^3\Sigma_u^+$
$^2\Sigma_g^+$
H(1s)-H(1s)
H_2^-
$^2\Sigma_u^+$
dissociative attachment
H(1s)-H$^-$
w''
$v''=0$
H_2
$X^1\Sigma_g^+$

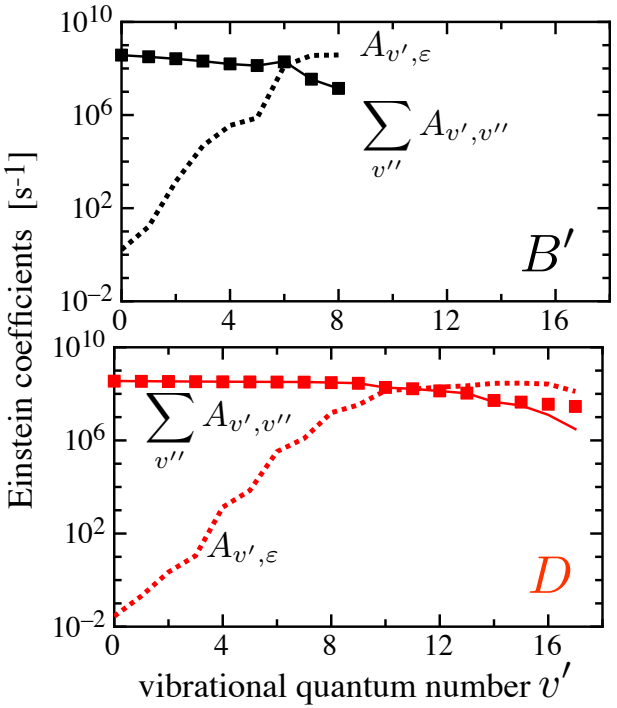

POTENTIAL ENERGY [eV]
INTERNUCLEAR DISTANCE [bohr]
0
5
10
15
0
2
4
6
8
$B'\,^1\Sigma_u^+$
H(1s)-H*(n = 2)
$B^1\Sigma_u^+$
$b^3\Sigma_u^+$
$^2\Sigma_g^+$
H_2^-
$^2\Sigma_u^+$
dissociative attachment
H(1s)-H(1s)
H(1s)-H$^-$
w''
$v'' > 0$
H_2
$X^1\Sigma_g^+$


$B'\,^1\Sigma_u^+$
H(1s)-H*($n=2$)
$H_2^\star$
$B^1\Sigma_u^+$
$h\nu$
H(1s)-H(1s)
v''
H_2
$X^1\Sigma_g^+$
POTENTIAL ENERGY [eV]
INTERNUCLEAR DISTANCE [bohr]
0
5
10
15
0
2
4
6
8

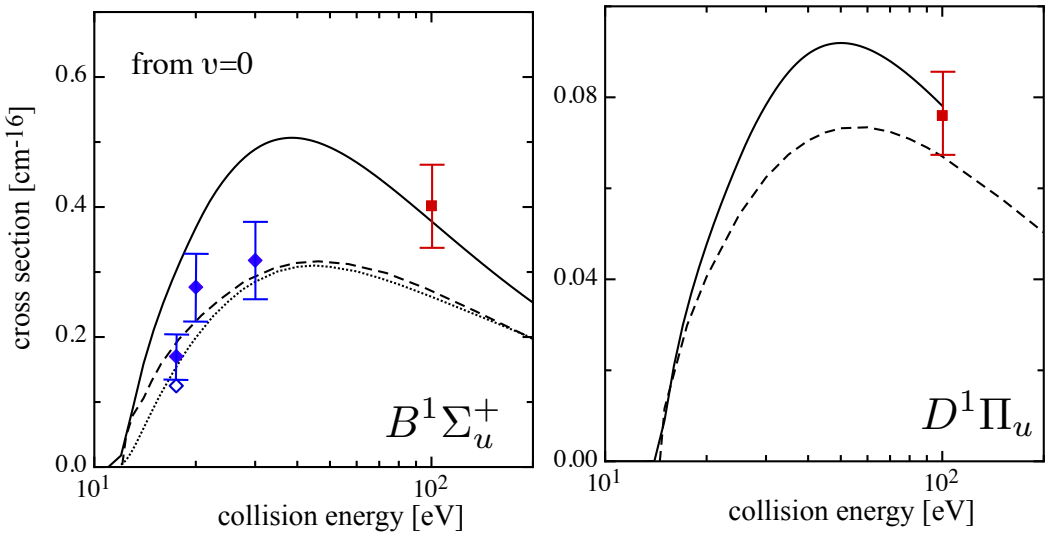

POTENTIAL ENERGY [eV]
INTERNUCLEAR DISTANCE [bohr]
0
5
10
15
0
2
4
6
8
$B'\,^1\Sigma_u^+$
H(1s)-H*(n = 2)
v'
$H_2^\star$
$B^1\Sigma_u^+$
collisional quenching
$h\nu$
H(1s)-H(1s)
v''
H_2
$X^1\Sigma_g^+$

Fast discharges in hydrogen
State resolved data

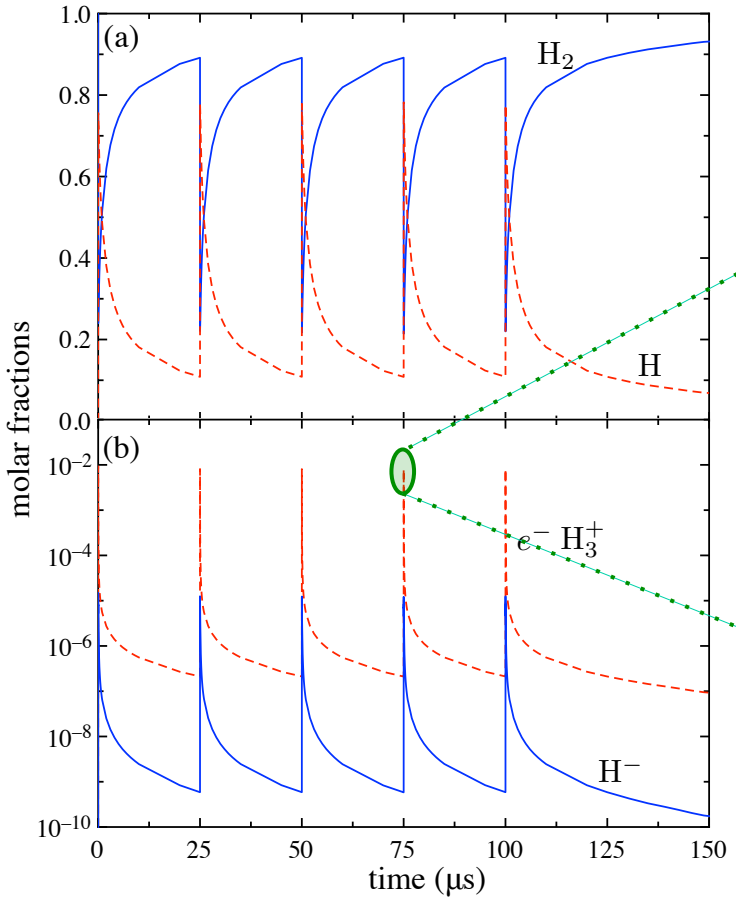
■ U. Fantz, D. Wünderlich, Atomic Data and Nuclear Data Tables 92, 853 (2006)

