Vibrational Kinetics, electron dynamics and elementary processes in H_2 and D_2 Plasmas for Negative Ion Production: Modelling Aspects

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Outline

1) Open problems (1985-1995) in Multipole Magnetic Plasmas
   a) Validation of Bari code with FOM experiments
   b) Extension to D_2 plasmas
   c) Pulsed discharges
   d) Rydberg states
   d) Wall effects
2) Cross Section Improvements (1995-2005)
   a) Electron-molecule cross sections
   b) Heavy particle collision cross sections
   c) Gas surface interaction
3) Kinetic models Improvements(1995-2005)
   a) New multipole zerodimensional code
   b) Parallel-plate 1D code
   c) RF and MW quasi 1D code
4) Conclusions

Vibrational excitation and negative ion kinetics

Multipole Magnetic Plasmas

Self-consistent non equilibrium vibrational kinetics coupled to the Boltzmann equation for the electron energy distribution function

Time Evolution
(heavy species)

$$\left(\frac{dN_v}{dt}\right) = \left(\frac{dN_v}{dt}\right)_{e-V} + \left(\frac{dN_v}{dt}\right)_{E-V} + \left(\frac{dN_v}{dt}\right)_{V-V} + \left(\frac{dN_v}{dt}\right)_{V-T} + \left(\frac{dN_v}{dt}\right)_{e-D} + \left(\frac{dN_v}{dt}\right)_{e-I} + \left(\frac{dN_v}{dt}\right)_{e-da} + \left(\frac{dN_v}{dt}\right)_{e-E} + \left(\frac{dN_v}{dt}\right)_{wall}$$

$$\frac{\partial n(\varepsilon,t)}{\partial t} = -\left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-M} - \left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-e} + In + Ion + Sup + S - L$$

$S = \dfrac{I}{Ve\Delta\varepsilon_p}$ Electron source term

$-\left(\dfrac{\partial J_{el}}{\partial \varepsilon}\right)_{e-M}$ Flux of electrons along energy axis due to elastic collisions

$-\left(\dfrac{\partial J_{el}}{\partial \varepsilon}\right)_{e-e}$ Flux of electrons along energy axis due to electron-electron collisions

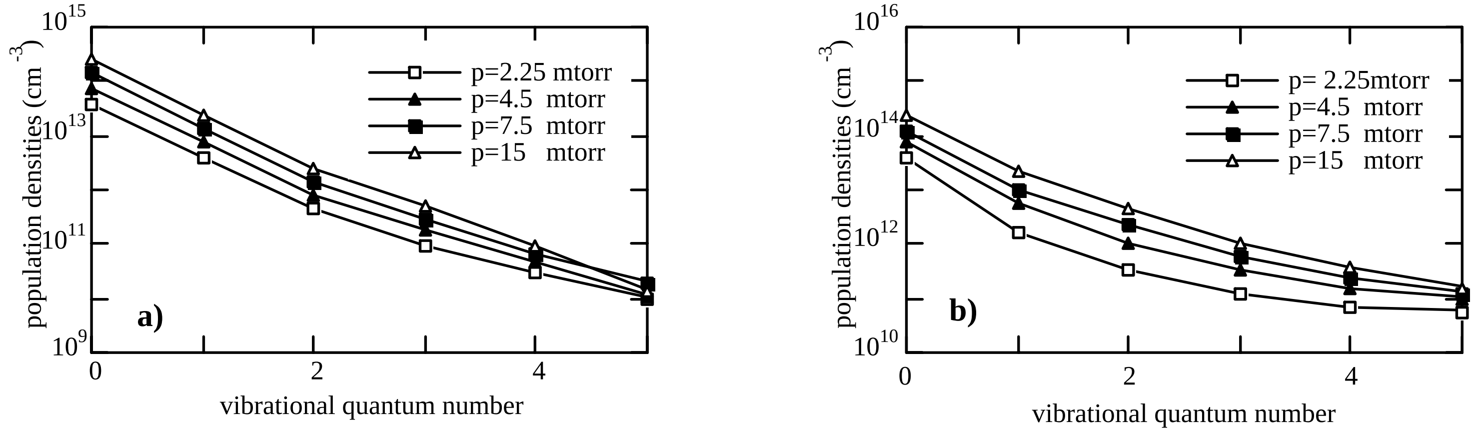
In Term due to inelastic collisions

Ion Term due to ionization collisions

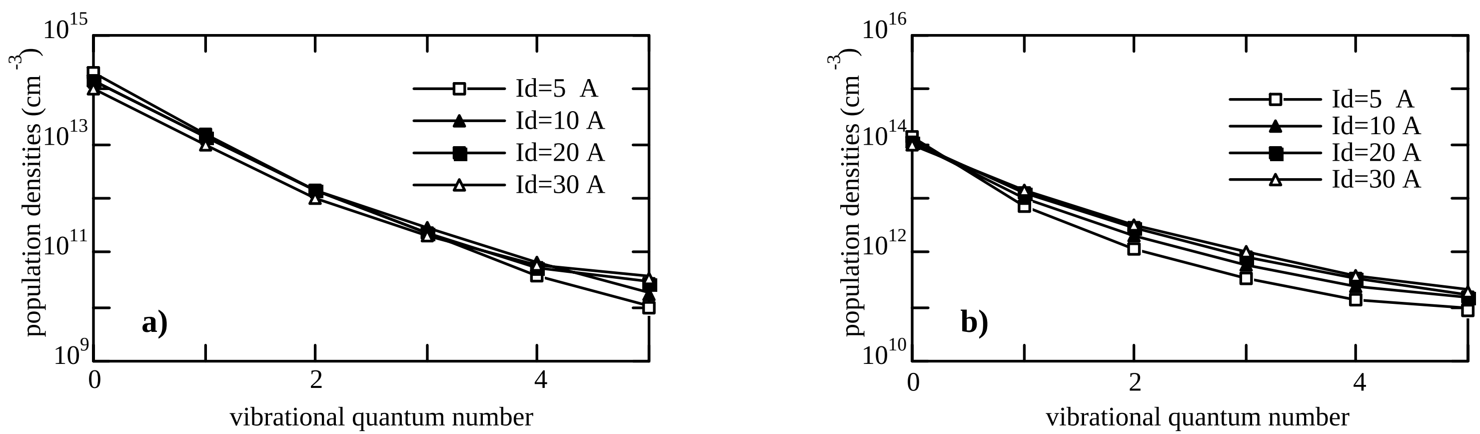
Sup Term due to superelastic collisions

L Electron loss term

Validation of Bari code with the FOM experiments (Gorse et al.1992)



comparison between experimental (a) and theoretical (b) vdfs at several pressures



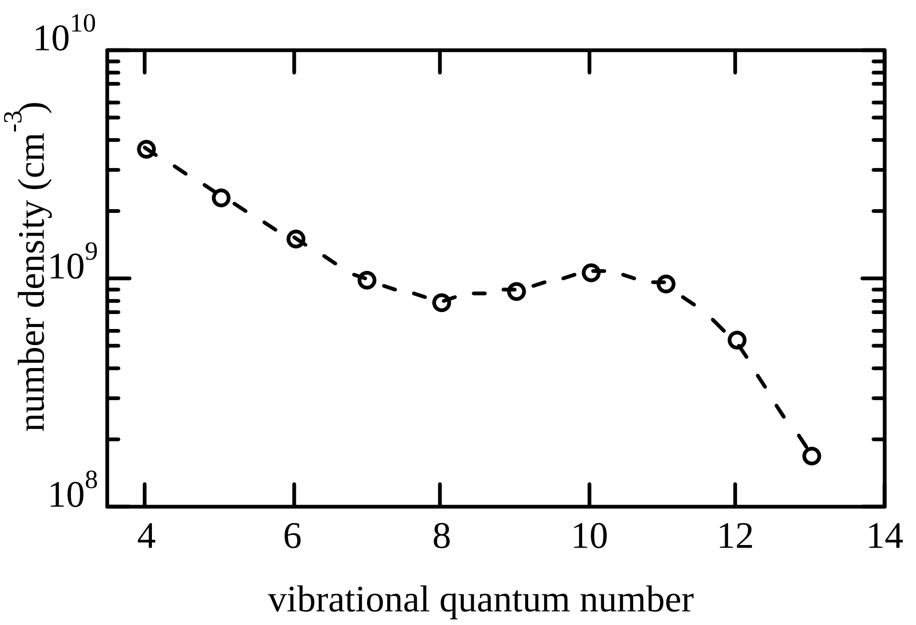
comparison between experimental (a) and theoretical (b) vdfs at several discharge currents I_d

Problems:

1) calculations overestimate by a factor 10 the high lying vibrational levels giving satisfactory agreement with negative ion concentrations

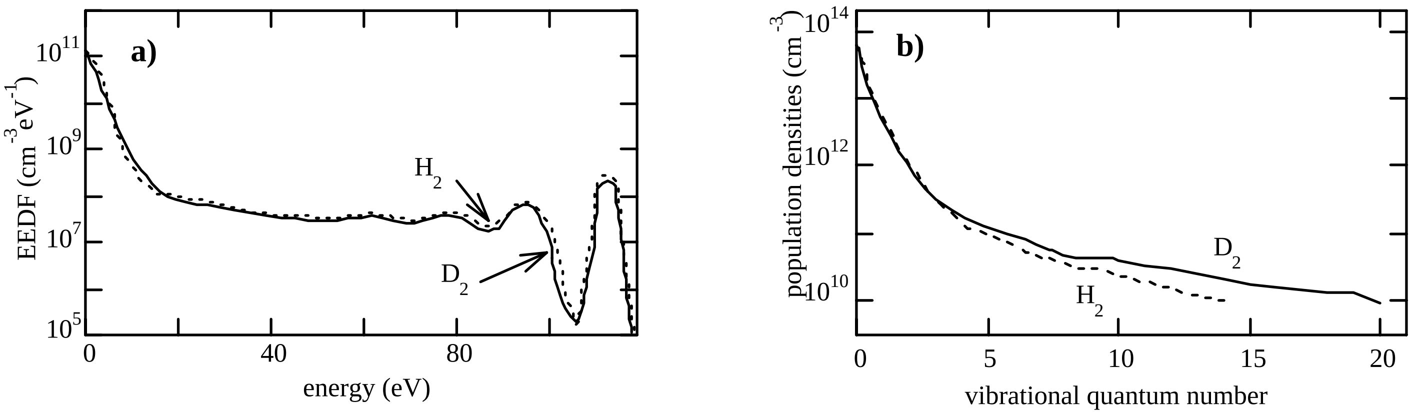
2) FOM experimental vibrational distributions limited to v=5

New: experimental determination by Mosbach and Dobele up to v=13

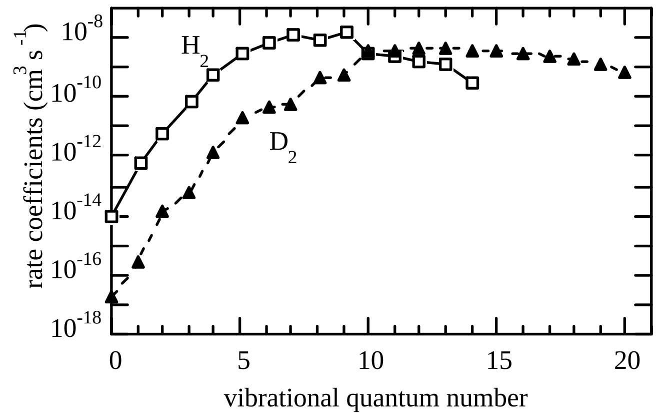


vibrational distribution N_v measured in a H_2 multicusp source (p = 11.25 mtorr, I_d = 0.5 A, V_d = 100 V)

