



Polytechnic of Bari, Italy



Institute of Nanot  
CNR - Bari, Ita

# From elementary processes to plasma modeling

Roberto Celiberto

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1<sup>st</sup> Research Coordination Meeting on  
*Atomic Data for Vapour Shielding in Fusion Devices*  
I.A.E.A. Vienna, March 2019

# Non-equilibrium low-temperature plasmas

- Molecular plasmas
- Non-Boltzmann population
- Non-Maxwellian electron energy distributions function
- State-to-state vibrational kinetics
- Large sets of cross section data

# Vibrational kinetics of electronically excited states in H<sub>2</sub> discharges

Colonna et al., Eur. Phys. J. D (2017)



The evolution of atmospheric pressure hydrogen plasma under the action of repetitively ns electrical pulse

## Input data

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$E_m/N = 200 \text{ } Td;$

Pulse = 20 ns;

Gas temperature = 1000 K

Gas pressure = 1 bar.

Molar fractions:

$$\chi_e = \chi_{H_2^+} = 10^{-10}$$

$$\chi_H = 2 \cdot 10^{-9}$$

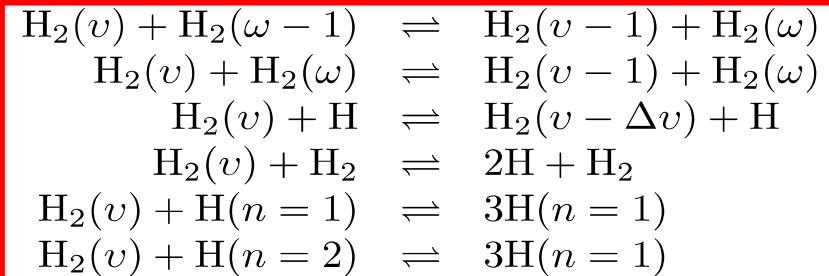
$$\chi_{H^+} = \chi_{H^-} = \chi_{H_3^+} = 0$$

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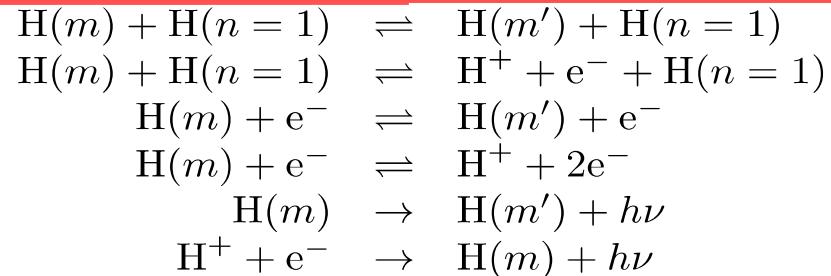
# H<sub>2</sub>/H STATE-TO-STATE KINETICS