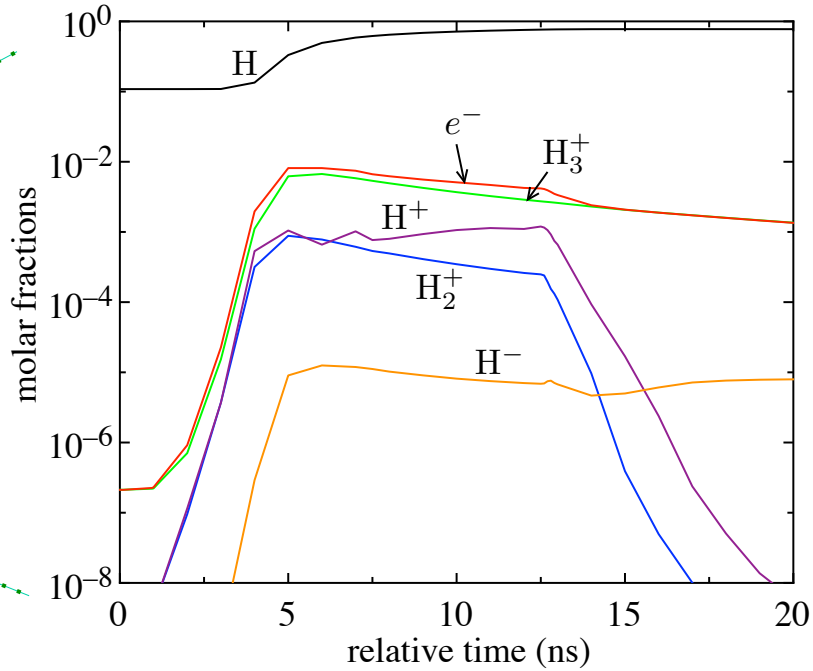


R. Celiberto et al., atomic data and nuclear data tables (2001)
H. Tanaka et al. Reviews of Modern Physics (2016)
Y.K. Kim, The Journal of chemical physics (2007)
◇ M.C. Zammit et al., Physical Review Letters (2016)
J. Ajello et al., Physical Review A (1984)
J. Wrkich et al., Journal of Physics B (2002)



Fast discharges in hydrogen
Multi pulse evolution





For n>2 periodic behavior is observed

H_2/H STATE-TO-STATE KINETICS

Updated model (f)

Singlets vibrational kinetics

$$
\begin{aligned}
H_2(X^1\Sigma_g^+, v'') + e^- &\rightleftharpoons H_2(^1Y^\star, \text{⊘}) + e^- \\
H_2(^1Y^\star, \text{⊘}) &\rightarrow H_2(X^1\Sigma_g^+, v'') + h\nu \\
H_2(^1Y^\star, \text{⊘}) &\rightarrow H_2(X^1\Sigma_a^+, \varepsilon) + h\nu \rightarrow 2H(n=1)
\end{aligned}
$$

$(f-q)$

Triples kinetics

$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v) &\rightleftharpoons e^- + H_2(a^3\Sigma_g^+) \\
H_2(a^3\Sigma_g^+) &\rightarrow H_2(b^3\Sigma_u^+) + h\nu \rightarrow 2H(n=1) \\
H_2(a^3\Sigma_g^+) + H_2/H &\rightleftharpoons H_2(c^3\Pi_u) + H_2/H \\
H_2(c^3\Pi_u) + H_2/H &\rightleftharpoons 2H + H_2/H
\end{aligned}
$$

Negative Ions kinetics

$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v'') &\rightleftharpoons H^- + H \\
e^- + H_2^+ &\rightleftharpoons H^- + H^+ \\
H^- + H^+ &\rightleftharpoons H(n=1) + H(n>1) \\
H^- + H_2^+ &\rightleftharpoons H_2(v''=0) + H(n=1) \\
H^- + H_3^+ &\rightleftharpoons H_2(v''=0) + H_2(v''=0)
\end{aligned}
$$

Trihydrogen cation kinetics

$$
\begin{aligned}
H^+ + 2H_2(v''=0) &\rightleftharpoons H_3^+ + H_2(v''=0) \\
H_2^+ + H_2(v''=0) &\rightleftharpoons H_3^+ + H(n=1) \\
e^- + H_3^+ &\rightleftharpoons e^- + H^+ + 2H(n=1) \\
e^- + H_3^+ &\rightarrow H_2^+ + H^- + h\nu \\
e^- + H_3^+ &\rightarrow H_2(v=0) + H(n=1) \\
e^- + H_3^+ &\rightarrow 3H(n=1)
\end{aligned}
$$

H_2/H STATE-TO-STATE KINETICS

Updated model (f)

Singlets vibrational kinetics

$$
\begin{aligned}
H_2(X^1\Sigma_g^+, v'') + e^- &\rightleftharpoons H_2(^1Y^\star, \text{⦻}) + e^- \\
H_2(^1Y^\star, \text{⦻}) &\rightarrow H_2(X^1\Sigma_g^+, v'') + h\nu \\
H_2(^1Y^\star, \text{⦻}) &\rightarrow H_2(X^1\Sigma_a^+, \varepsilon) + h\nu \rightarrow 2H(n=1)
\end{aligned}
$$

$(f-q)$

Triples kinetics

$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v) &\rightleftharpoons e^- + H_2(a^3\Sigma_g^+) \\
H_2(a^3\Sigma_g^+) &\rightarrow H_2(b^3\Sigma_u^+) + h\nu \rightarrow 2H(n=1) \\
H_2(a^3\Sigma_g^+) + H_2/H &\rightleftharpoons H_2(c^3\Pi_u) + H_2/H \\
H_2(c^3\Pi_u) + H_2/H &\rightleftharpoons 2H + H_2/H
\end{aligned}
$$

Negative Ions kinetics

$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v'') &\rightleftharpoons H^- + H \\
e^- + H_2^+ &\rightleftharpoons H^- + H^+ \\
H^- + H^+ &\rightleftharpoons H(n=1) + H(n>1) \\
H^- + H_2^+ &\rightleftharpoons H_2(v''=0) + H(n=1) \\
H^- + H_3^+ &\rightleftharpoons H_2(v''=0) + H_2(v''=0)
\end{aligned}
$$

Trihydrogen cation kinetics

$$
\begin{aligned}
H^+ + 2H_2(v''=0) &\rightleftharpoons H_3^+ + H_2(v''=0) \\
H_2^+ + H_2(v''=0) &\rightleftharpoons H_3^+ + H(n=1) \\
e^- + H_3^+ &\rightleftharpoons e^- + H^+ + 2H(n=1) \\
e^- + H_3^+ &\rightarrow H_2^+ + H^- + h\nu \\
e^- + H_3^+ &\rightarrow H_2(v=0) + H(n=1) \\
e^- + H_3^+ &\rightarrow 3H(n=1)
\end{aligned}
$$

H_2/H STATE-TO-STATE KINETICS

Updated model (f)

Singlets vibrational kinetics

$$
\begin{aligned}
H_2(X^1\Sigma_g^+, v'') + e^- &\rightleftharpoons H_2(^1Y^\star, \text{⦻}) + e^- \\
H_2(^1Y^\star, \text{⦻}) &\rightarrow H_2(X^1\Sigma_g^+, v'') + h\nu \\
H_2(^1Y^\star, \text{⦻}) &\rightarrow H_2(X^1\Sigma_a^+, \varepsilon) + h\nu \rightarrow 2H(n=1)
\end{aligned}
$$

$(f-v)$

$(f-q)$

Triples kinetics

$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v) &\rightleftharpoons e^- + H_2(a^3\Sigma_g^+) \\
H_2(a^3\Sigma_g^+) &\rightarrow H_2(b^3\Sigma_u^+) + h\nu \rightarrow 2H(n=1) \\
H_2(a^3\Sigma_g^+) + H_2/H &\rightleftharpoons H_2(c^3\Pi_u) + H_2/H \\
H_2(c^3\Pi_u) + H_2/H &\rightleftharpoons 2H + H_2/H
\end{aligned}
$$

Negative Ions kinetics

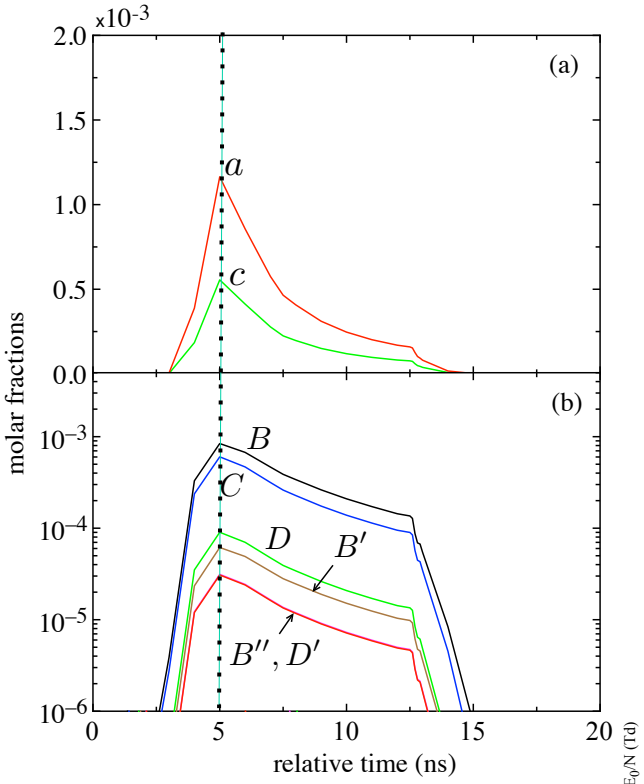
$$
\begin{aligned}
e^- + H_2(X^1\Sigma_g^+, v'') &\rightleftharpoons H^- + H \\
e^- + H_2^+ &\rightleftharpoons H^- + H^+ \\
H^- + H^+ &\rightleftharpoons H(n=1) + H(n>1) \\
H^- + H_2^+ &\rightleftharpoons H_2(v''=0) + H(n=1) \\
H^- + H_3^+ &\rightleftharpoons H_2(v''=0) + H_2(v''=0)
\end{aligned}
$$