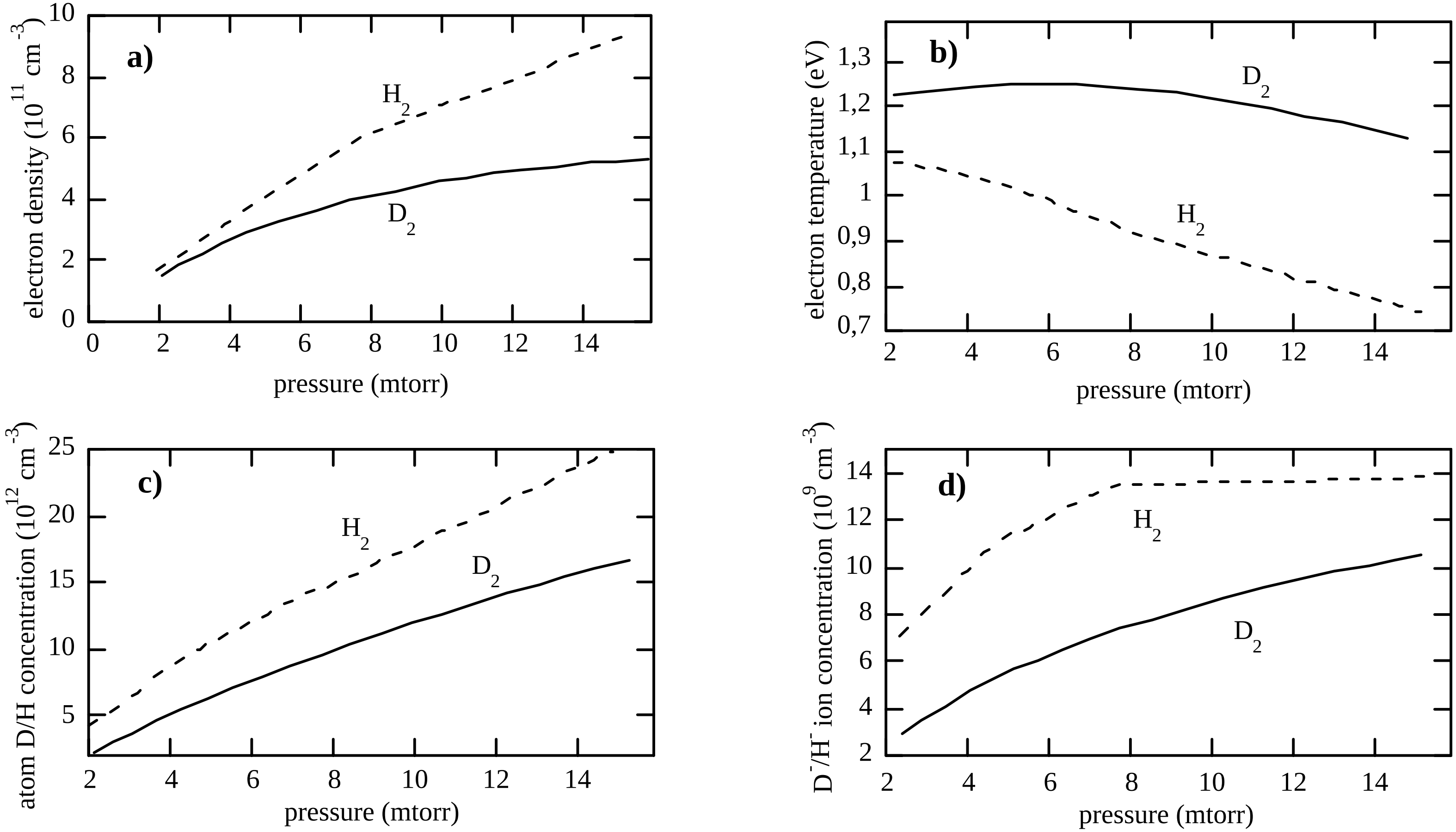
Extension to D_2 plasmas



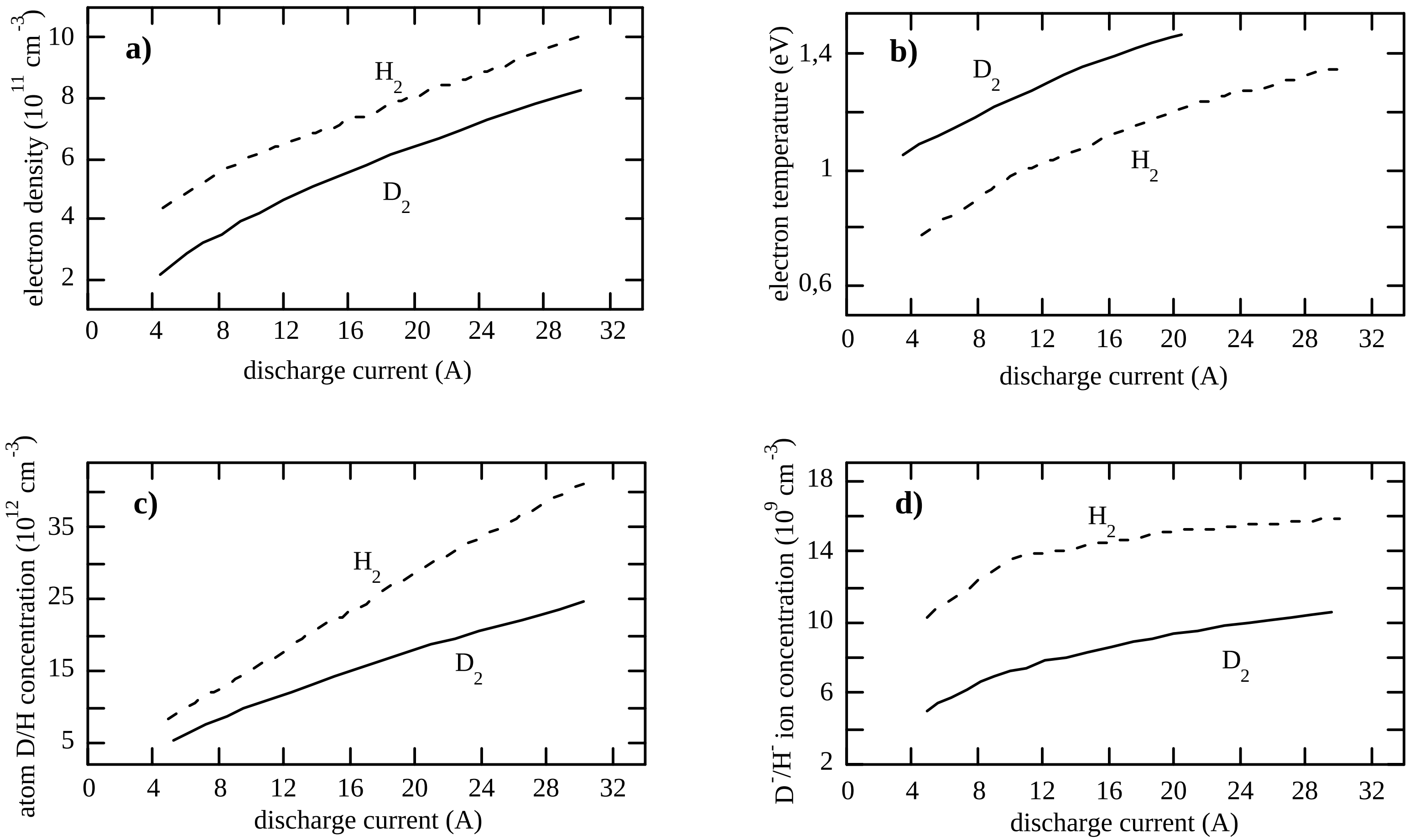
Theoretical *EEDF* (a) and N_v (b) in H_2 and D_2 sources (p = 4.5 mtorr, I_d = 10 A, V_d = 115 V, plasma potential V_p = 2.9 V)



Dissociative attachment rates versus vibrational quantum number for H_2 and D_2 molecules



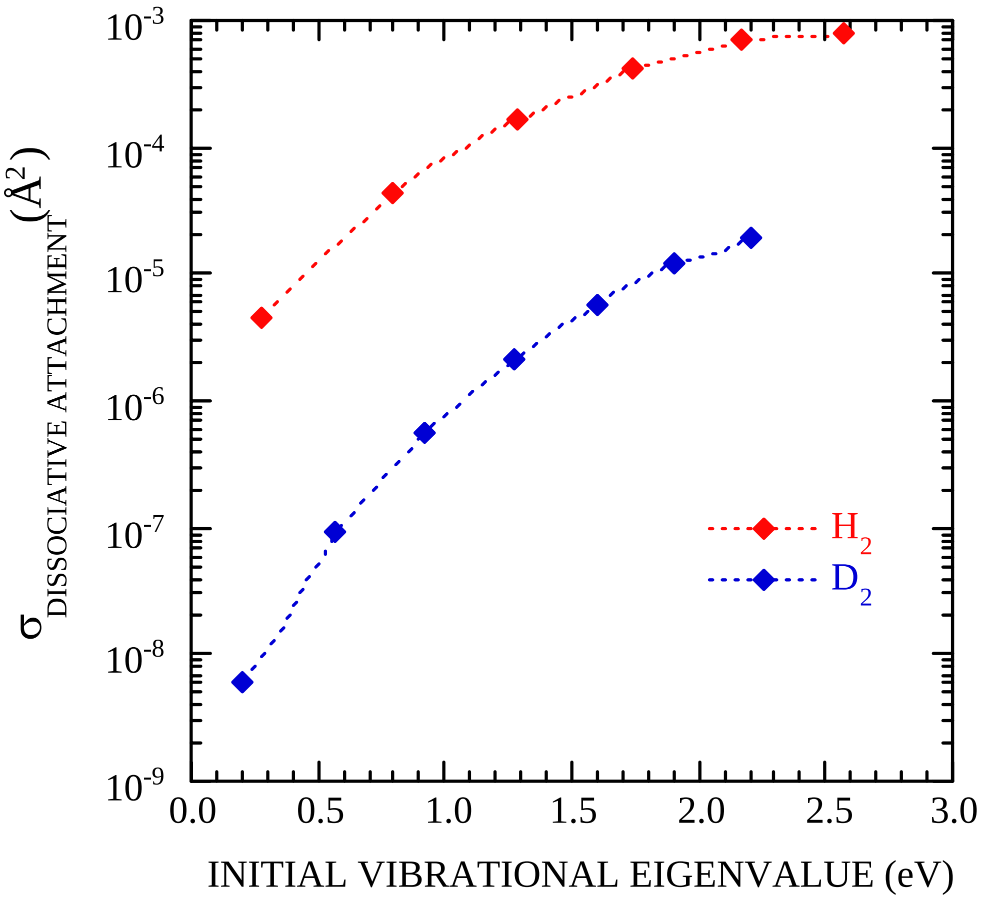
The behavior of electron density *ne* (a), electron temperature *Te* (b), atomic concentration [H]/[D] (c), and negative ion concentration $[H^-]/[D^-]$ (d), for H_2 and D_2 systems versus pressure p (I_d = 10 A, V_d = 115 V)



The behavior of electron density *ne* (a), electron temperature *Te* (b), atomic concentration [H]/[D] (c), and negative ion concentration $[H^-]/[D^-]$ (d), for H_2 and D_2 systems versus current I_d (p = 7.5 mtorr, V_d = 115 V) [37]

DISSOCIATIVE ATTACHMENT: H_2 ($X\ ^1\Sigma_g$, ν) + e → H_2^- → H^- + H

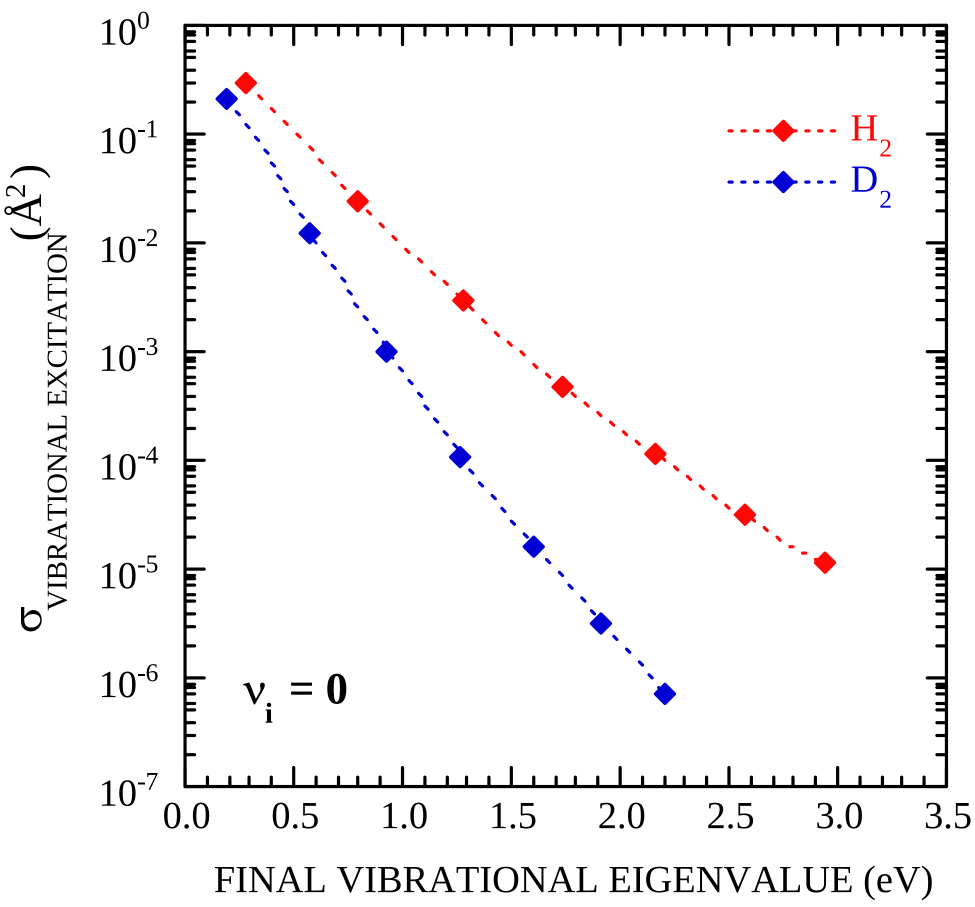
E = 4.5 eV



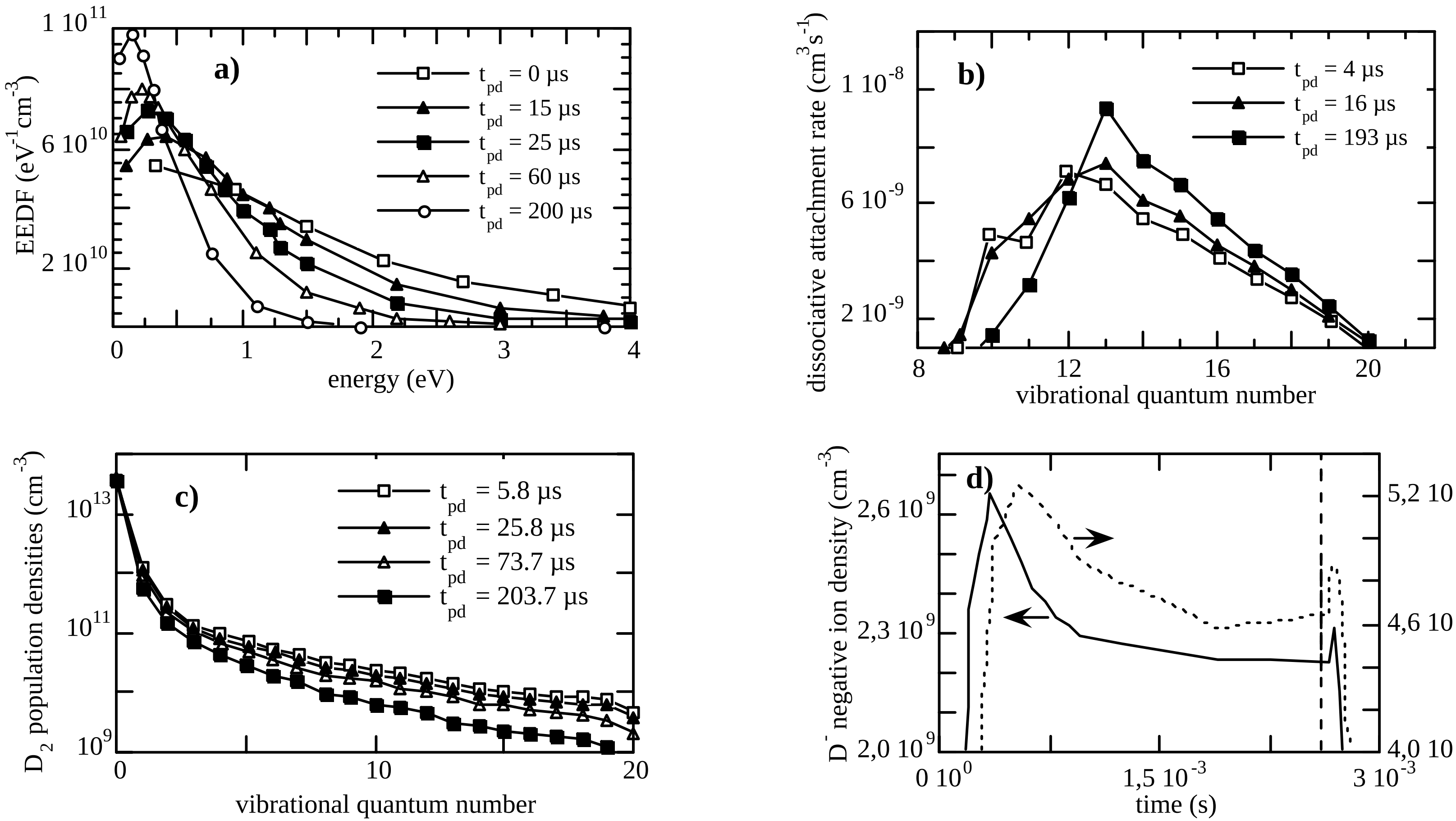
RESONANT VIBRATIONAL EXCITATION:

$H_2\ (X\ ^1\Sigma_g, \nu_i) + e \rightarrow H_2^- \rightarrow H_2\ (X\ ^1\Sigma_g, \nu_f) + e$