## Ground state vibrational kinetics

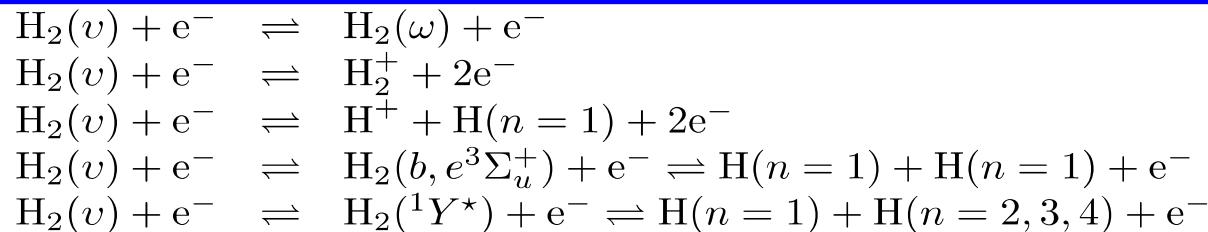
### Ground state vibrational kinetics



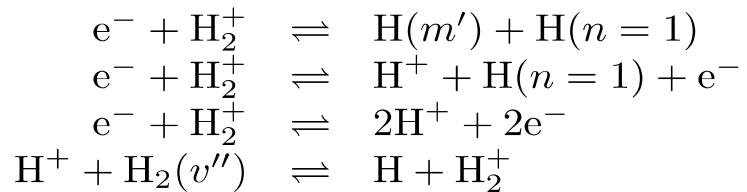
### Atomic level kinetics



### Electron impact induced processes



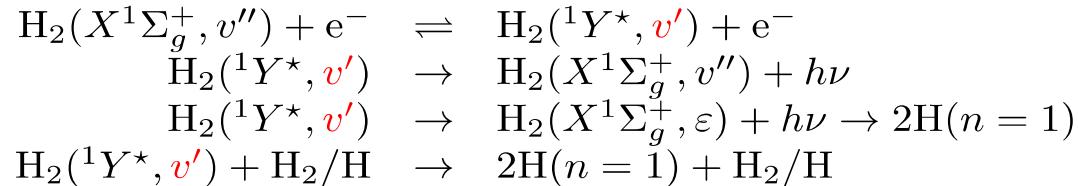
### Molecular ion kinetics



## H<sub>2</sub>/H STATE-TO-STATE KINETICS

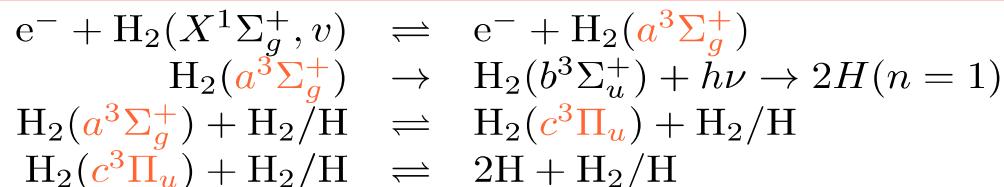
### Updated model

#### Singlets vibrational kinetics



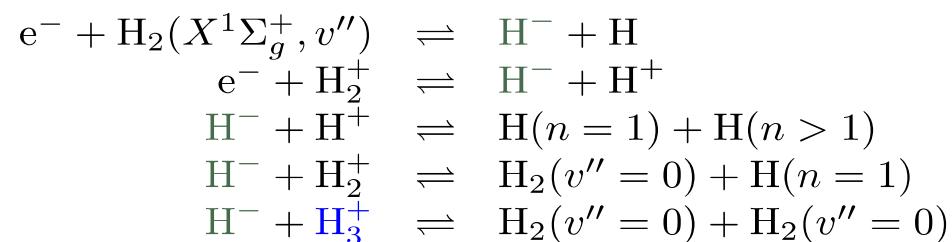
$${}^1Y^* = \begin{cases} {}^1\Sigma_g^+ : B, B', B'' \\ {}^1\Pi_g : C, D, D' \end{cases}$$