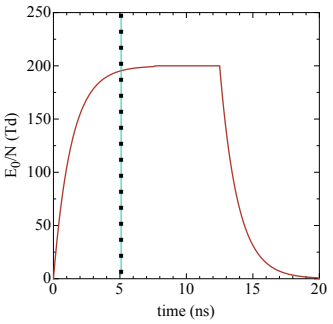
Trihydrogen cation kinetics

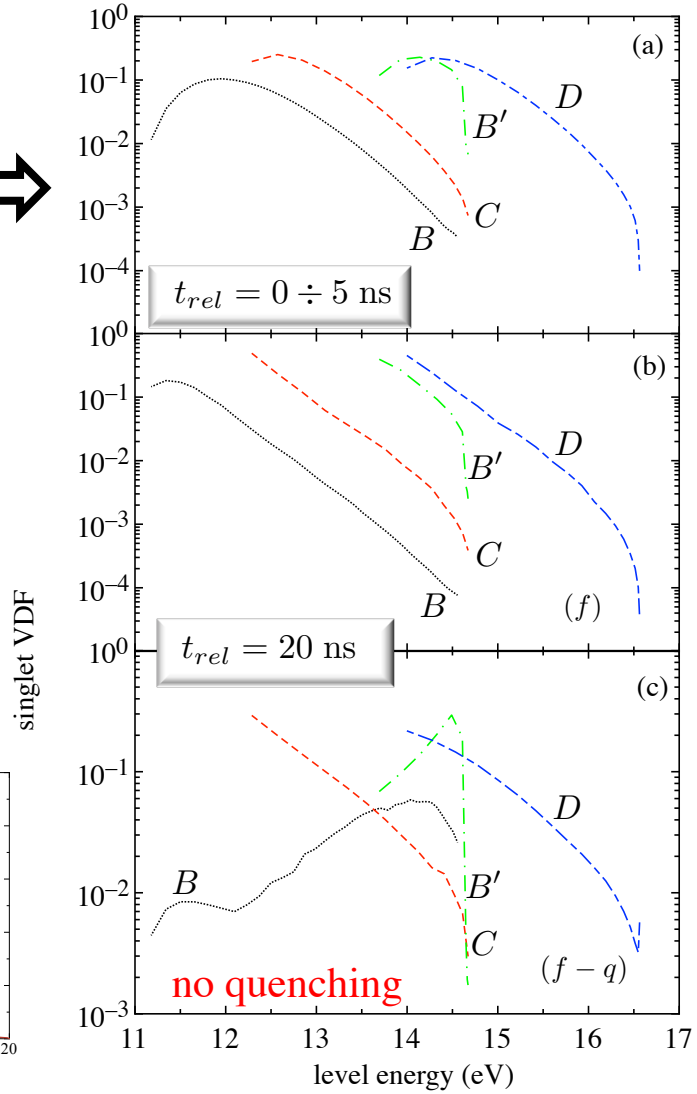
$$
\begin{aligned}
H^+ + 2H_2(v''=0) &\rightleftharpoons H_3^+ + H_2(v''=0) \\
H_2^+ + H_2(v''=0) &\rightleftharpoons H_3^+ + H(n=1) \\
e^- + H_3^+ &\rightleftharpoons e^- + H^+ + 2H(n=1) \\
e^- + H_3^+ &\rightarrow H_2^+ + H^- + h\nu \\
e^- + H_3^+ &\rightarrow H_2(v=0) + H(n=1) \\
e^- + H_3^+ &\rightarrow 3H(n=1)
\end{aligned}
$$