E = 5 eV

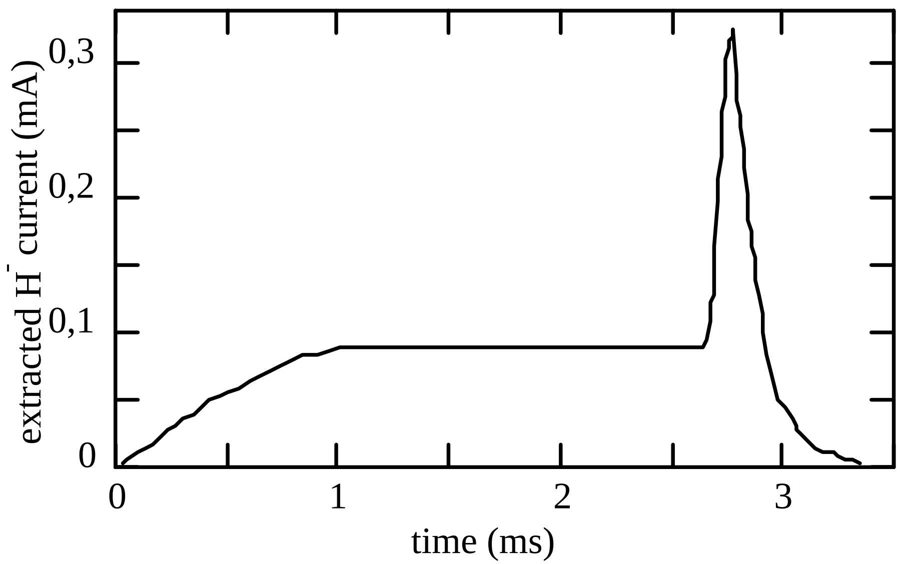


Pulsed discharges: model



Relaxation of several quantities (*EEDF* (a), e-da rate coefficient (b), N_v (c), D^- density (d)) in the D_2 post-discharge regime

Pulsed discharges: experiment



Extracted H^- current in a pulsed hydrogen discharge with a 2.7 ms pulse length and a 87 Hz repetition rate (p = 2.4 mtorr, I_d = 15 A)

Rydberg states: hystorical Scenario/1

Pinnaduwage et al. Phys. Rev. Lett. **70**, 754 (1993)

$e + H_2^* \rightarrow H + H^-$ $K_{da}(Ryd)=10^{-6}\ cm^3/sec$

Garscadden and Nagpal Plasma Sources Sci. Technol. **4**, 268 (1995)

Simplified model: (lumped excitation cross section on Rydberg states + lifetime of Rydberg states of 10^{-6}sec + $K_{da}(Ryd)=10^{-6}\ cm^3/sec$)

Result: Contribution from Rydberg states 10 times the one from vibrationally excited states

Gorse et al. AIP Conf. Proc. **380**, 109 (1995)

Model: Insertion of Garscadden model in the selfconsistent kinetics in multipole magnetic plasmas

Result: enhancement by a factor 2

Hiskes Appl. Phys. Lett. **69**, 755 (1996)

Model: collisional radiative model for H_2^* Rydberg states + $K_{da}(Ryd)=10^{-6}\ cm^3/sec$

Result: lifetime of Rydberg states of the order of 10^{-8}sec

Consequence: contribution of Rydberg states 1%

Rydberg states: Hystorical Scenario/2

Pinnaduwage et al. Phys. Rev. A **55**, 4131 (1997)

$e + H_2^* = H + H^-$ $K_{da}(Ryd) = 5\ 10^{-5}\ cm^3/sec$

Hassouni et al. Chem. Phys. Lett. **290**, 502 (1998)

Model: collisional radiative model for H_2^* Rydberg states +

$K_{da}(Ryd) = 5\ 10^{-5}\ cm^3/sec$

Result: enhancement by factor 2.7

problem: Rydberg state from n>3

Pinnaduwage et al. J.Appl.Phys. **85**, 7064 (1999)

scaling law for Rydberg states $k_{da}(n) = 10^{-8}\ n^{7/2}\ cm^3 \cdot s^{-1}$

which corresponds to n=12

An estimation

$$6\ 10^{-5} \sum_{n>12} H_2(n) = 10^{-8} \sum_{v>4} H_2(v)$$

For a plateau between 10^{10}-$10^{12} cm^{-3}$ Rydberg concentrations of the order of 1/6 10^7 to 1/6 10^9 cm^{-3} can be of the same importance as the dissociative attachment from vibrationally excited molecules

Future Improvements

- Collisional radiative model for Rydberg states
- Scaling law for the excitation of Rydberg states
- Lifetimes of Rydberg states
- Scaling law for dissociative attachment from Rydberg states

Wall effects

Historical scenario

Hiskes and Karo

Model: Trajectory calculations

Results: strong deactivation of vibrationally excited molecules on iron surfaces- Widely used in multicusp modelling

Billing and Cacciatore

Model: semiclassical ; classical for describing atoms and molecules reaching the surface; quantum description of the interaction of the molecule/atom with the phononic and electronic structure of the metal

Results : small deactivation of vibrationally excited molecules on copper surfaces

Dissociation Probabilities And Energy Accommodation For $H_2(v,j)$ Colliding With A Cu(100) Surface As A Function Of Vibrational And Rotational Angular Momenta *v* And *j* And Initial Kinetic Energy

v	j	E_{kin} (eV)	P_D [a)]	v' [b)]	j' [b)]	E^{int} [b),c)] (eV)
5	0	1,0	0,0	5	0,1	0,016
		2,0	0,70	5	1	0,026
6	0	0,2	0,0	6	0,1	0,0024
		0,4	0,0	6	0,1	0,0060
		0,6	0,0	6	1	0,0095
		1,0	0,62	6	1	0,014
8	0	0,05	0,0	8 (7)	0	0,001
		0,2	1,0			
10	0	0,05	0,95			
		0,1	1,0			

[a)] Dissociation probability.
[b)] Averaged values for reflected trajectories.
[c)] Energy transferred to surface phonons.

Formation of vibrationally excited states from heterogeneous atom recombination

H(gas) + H_{ads} ----> $H_2(v)$ Direct Eley Rideal(E-R) mechanism

H(gas) ----> H (trapped)

H(trapped) + H_{ads} ----> $H_2(v)$ Hot atom mech.(HA)

H_{ads} + H_{ads} ----> $H_2(v)$ Hinshelwood-Langmuir (H-L) mechanism

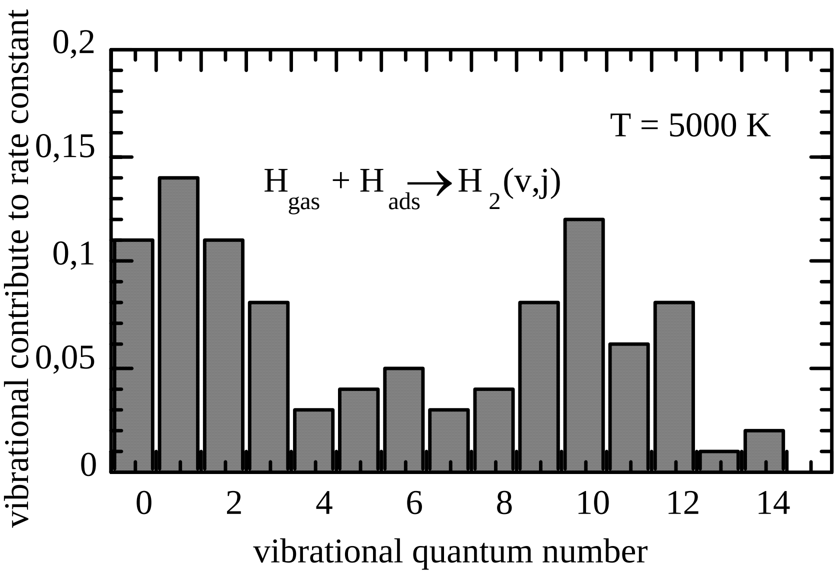
Different energetics depending on the nature of the adsorbed atom e.g. physi-adsorbed; chemi-adsorbed

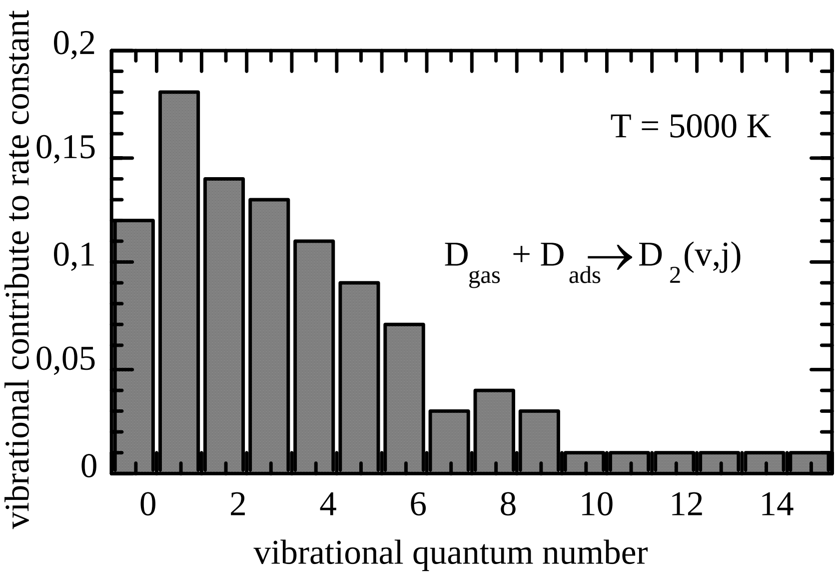
Physi-adsorbed: practically all the recombination energy can go into vibrational excitation of desorbed molecules in both E-R and H-L mechanisms

Chemi-adsorbed: only the difference between the dissociation energy of the diatom and the adsorption energy of atom(s) can go into vibrational energy of the desorbed molecules

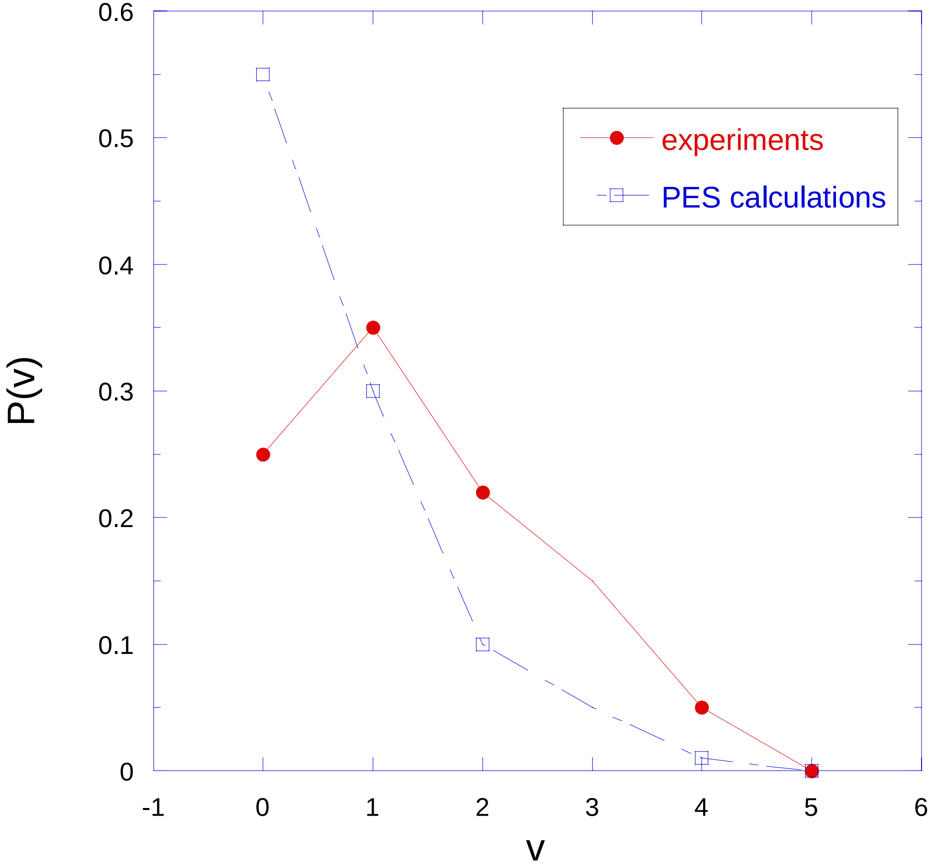
Results

Vibrational distributions from physiadsorbed H and D atoms on copper (E-R mech. Billing-Cacciatore)

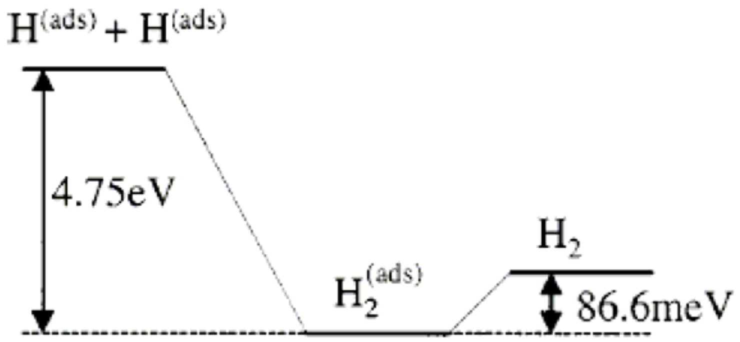




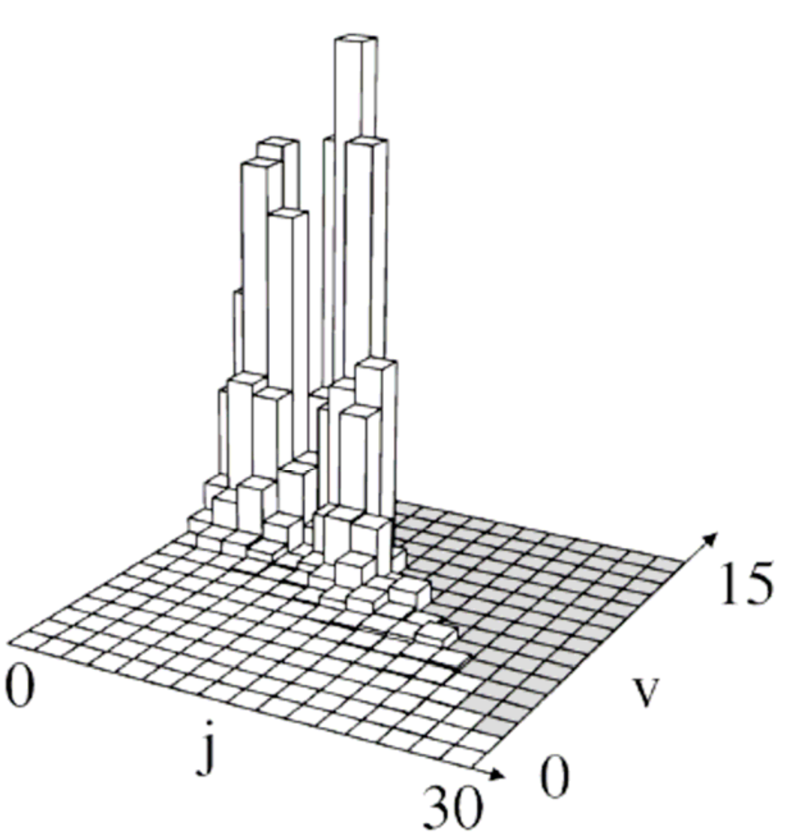
Vibrational distributions from chemiadsorbed H atoms on copper (HA-Shalashilin et al.) for the reaction H(gas) + Dads -->HD(v)