Fast discharges in hydrogen

Excited state concentration & singlets vibrational distributions

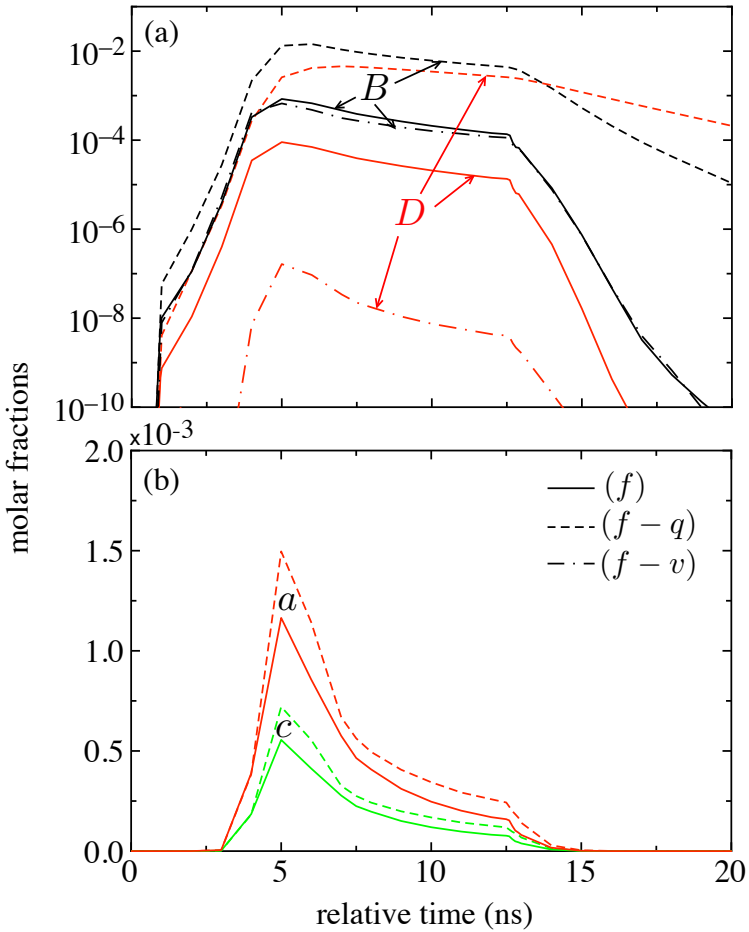




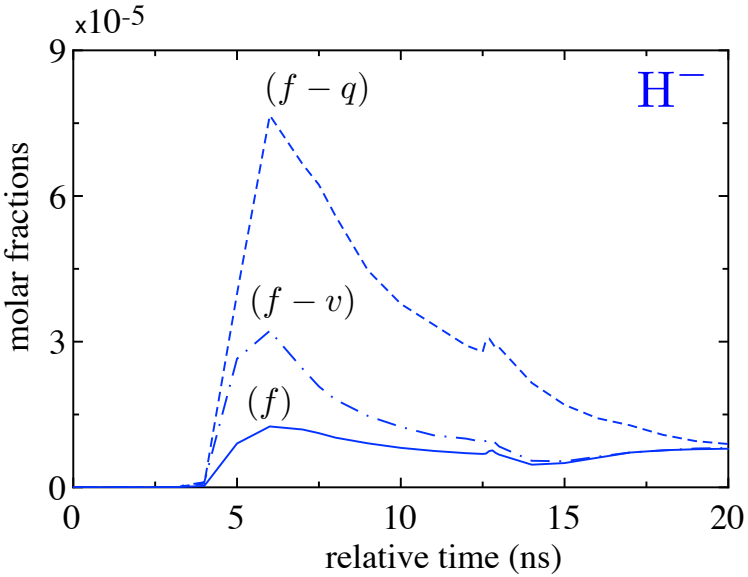


Fast discharges in hydrogen
Effect of reduced models

on electronically excited states

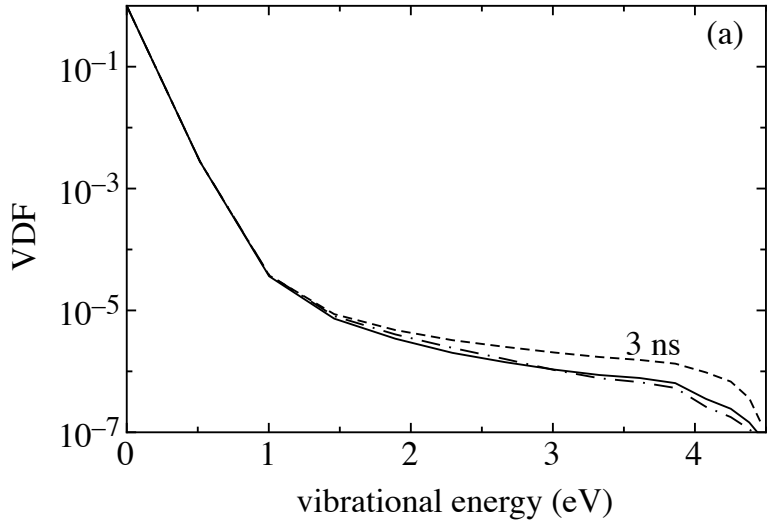


& on hydrogen negative ion



Fast discharges in hydrogen
Effect of reduced models

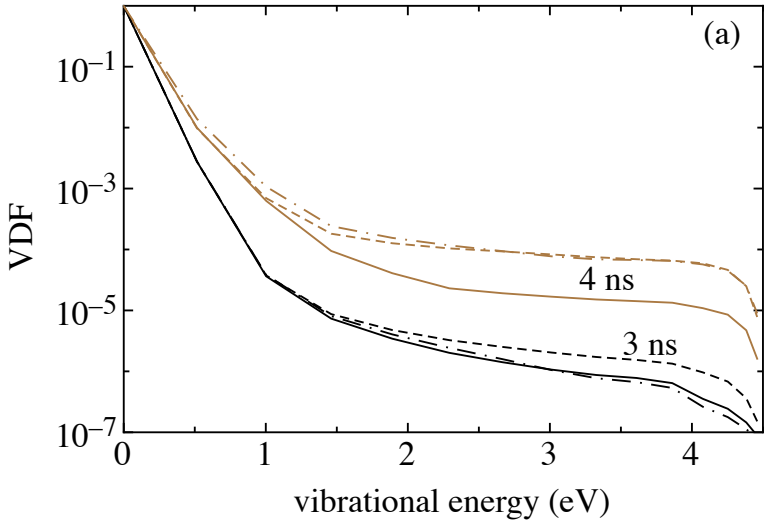
on ground state vibrational distributions



—— (f)
---- $(f-q)$
– · – $(f-v)$

Fast discharges in hydrogen
Effect of reduced models

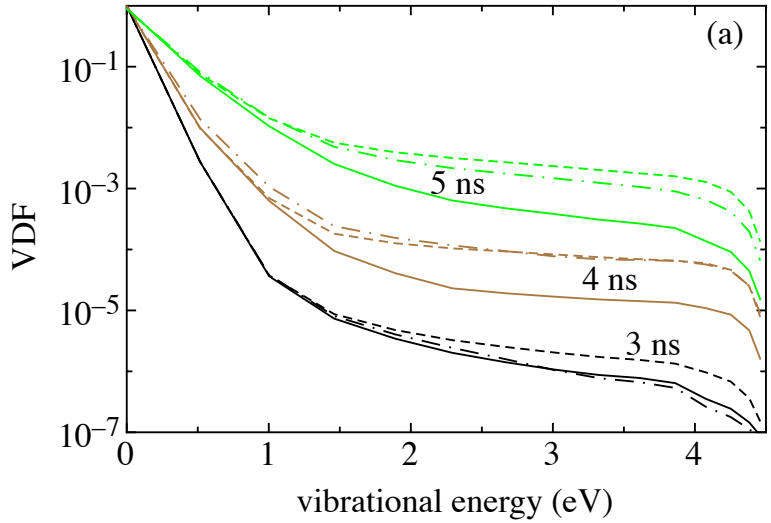
on ground state vibrational distributions



—— (f)
---- $(f-q)$
– · – $(f-v)$

Fast discharges in hydrogen
Effect of reduced models

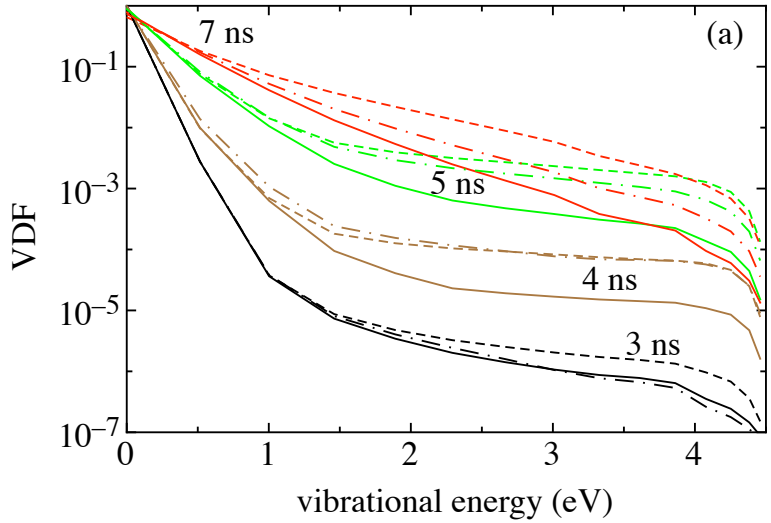
on ground state vibrational distributions



—— (f)
----$(f-q)$
– · –$(f-v)$

Fast discharges in hydrogen
Effect of reduced models

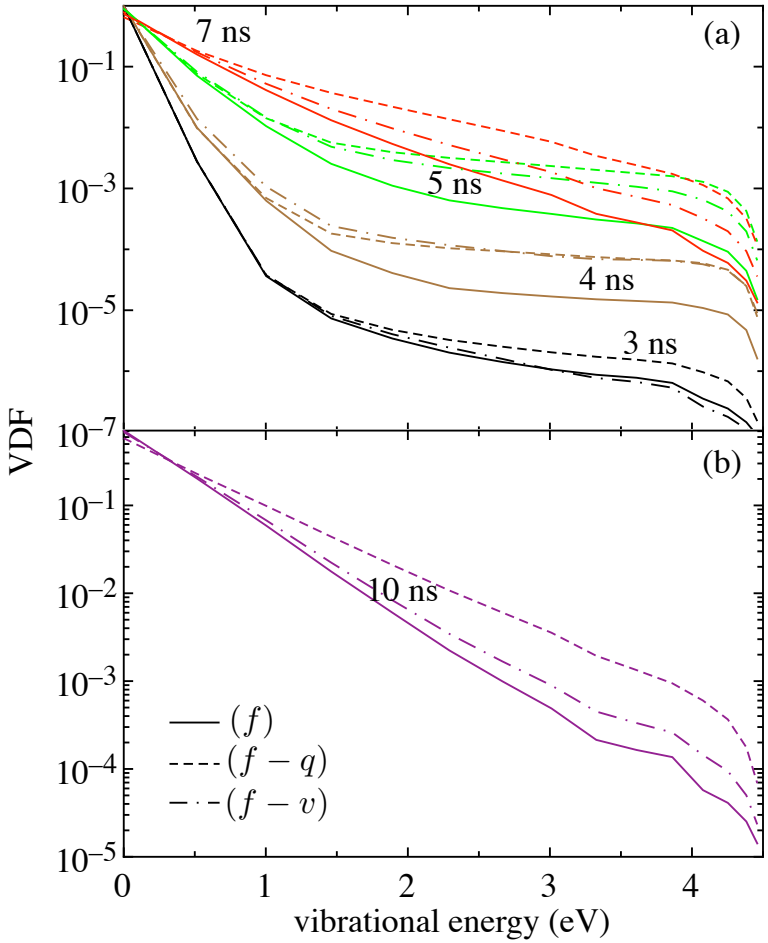
on ground state vibrational distributions



—— (f)
---- $(f-q)$
– · – $(f-v)$

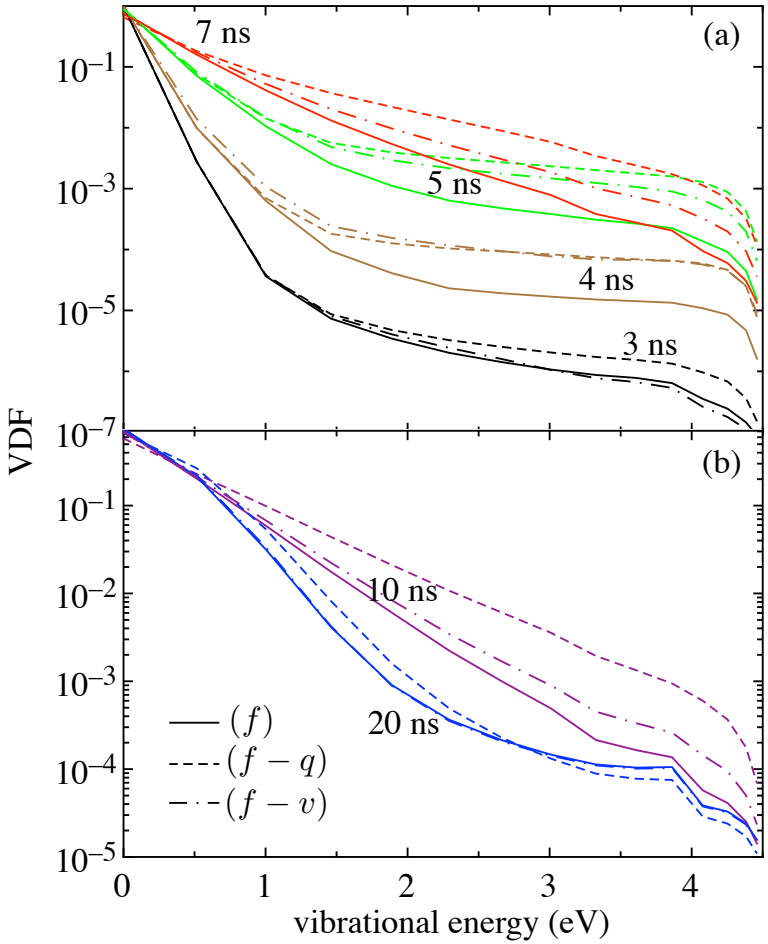
Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions

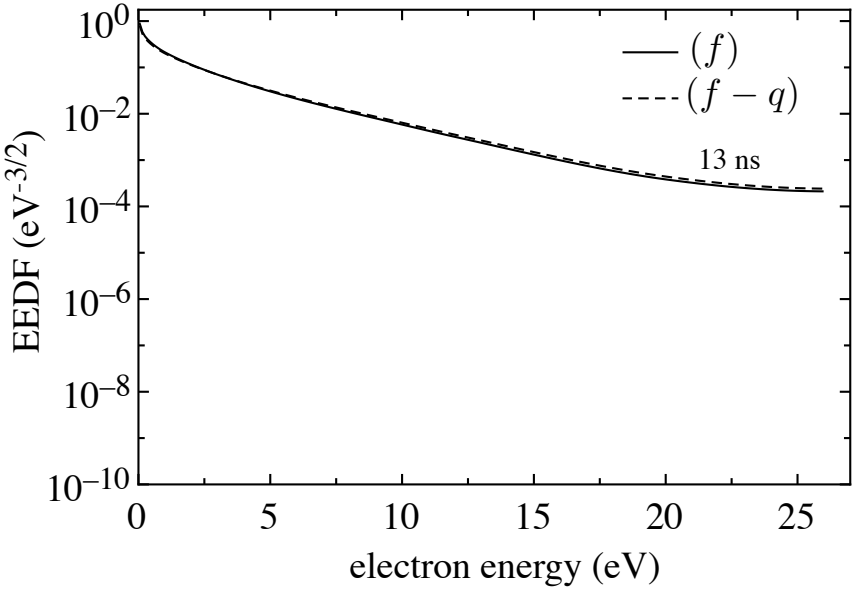


Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions

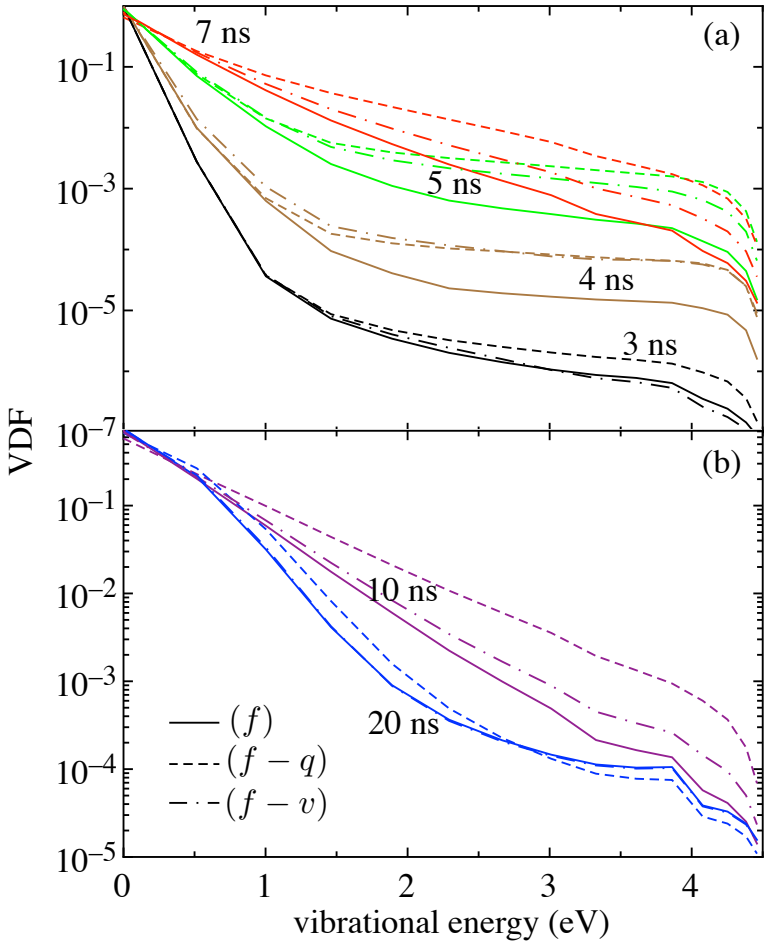


& on electron energy distribution

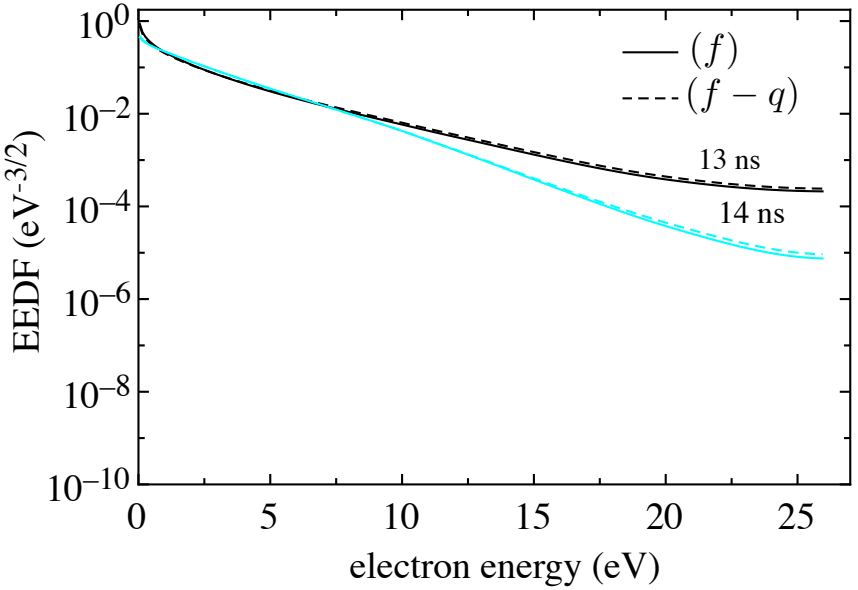


Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions

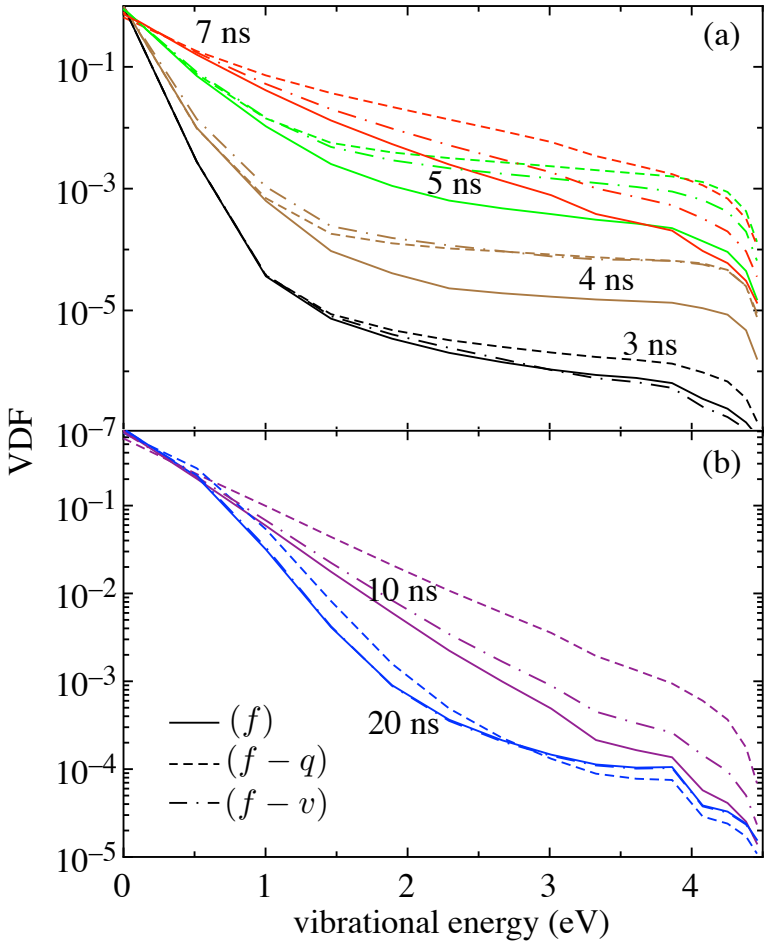


& on electron energy distribution

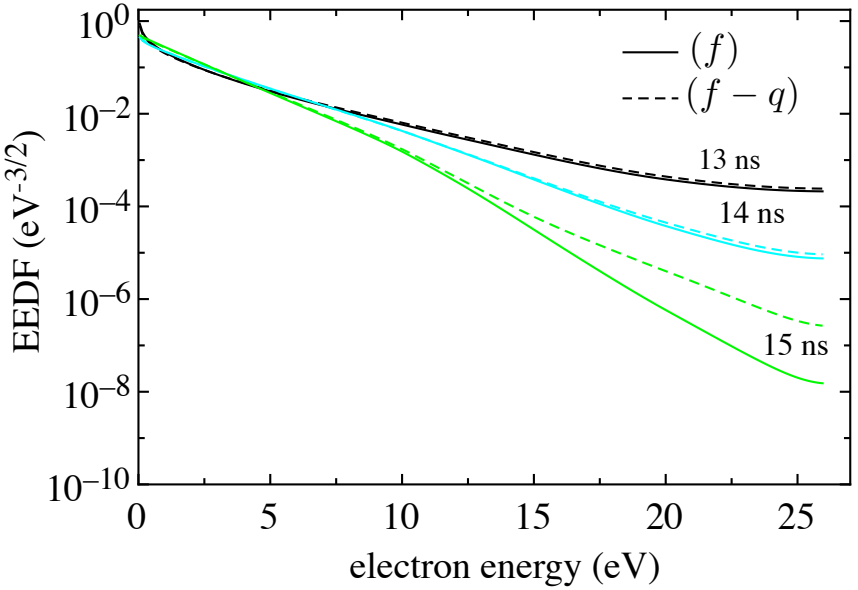


Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions

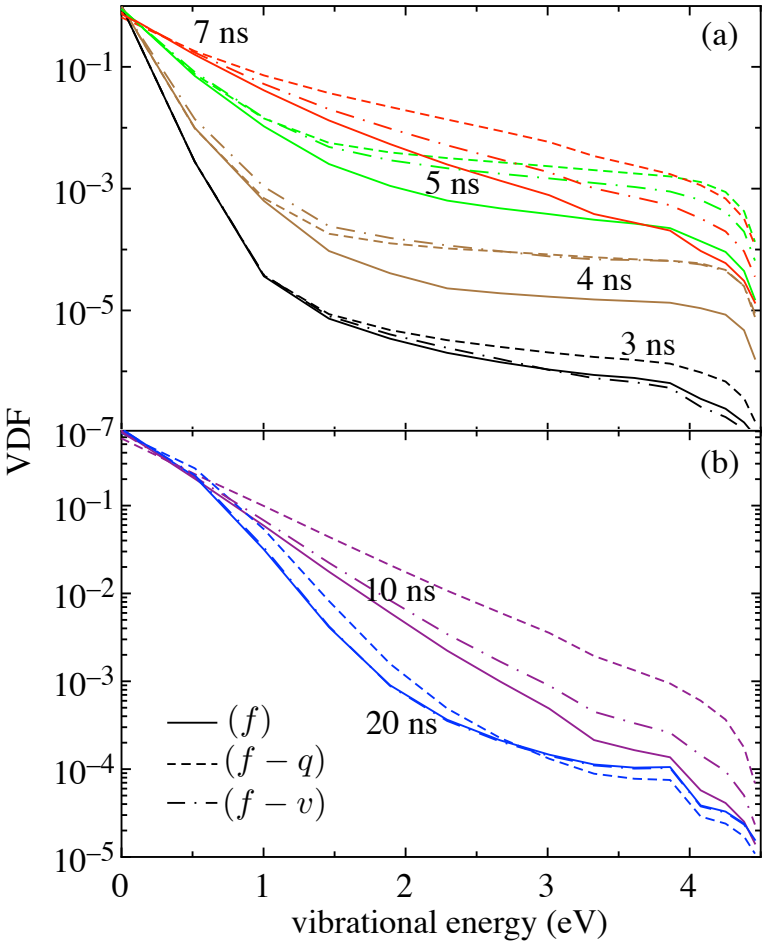


& on electron energy distribution

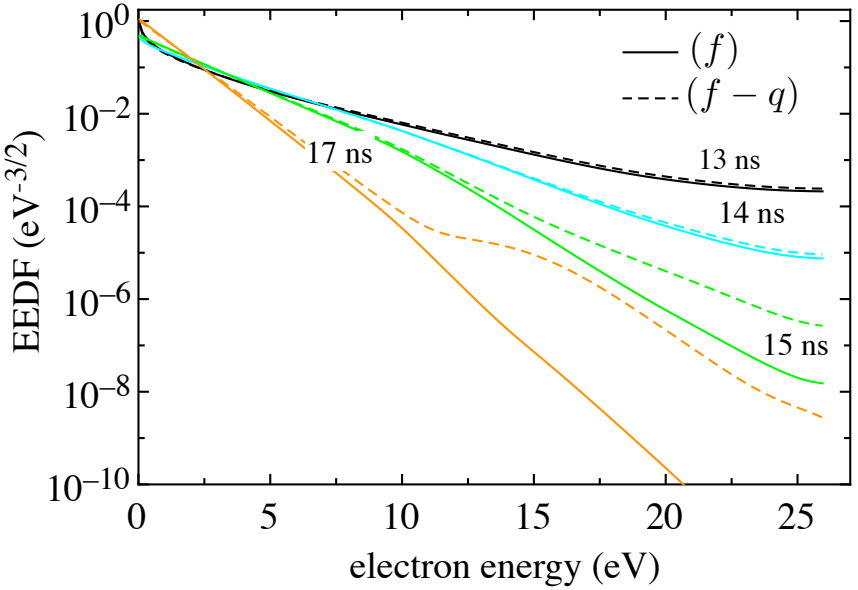


Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions

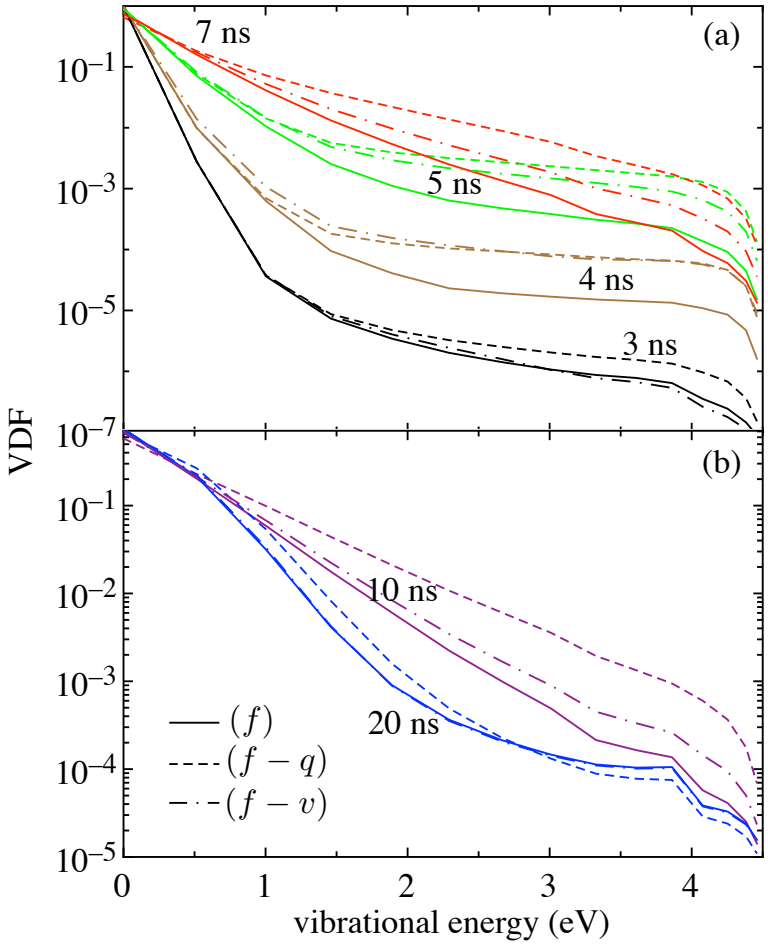


& on electron energy distribution

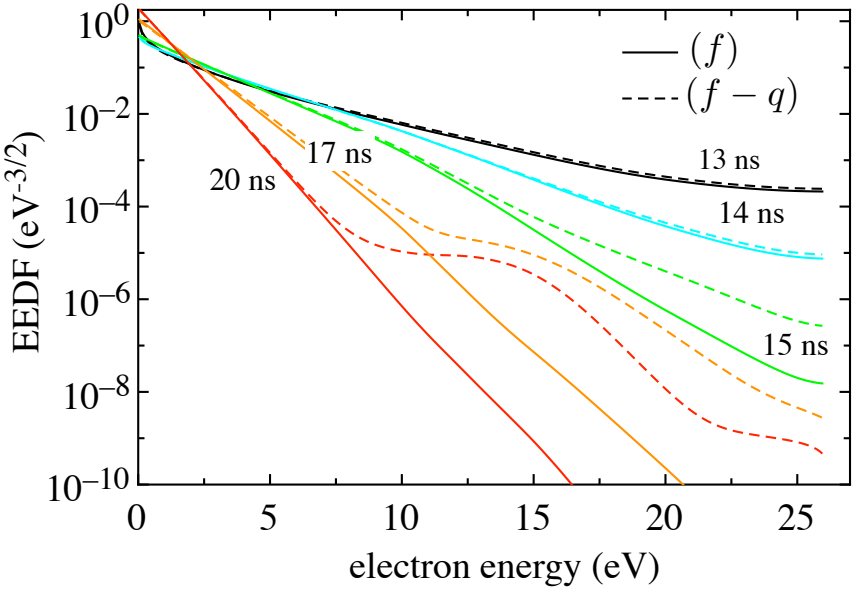


Fast discharges in hydrogen
Effect of reduced models

on ground state vibrational distributions