Vibrational distributions from physiadsorbed H atoms on graphite (E-R, H-L Sidis-Morisset)

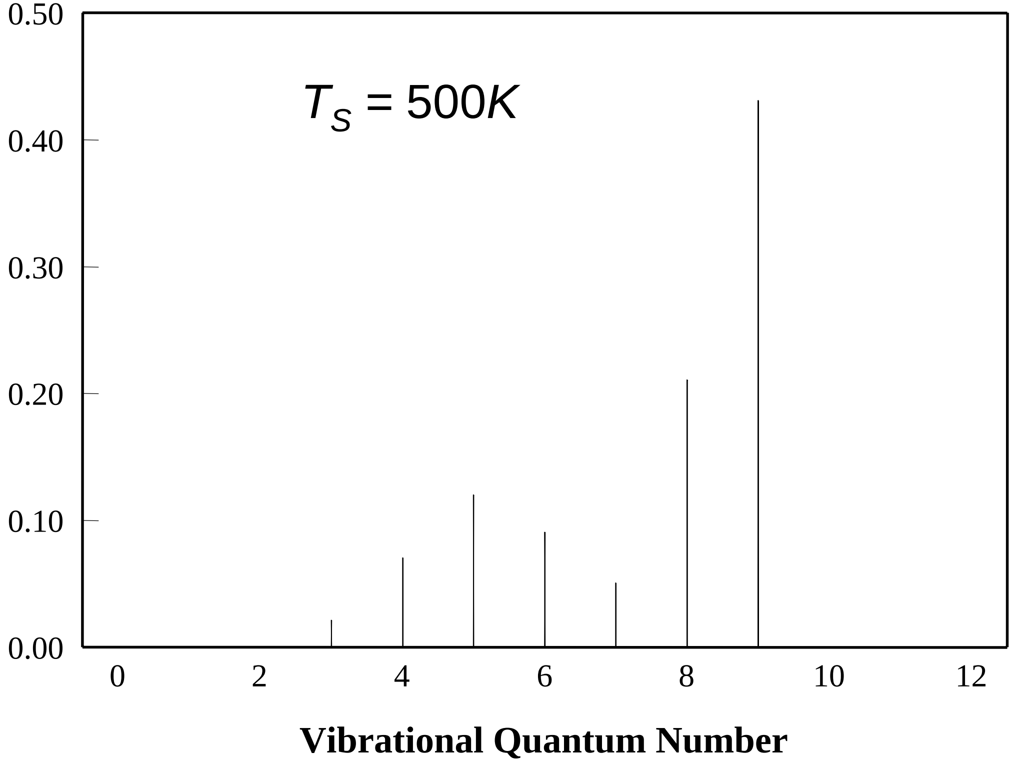


Scheme of the reaction path



(v, j) distribution of the H_2 product

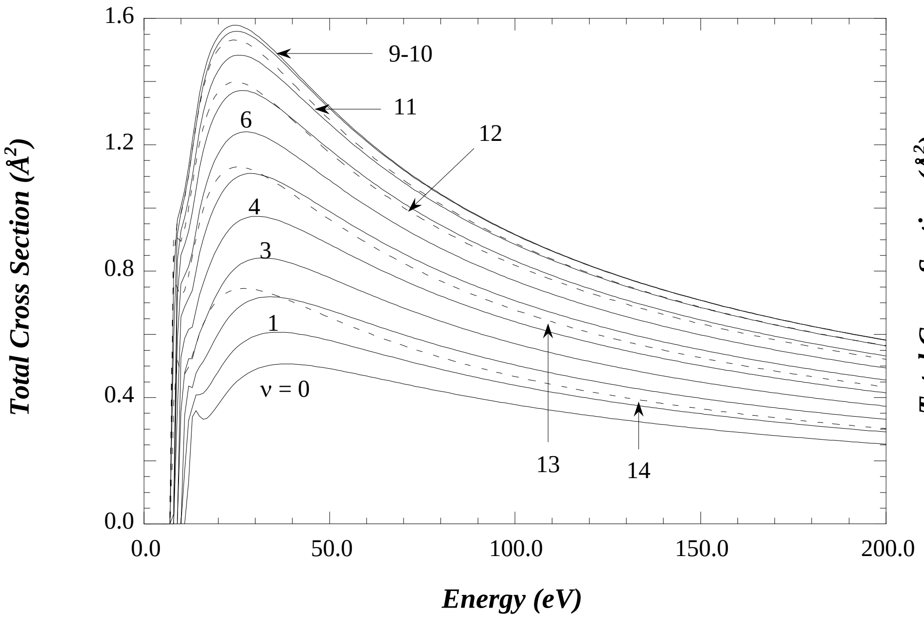
Vibrational distributions from physiadsorbed H atoms on graphite (E-R-Billing-Cacciatore)



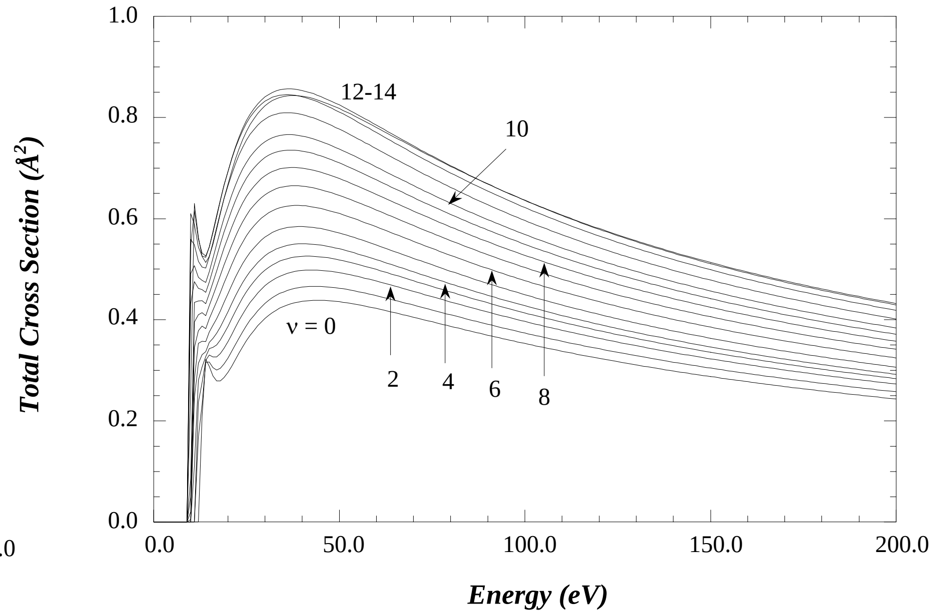
Cross sections improvements

ELECTRONIC EXCITATION to the lowest SINGLETS

$X\ ^1\Sigma_g\ (\nu_i) \rightarrow B\ ^1\Sigma_u$

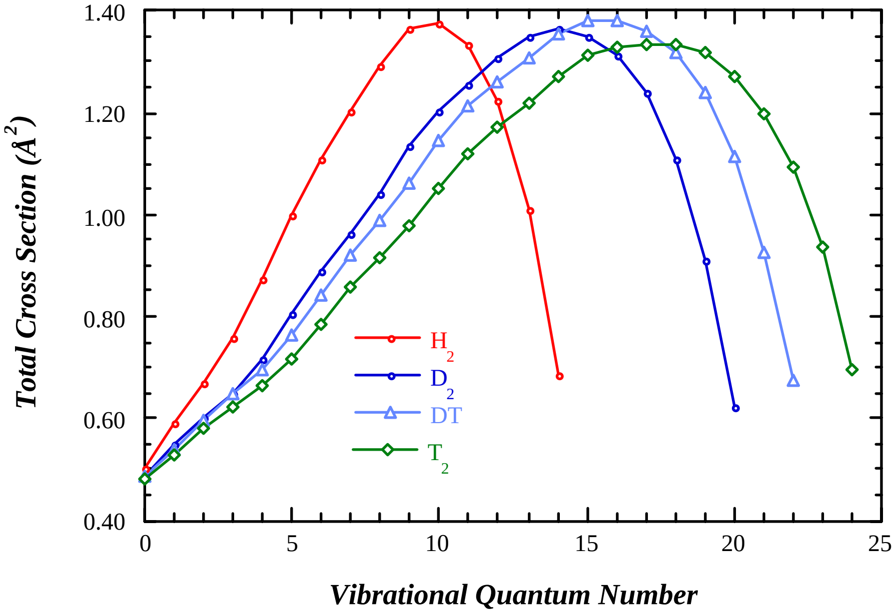


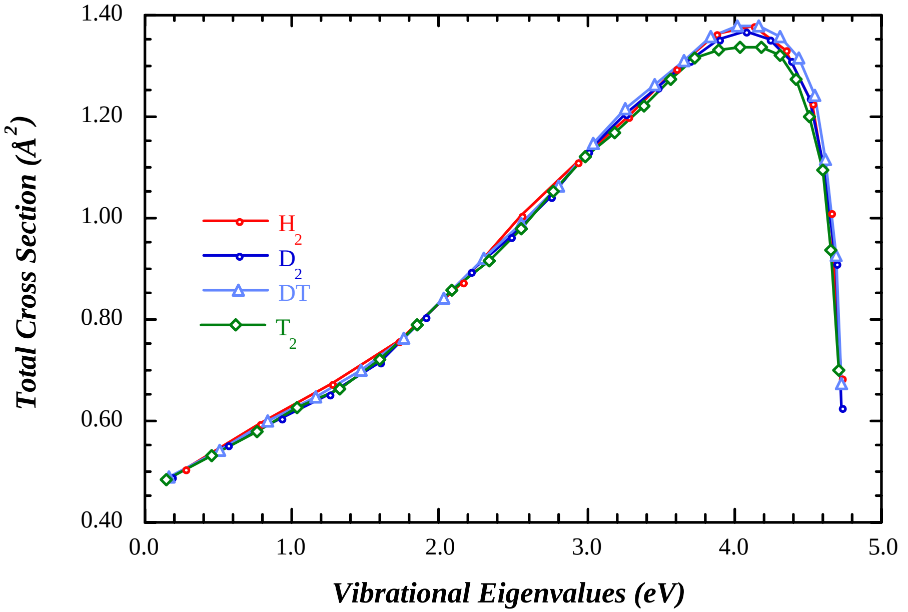
$X\ ^1\Sigma_g\ (\nu_i) \rightarrow C\ ^1\Pi_u$



CROSS SECTIONS for H_2 ISOTOPIC VARIANTS

$X\ ^1\Sigma_g\ (\nu_i) \rightarrow B\ ^1\Sigma_u$ E = 40 eV

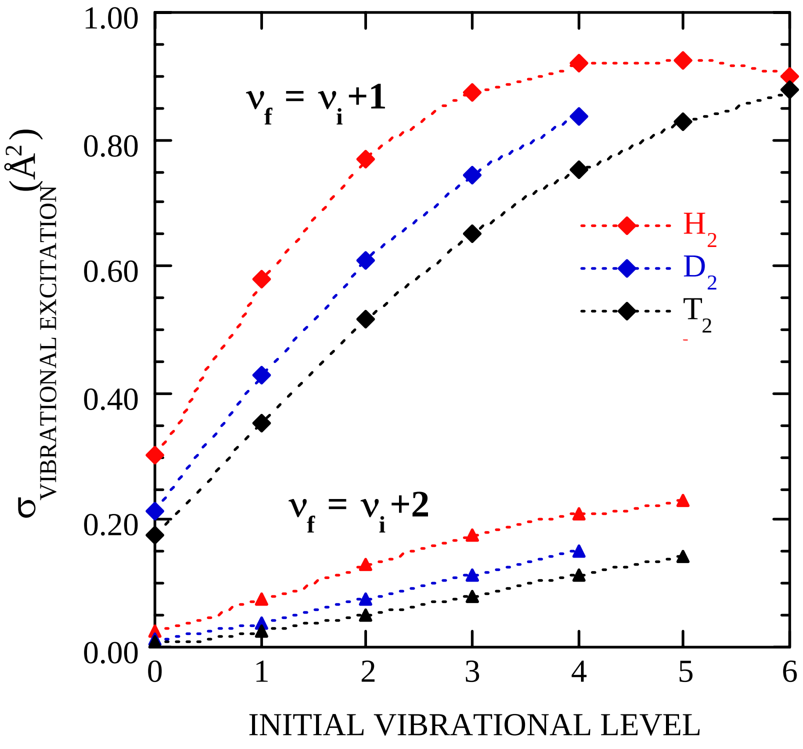


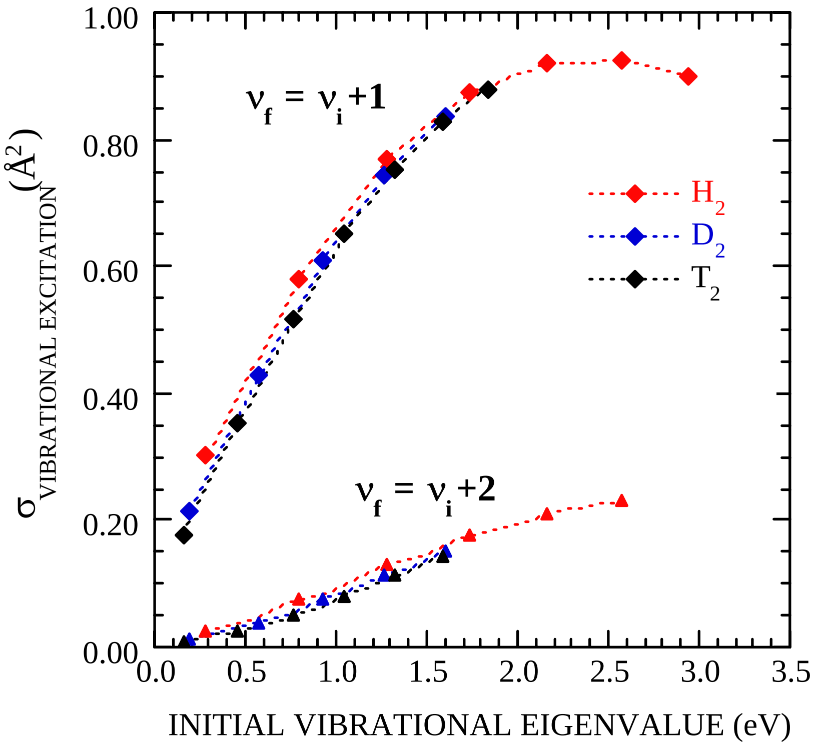


RESONANT VIBRATIONAL EXCITATION

$H_2 (X\ ^1\Sigma_g, \nu_i) + e \rightarrow H_2^- \rightarrow H_2 (X\ ^1\Sigma_g, \nu_f) + e$