& on electron energy distribution



Dissociation by Pure Vibrational Mechanism (PVM)

- **eV** (**electron-vibration**) processes;
- **VV** (**vibration-vibration**) and
- **VT** (**vibrational-translation**) processes;
- **Dissociation** from the last vibrational level.

PVM Upper Limit dissociation rate

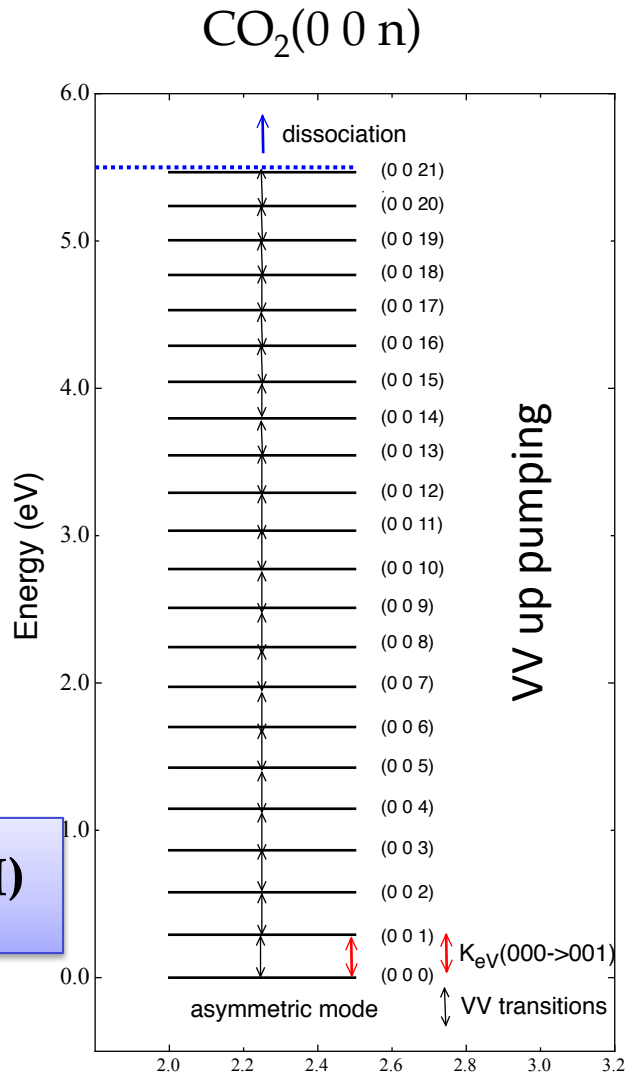
$$K_d^{(ulPVM)} = \frac{1}{\upsilon_{\max}} k_{eV}\left(000 \rightarrow 001\right)$$

including the effect of excited asymmetric mode vibrational levels

$$K_d^{(ulPVM)}\left(all\right) = \frac{1}{v_{\max}} \sum_n \frac{\varepsilon_{v_n}}{\varepsilon_{v_1}} k_{eV}(v_0 \rightarrow v_n)$$

Dissociation by Electron impact Mechanism (DEM)

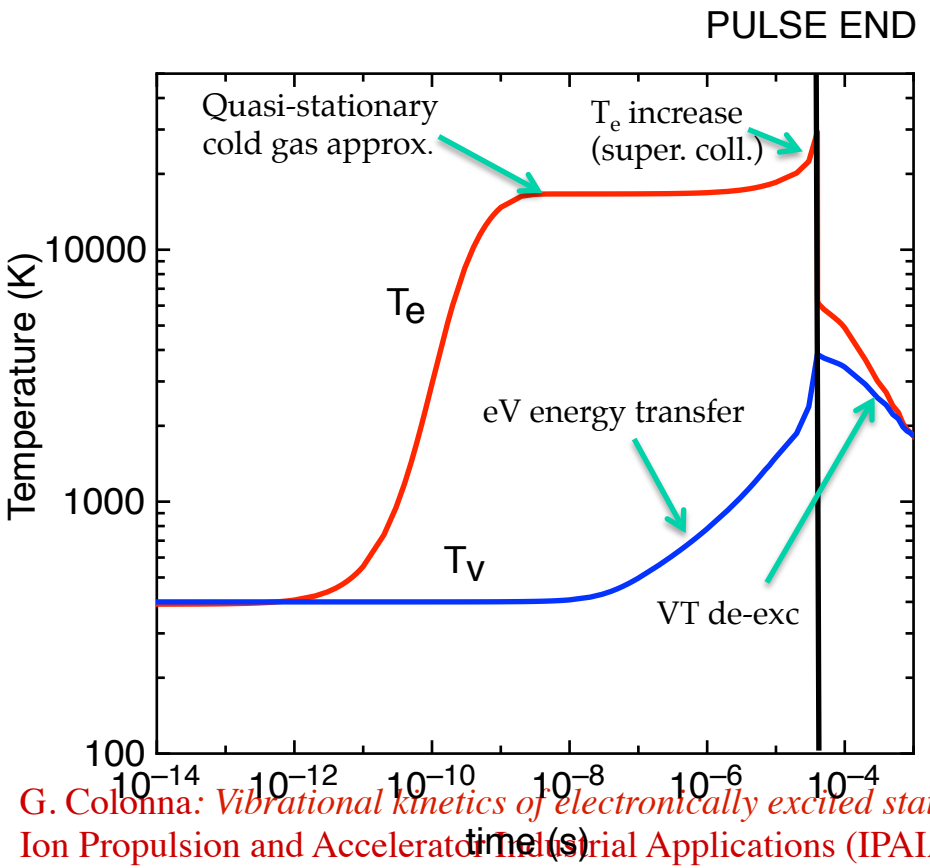
$$k_d(000) = \int_{E_{thr}} f(\varepsilon)\sigma_D(\varepsilon)v(\varepsilon)d\varepsilon$$