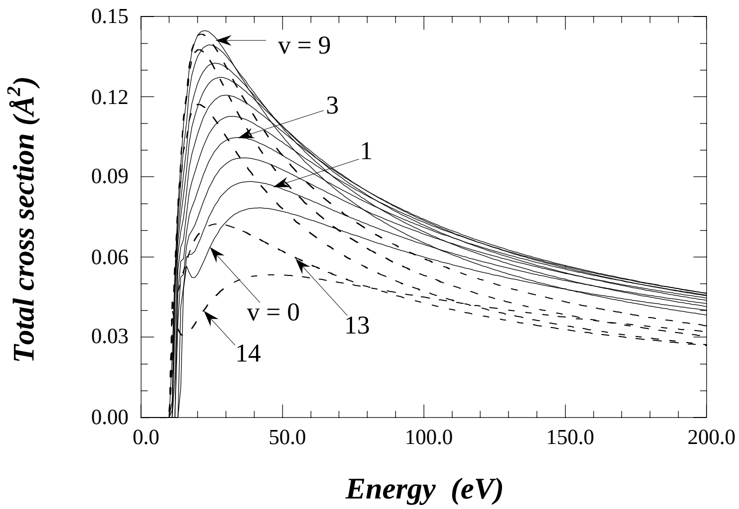
E = 5 eV



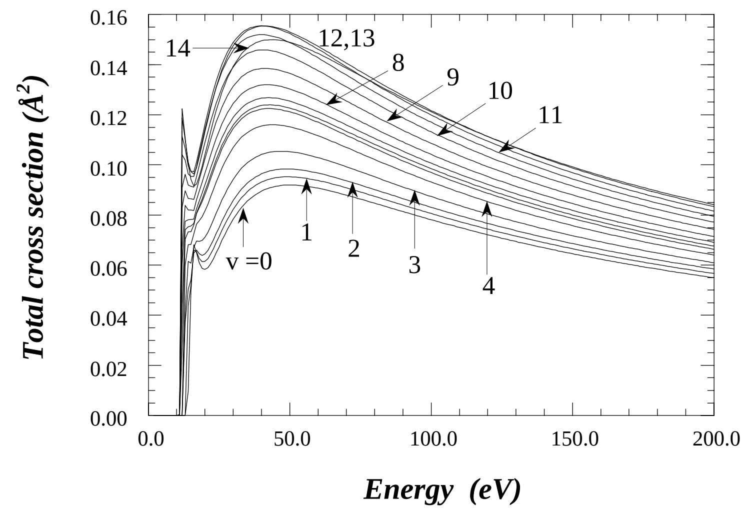


EXCITATION of low-lying RYDBERG STATES

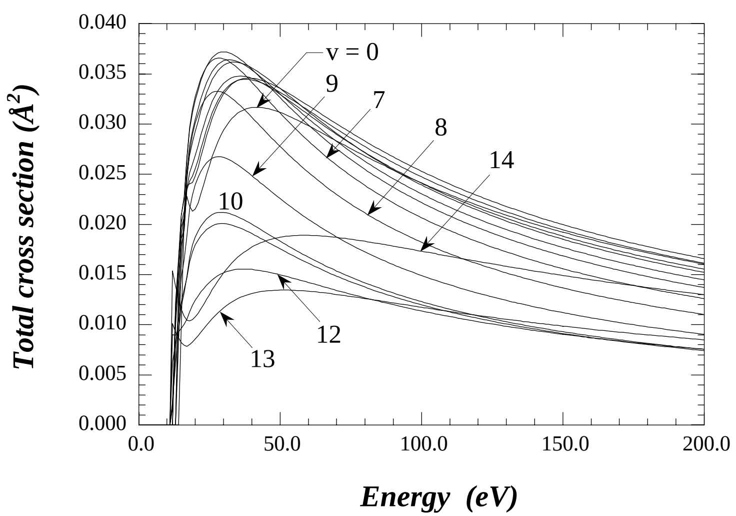
$X\ {}^1\Sigma_g (\nu_i) \rightarrow B'\ {}^1\Sigma_u$



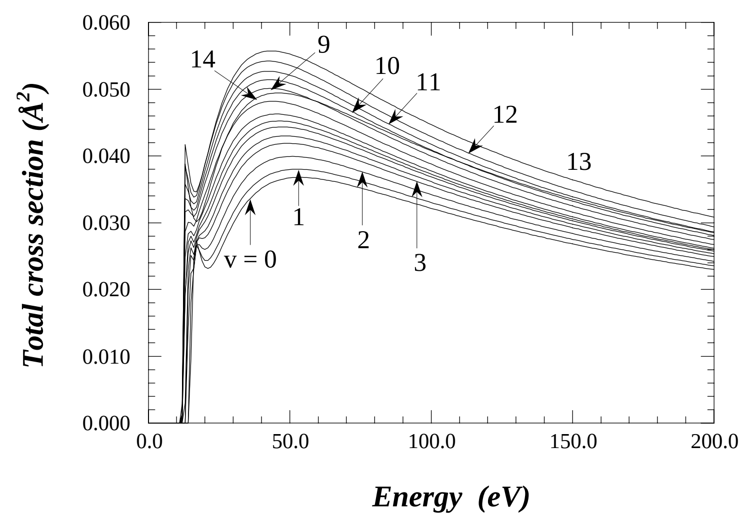
$X\ {}^1\Sigma_g (\nu_i) \rightarrow D\ {}^1\Pi_u$

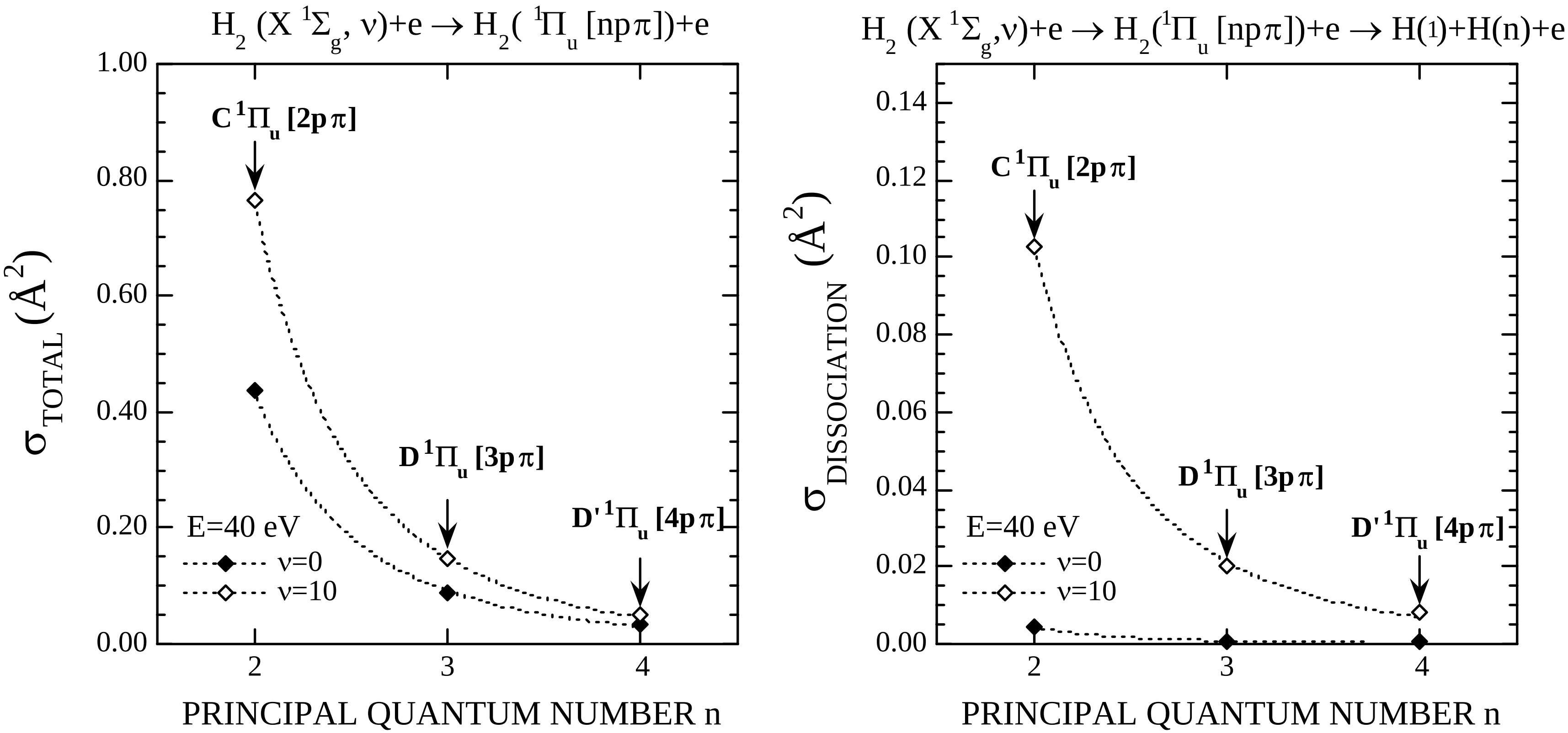


$X\ {}^1\Sigma_g (\nu_i) \rightarrow B''\ {}^1\Sigma_u$



$X\ {}^1\Sigma_g (\nu_i) \rightarrow D'\ {}^1\Pi_u$





$$\sigma \propto n^{-4}$$

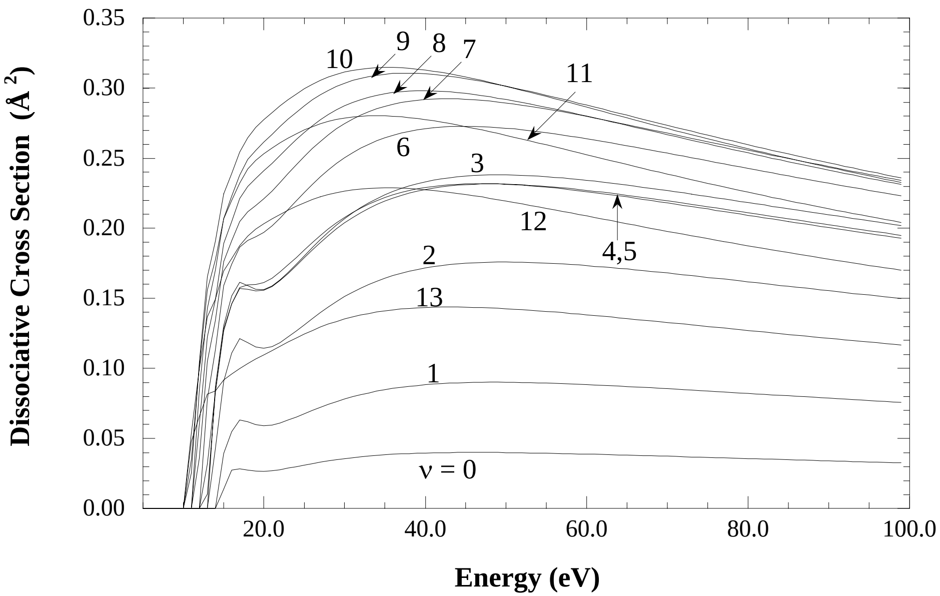
DISSOCIATION

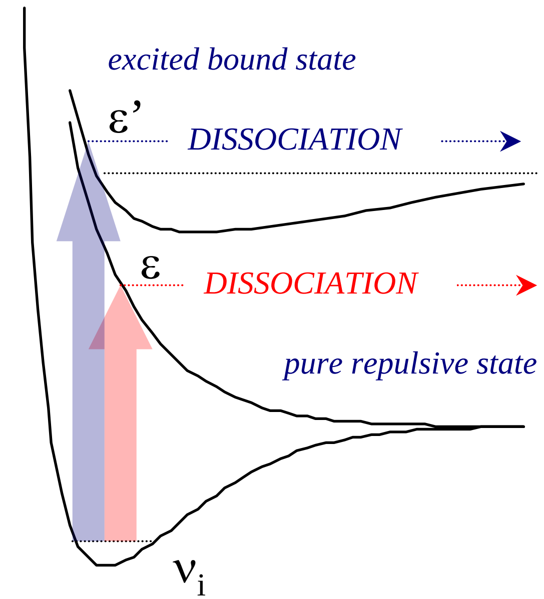
DIRECT DISSOCIATION through EXCITED STATES

$$H_2(X\,^1\Sigma_g^+, \nu_i) + e \rightarrow H_2(b\,^3\Sigma_u^+, \varepsilon) + e \rightarrow H + H + e$$

$$H_2(X\,^1\Sigma_g^+, \nu_i) + e \rightarrow H_2(\text{singlets}, \varepsilon') + e \rightarrow H + H + e$$

B $^1\Sigma_u$ and C $^1\Pi_u$ + low-lying RYDBERG STATES B', B" $^1\Sigma_u$, D, D' $^1\Pi_u$