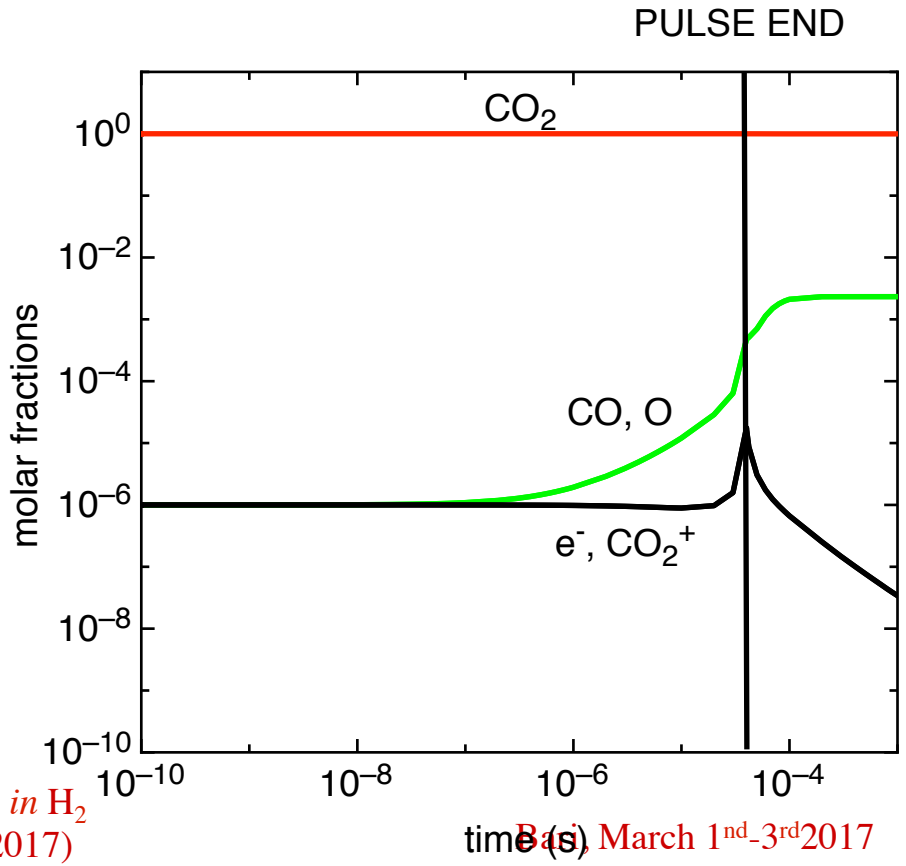


Selfconsistent results

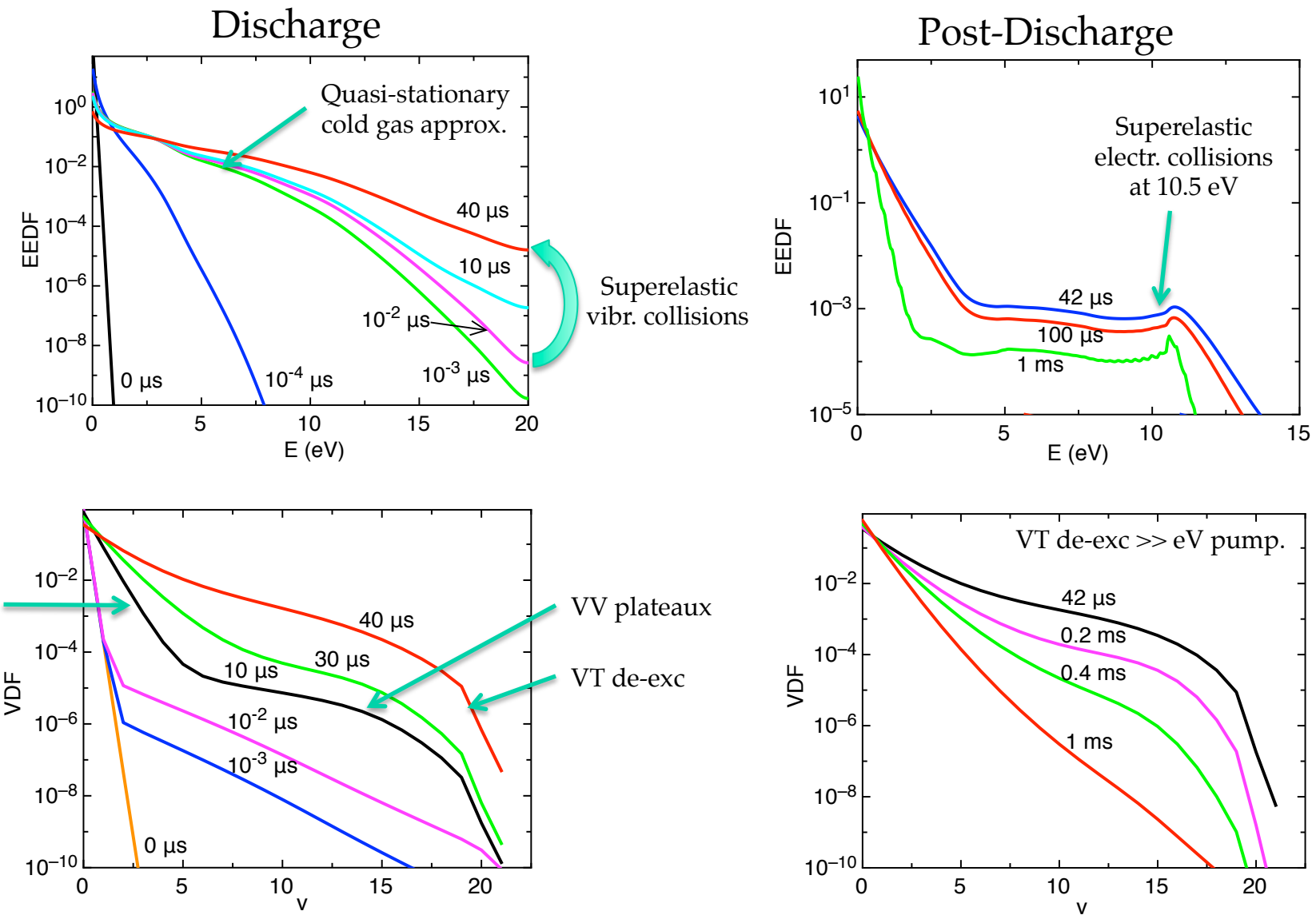
Study case 1: P=20 torr, τ_{pulse}=40 μs, E/N=50 Td, T_{gas}=400 K, $\chi_e(t=0)=10^{-6}$, α=0.8

τ_{pulse}	$\tau_{eedf}=\left(n_{CO_2}K_{eV}^{1,0}\right)^{-1}$	$\tau_{eV}=\left(n_e K_{eV}^{1,0}\right)^{-1}$	$\tau_{VV}=\left(n_{CO_2}K_{1,0}^{0,1}\right)^{-1}$	$\tau_{VT}=\left(n_{CO_2}K_{VT}^{1,0}\right)^{-1}$
$4\ 10^{-5}$ s	$3.69\ 10^{-10}$ s	$2.09\ 10^{-5}$ s	$1.50\ 10^{-8}$ s	$1.94\ 10^{-4}$ s





Study case 1: EEDF and VDF



Conclusions

- Self-consistent chemical kinetics has been applied to model gas discharges in hydrogen and CO_2.
- The self-consistent approach put in evidence the synergy between EEDF, level distributions and composition, including superelastic collisions.
- DB of electron impact cross sections has been improved by adding transitions from excited vibrational level of $X^1\Sigma$ state.
- Vibrational kinetics of singlet states have been included to properly consider dissociative channels and radiative decay.
- Positive and negative ion kinetics has been improved.
- FUTURE WORK (in progress): Improvement of DBD model.