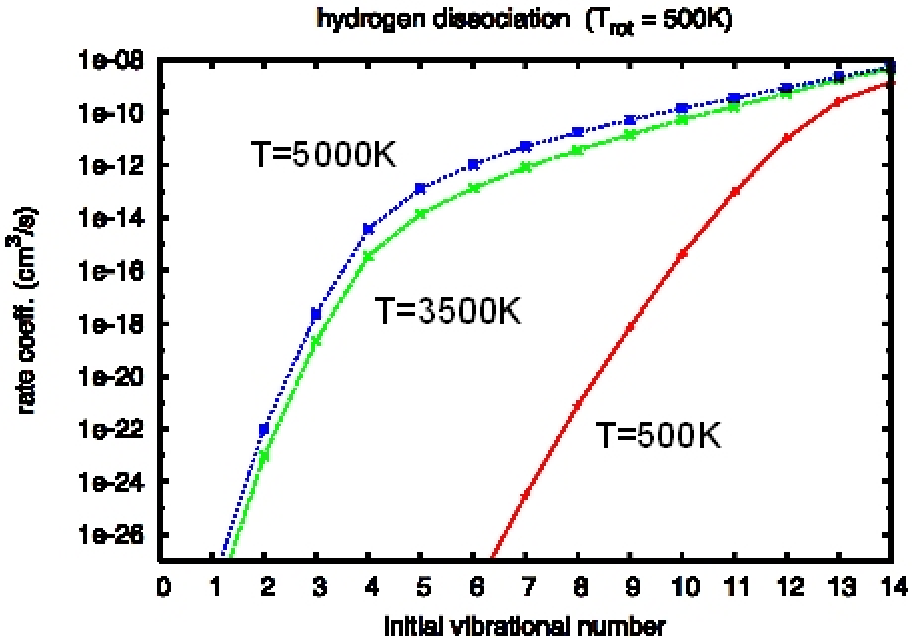




Rate coefficients for the process: $H+H_2(v,T_{rot})\text{->}3H$

different translational temperatures

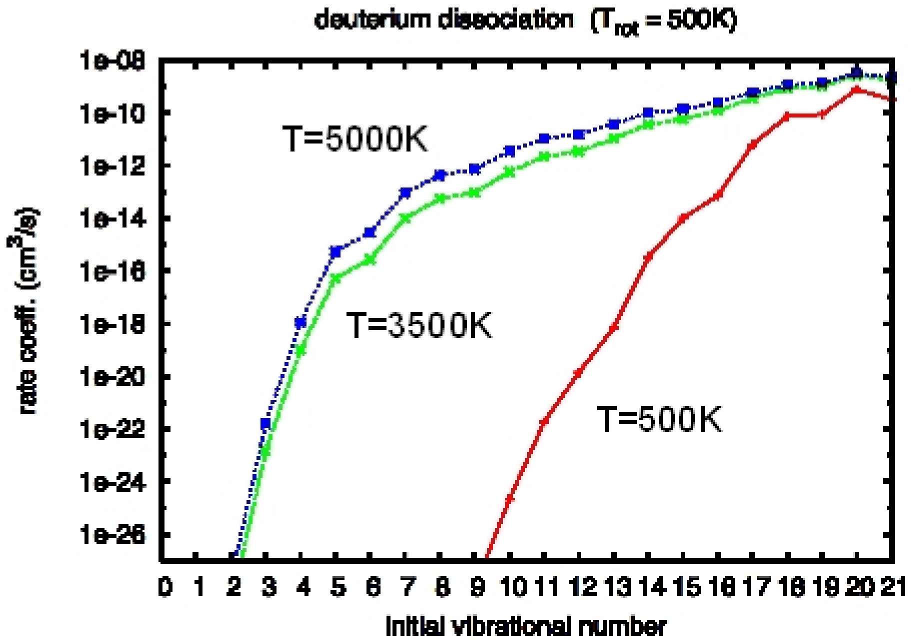
Rotational temperature is fixed to 500K



Deuterium dissociation rate coefficients

different translational temperatures

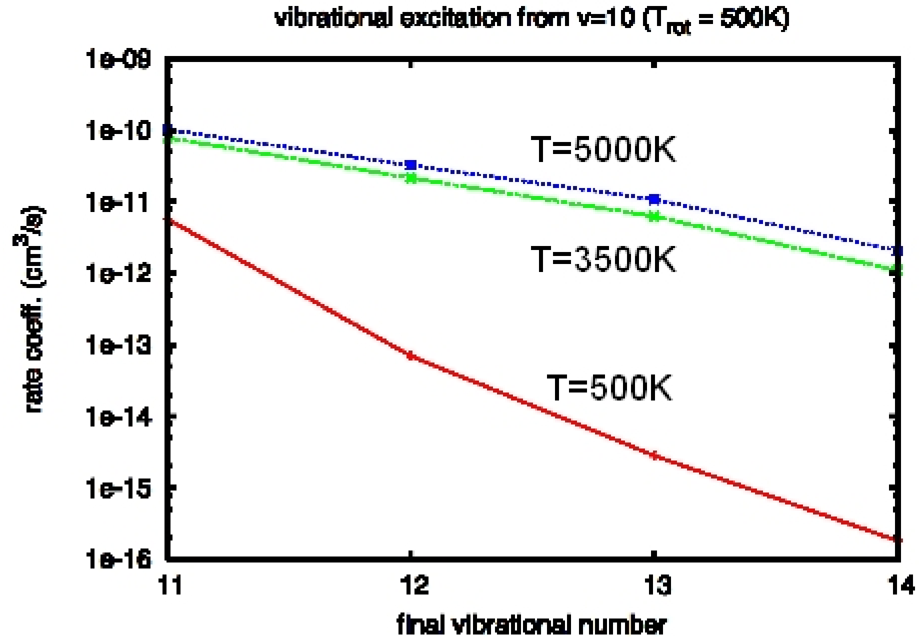
Rotational temperature is fixed to 500K



Hydrogen vibrational excitation rate coefficients
as a function of final vibrational quantum number

different translational temperatures

Rotational temperature is fixed to 500K

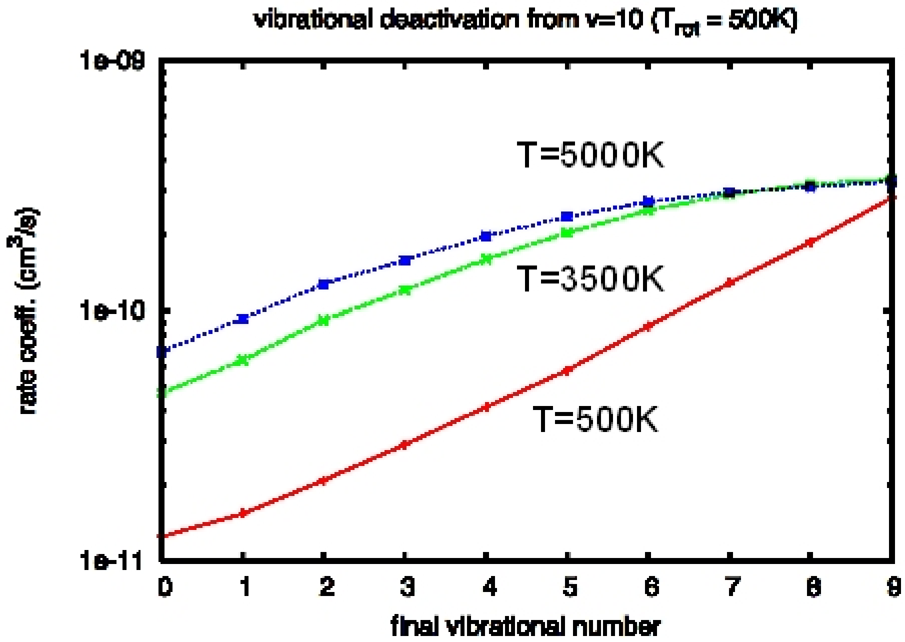


$$H_2(v = 10, T_{rot} = 500K) + H \rightarrow H_2(v = 10+n, T_{rot} = 500K) + H$$

Hydrogen vibrational deactivation rate coefficients
as a function of final vibrational quantum number

different translational temperatures

Rotational temperature is fixed to 500K

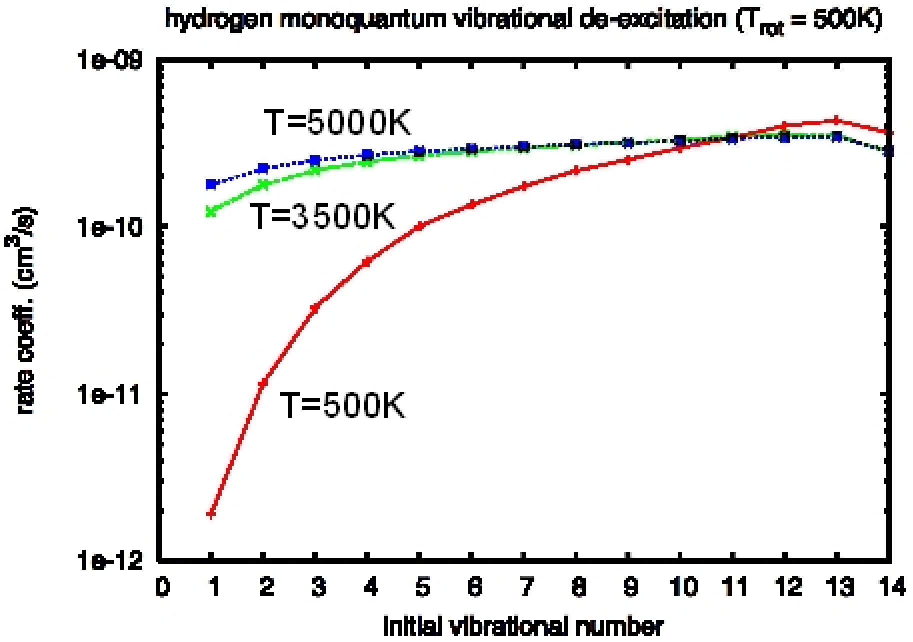


$$H_2(v = 10, T_{rot} = 500K) + H \rightarrow H_2(v = 10 - n, T_{rot} = 500K) + H$$

Hydrogen vibrational monoquantum deactivation rate coefficients

different translational temperatures

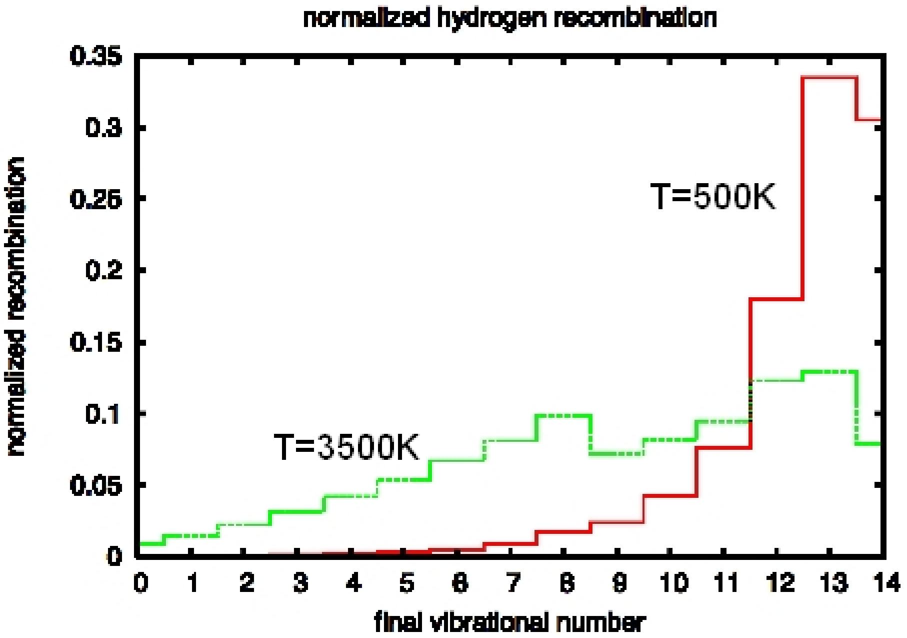
Rotational temperature is fixed to 500K



$$H_2(v\ ,\ T_{rot} = 500K) + H \rightarrow H_2(v\ -1,\ T_{rot} = 500K) + H$$

Hydrogen recombination rate coefficients
as a function of final vibrational quantum number

normalized to total recombination, at different temperatures



$H + H + H \rightarrow H_2(v) + H$

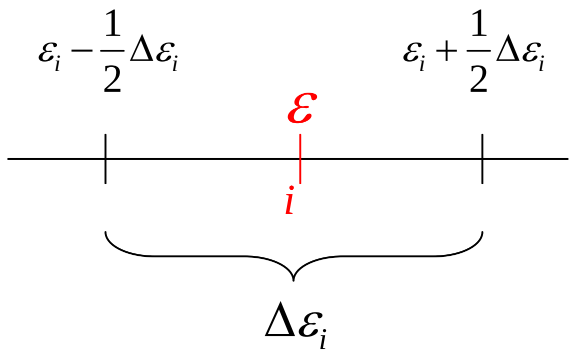
Kinetic models improvements

Multipole H_2 discharges

Time dependent electron kinetics and vibrational kinetics treated at the same level

Electron energy discretization

$$n(\varepsilon,t) \approx n(\varepsilon_i,t) \quad \text{for} \quad \varepsilon_i - \frac{1}{2}\Delta\varepsilon_i \le \varepsilon \le \varepsilon_i + \frac{1}{2}\Delta\varepsilon_i$$



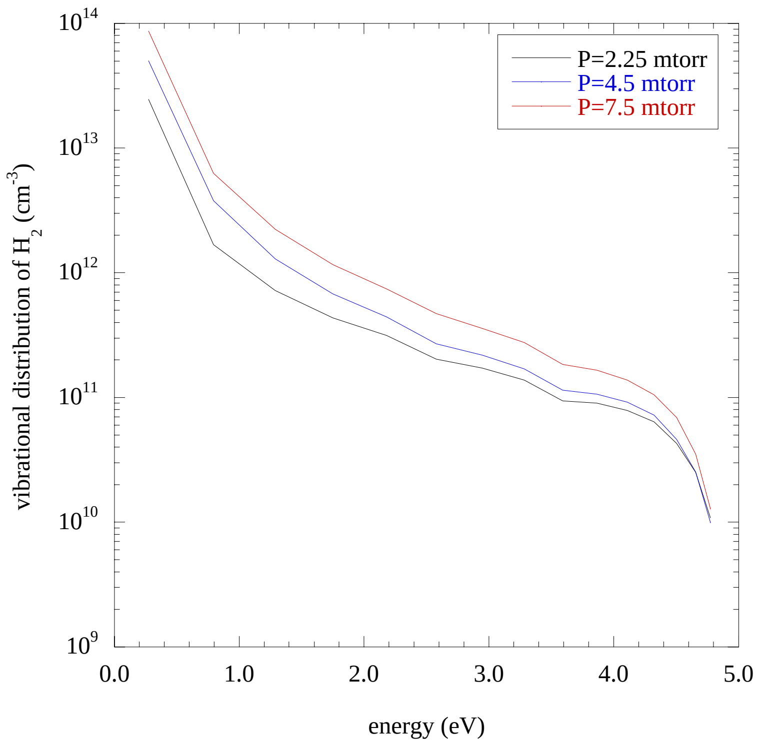
Each electron energy sub-interval → A "**different electron**" characterized by a **representative energy** *ε_i (sub-interval mean energy)*

Electrons state-to-state kinetics

(electrons with different energies as molecular energy levels) → **Discretized electron rate coefficients**:

$$k_i^e = \sigma_i(\varepsilon)v(\varepsilon)$$

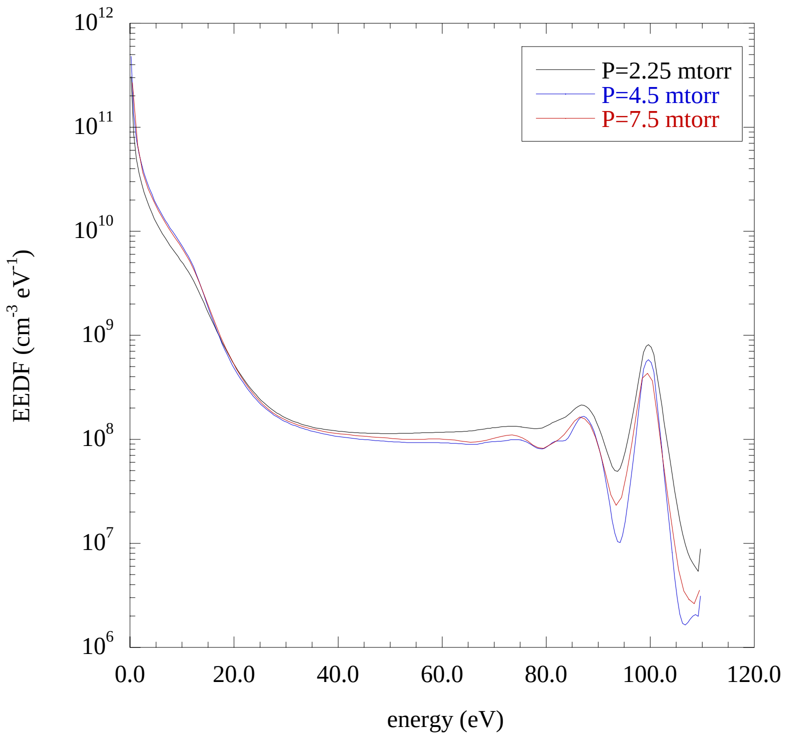
VDF and EEDF for different Pressures



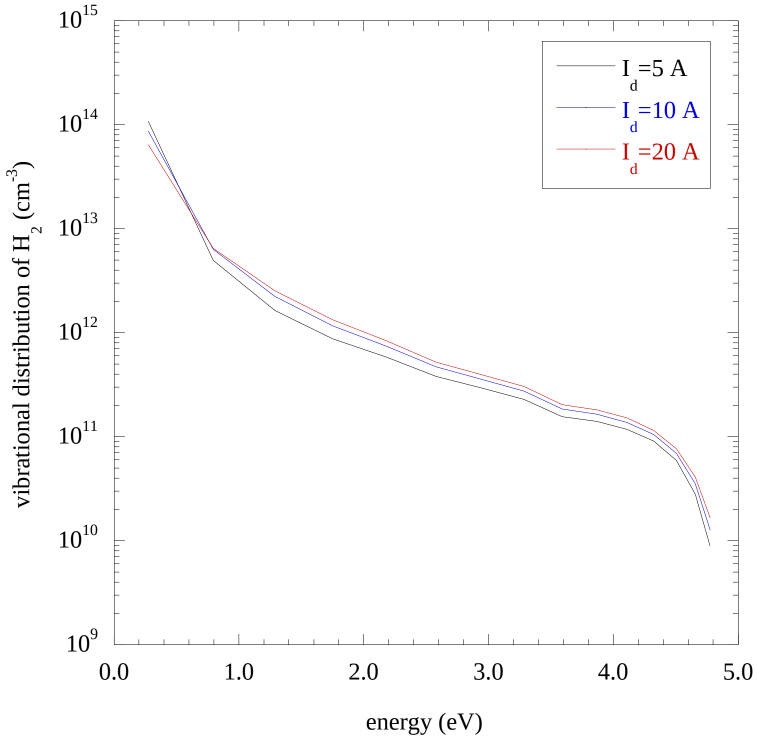
T_g=500 K

Discharge current=10 A

Discharge voltage=100 V



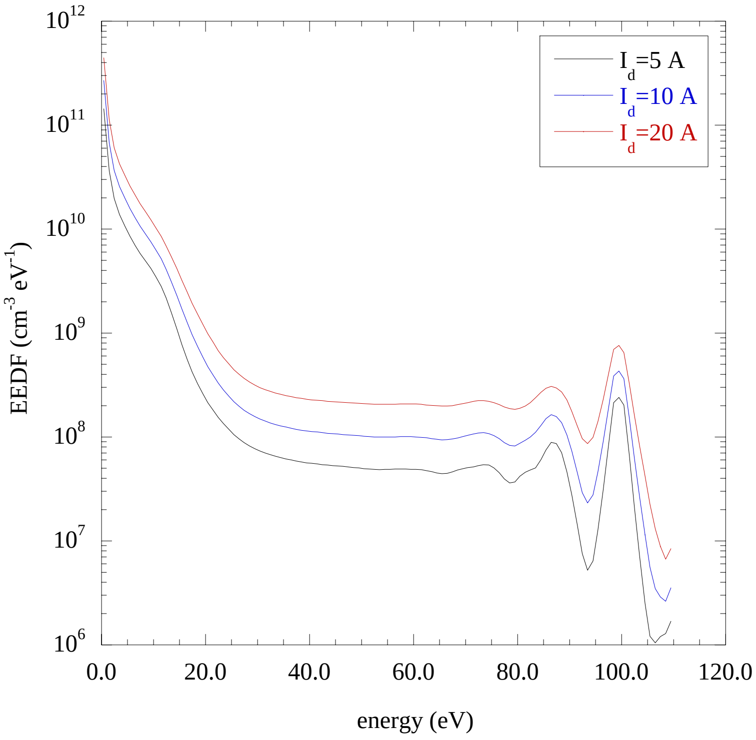
VDF and EEDF for different Currents



T_g=500 K

Pressure=7.5 mtorr

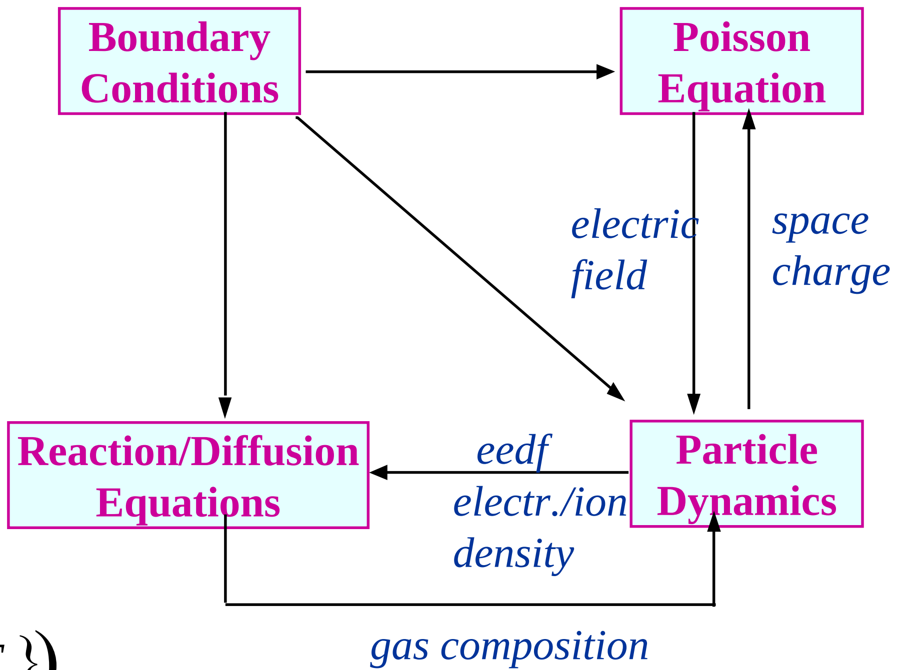
Discharge voltage=100 V



RF Discharges: Parallel Plates

1D(r)2D(v) self-consistent particle/continuum model

- **PIC/MCC** applied to **electrons** and **ionic species**
- **Grid-discretized relaxation technique** for **reaction-diffusion** part



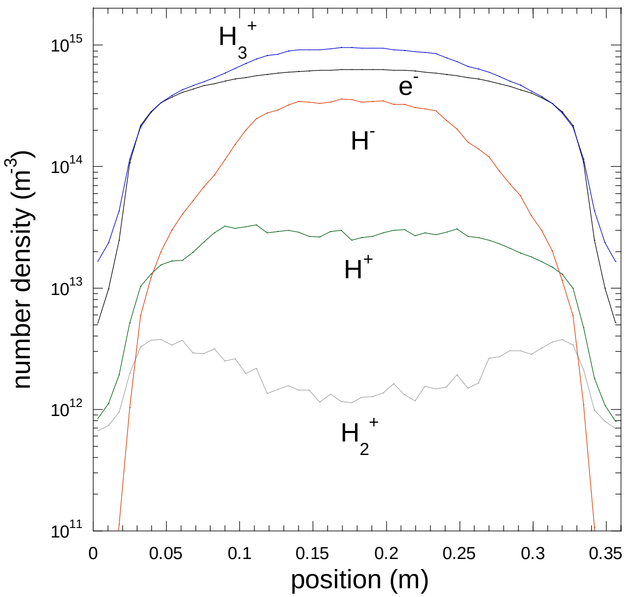
$$\left(\frac{\partial}{\partial t} + v_x \frac{\partial}{\partial x} - \frac{q_s}{m_s}\frac{\partial \varphi(x,t)}{\partial x}\frac{\partial}{\partial v_x}\right) f_s(x,\mathbf{v},t) = C_s(\{F_c\})$$

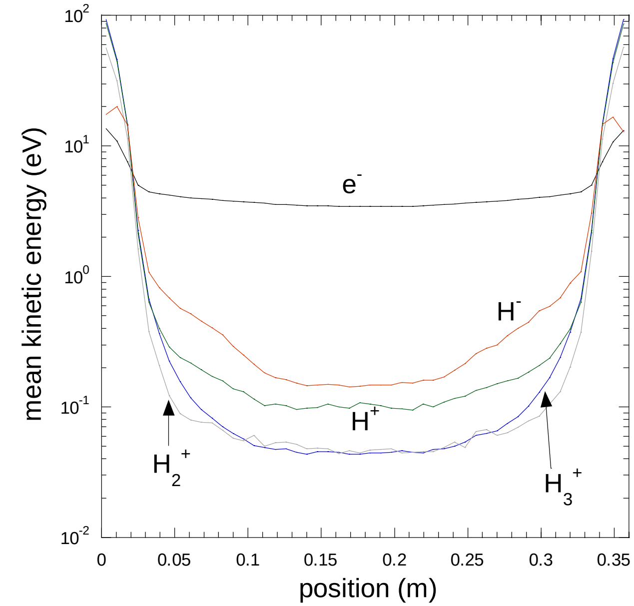
$$\frac{\partial^2 \varphi(x,t)}{\partial x^2} = -\frac{1}{\varepsilon_0}\sum_s q_s \int d^3 v f_s(x,\mathbf{v},t)$$

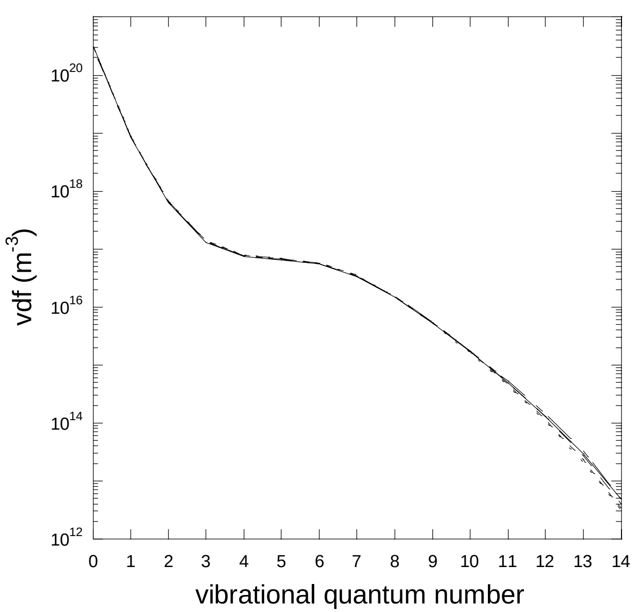
$$-D_c \frac{\partial^2 n_c(x)}{\partial x^2} = \sum_r (\nu'_{rc} - \nu_{rc}) k_r(\langle f_e \rangle_t) \prod_{c'} n_{c'}^{\nu_{rc'}}$$

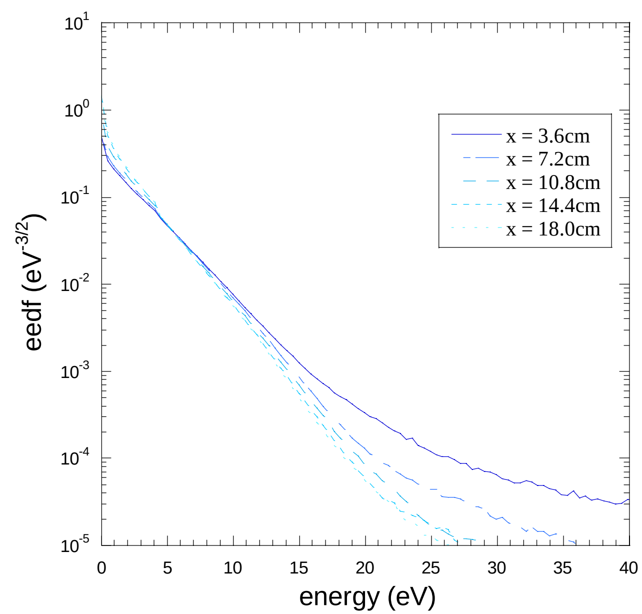
C_s: Boltzmann collision integral for charged/neutral collisions

p = 10mtorr, d = 36cm, V_{rf} = 300V









RF Discharges: Inductive Coupling

Classical approach to couple heavy particle and electron kinetics

→

Simultaneous solution of ***master equations*** *and*

Boltzmann equation *including an electric field*

RF discharges *(Microwave):*

$$\frac{\partial n(\varepsilon,t)}{\partial t} = -\left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{field} - \left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-M} - \left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-e} + In + Ion + Sup - L$$

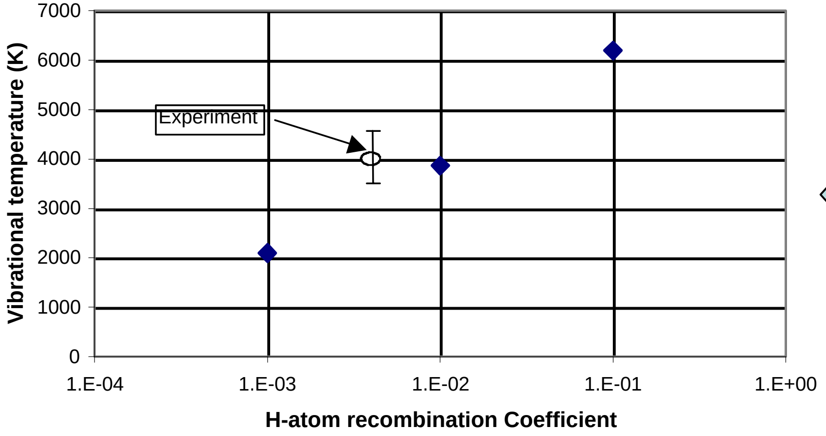
$-\left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{field}$ Flux of electrons along energy axis due to the electric field

$$E_{rms} = \left(RFPD\frac{m_e}{n_e e^2}\right)^{1/2}\left(\int_{\varepsilon}\frac{\nu}{\nu^2+\omega^2}f(\varepsilon)d\varepsilon\right)^{1/2}$$

RFPD: absorbed RF power density

Vibrational Temperature as a function of γ_H:

comparison with CARS measurements



Pressure= 1 torr

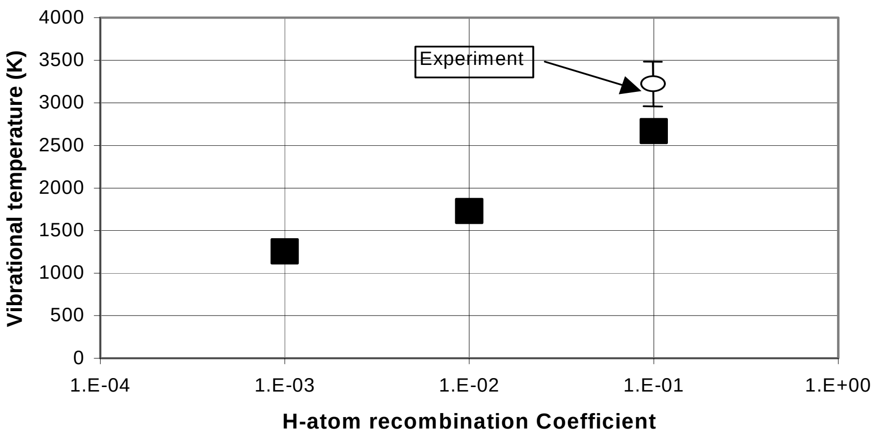
Injected power= 0.5 W

T_w=370 K

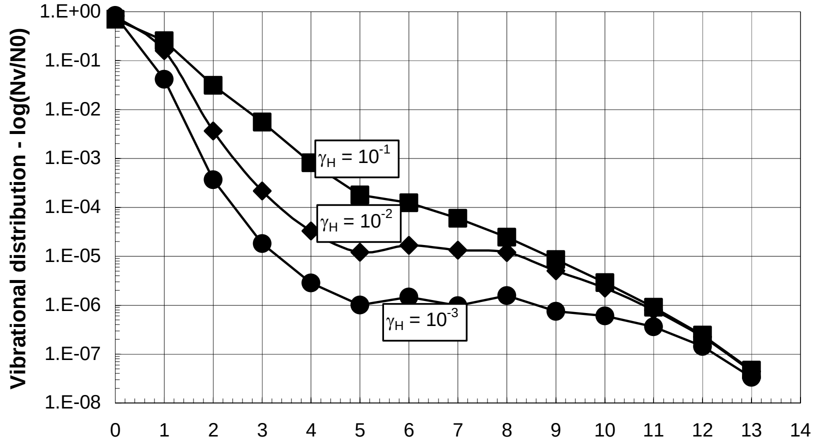
Pressure=6 torr

Injected power= 2.0 W

T_w=550 K



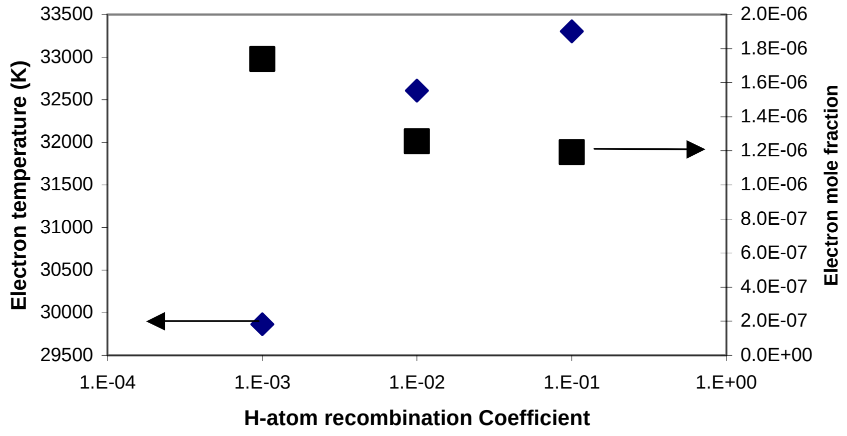
VDF and EEDF for different γ_H

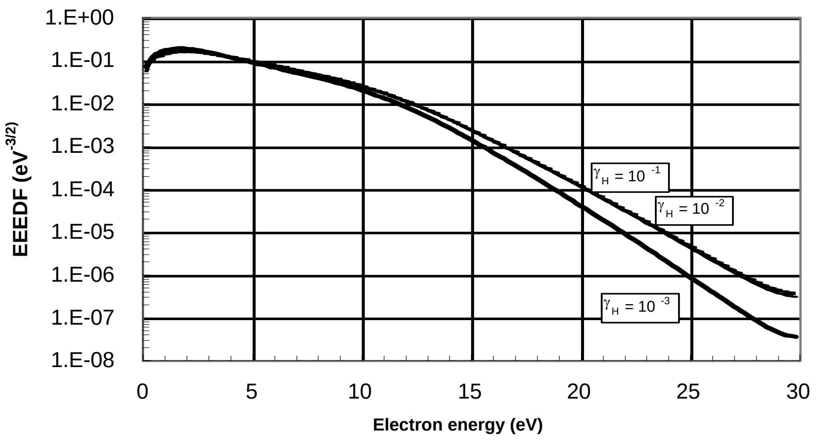


Pressure= 1 torr

Injected power= 0.5 W

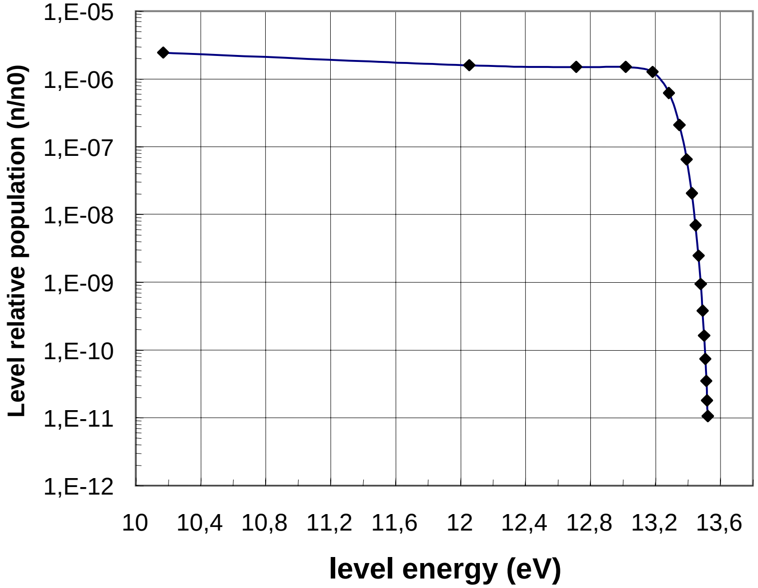
T_w=370 K



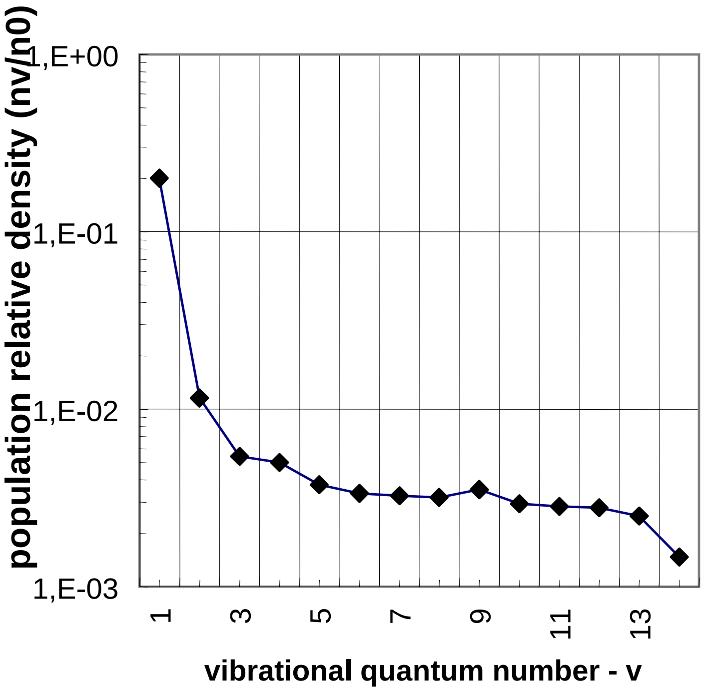


MW discharges

p= 5 mtorr , MWPD = 1.5 W/cm^3 (this corresponds to 1.5 kW / 2 l discharge)

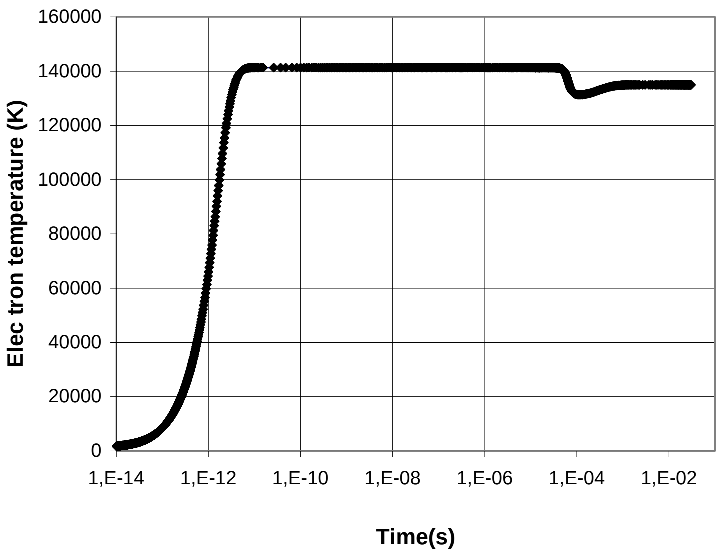


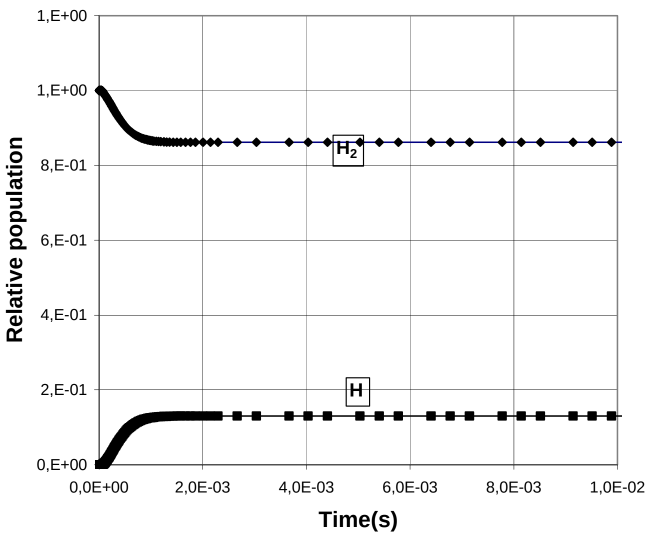
Population distribution of H-atom excited states

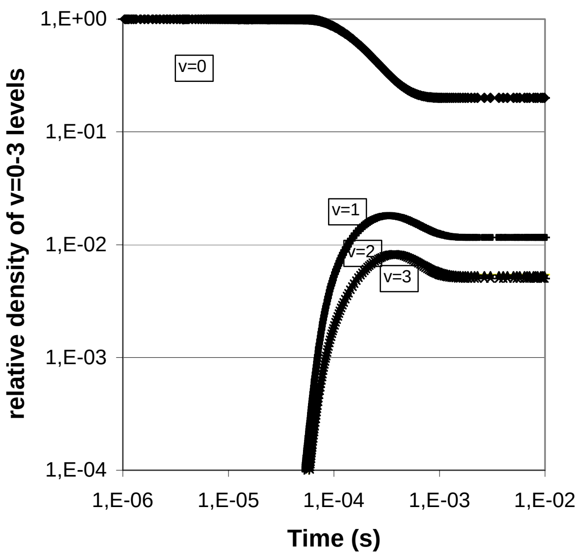


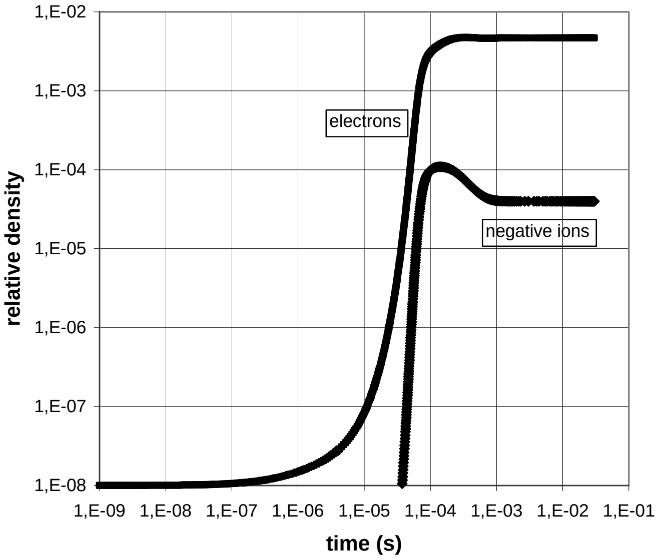
Vdf with very large and very populated plateau

Time evolution

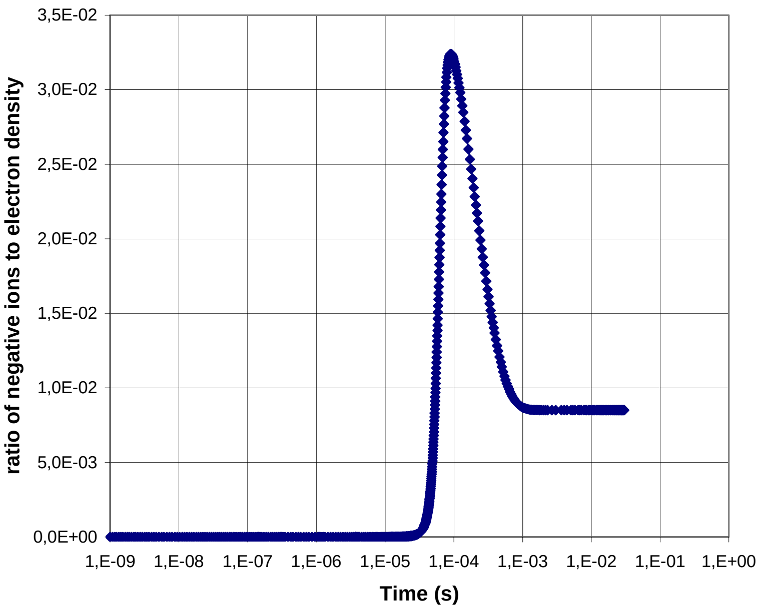


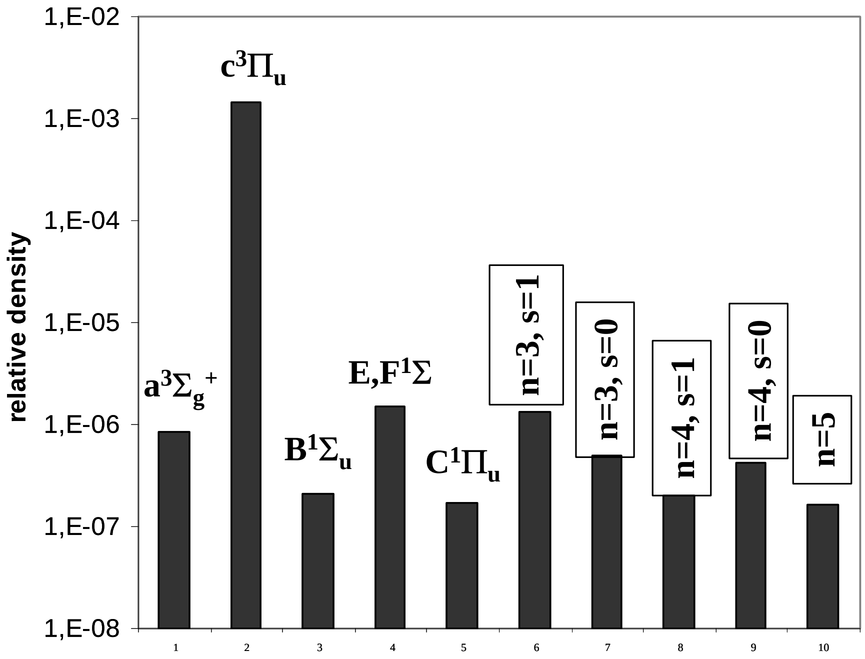






Time-evolution of electron to negative ion densities





steady state relative densities of H_2 electronically excites states

Future Steps

1) Construction of a data base of cross sections for H_2 and isotopes
2) Rydberg kinetics and gas-surface interactions
3) Insertion of the complete data base in 1D-2D codes
4) Extension to surface sources
5) Validation of the predictive code with dedicated experiments
6) Linking with the IAEA- CRP (Coordinated Research Project) on "Atomic and Molecular Data for Plasma Modelling" starting September 2005
7) Agreement protocol with ITER Programme