#### Triplets kinetics

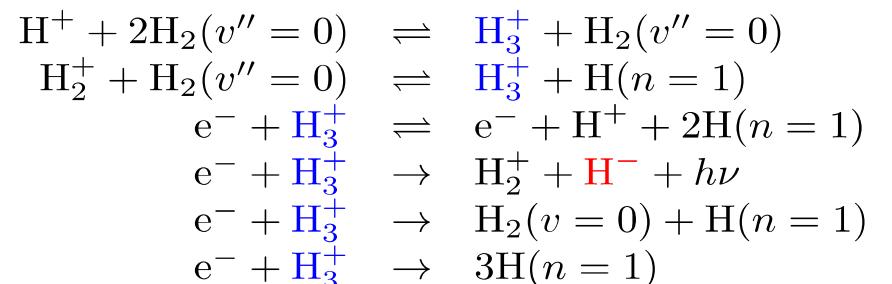


$$b^3\Sigma_u^+, a^3\Sigma_g^+, c^3\Pi_u$$

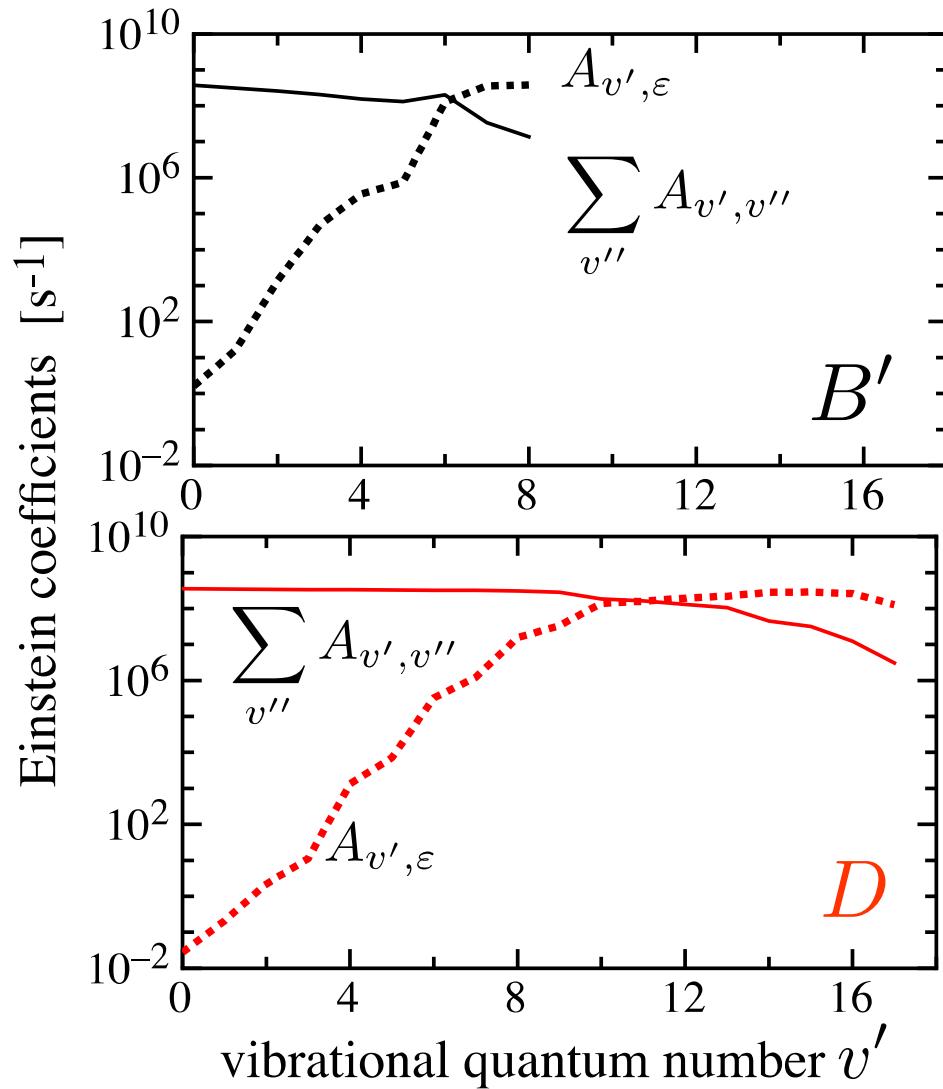
#### Negative Ions kinetics



#### H<sub>3</sub><sup>+</sup> cation kinetics

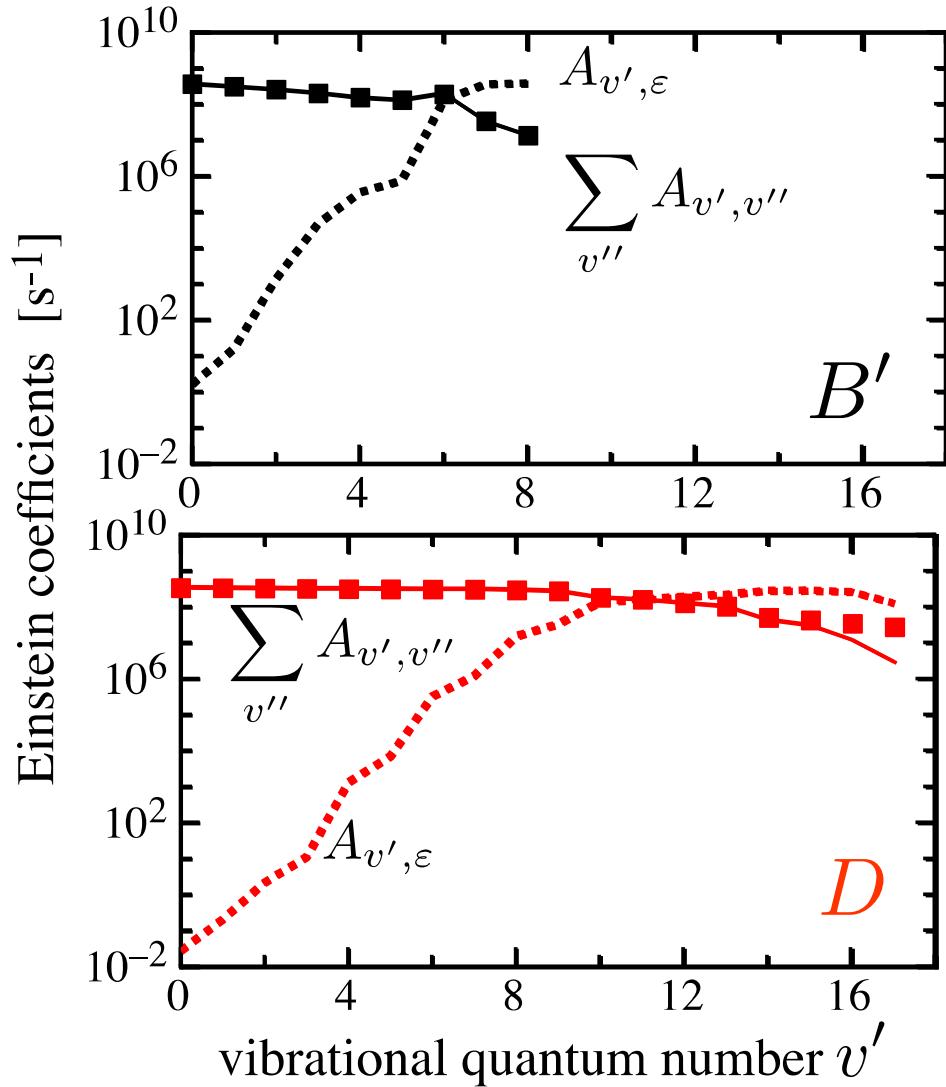


- ✓ state-to-state
- ✓ radiative processes

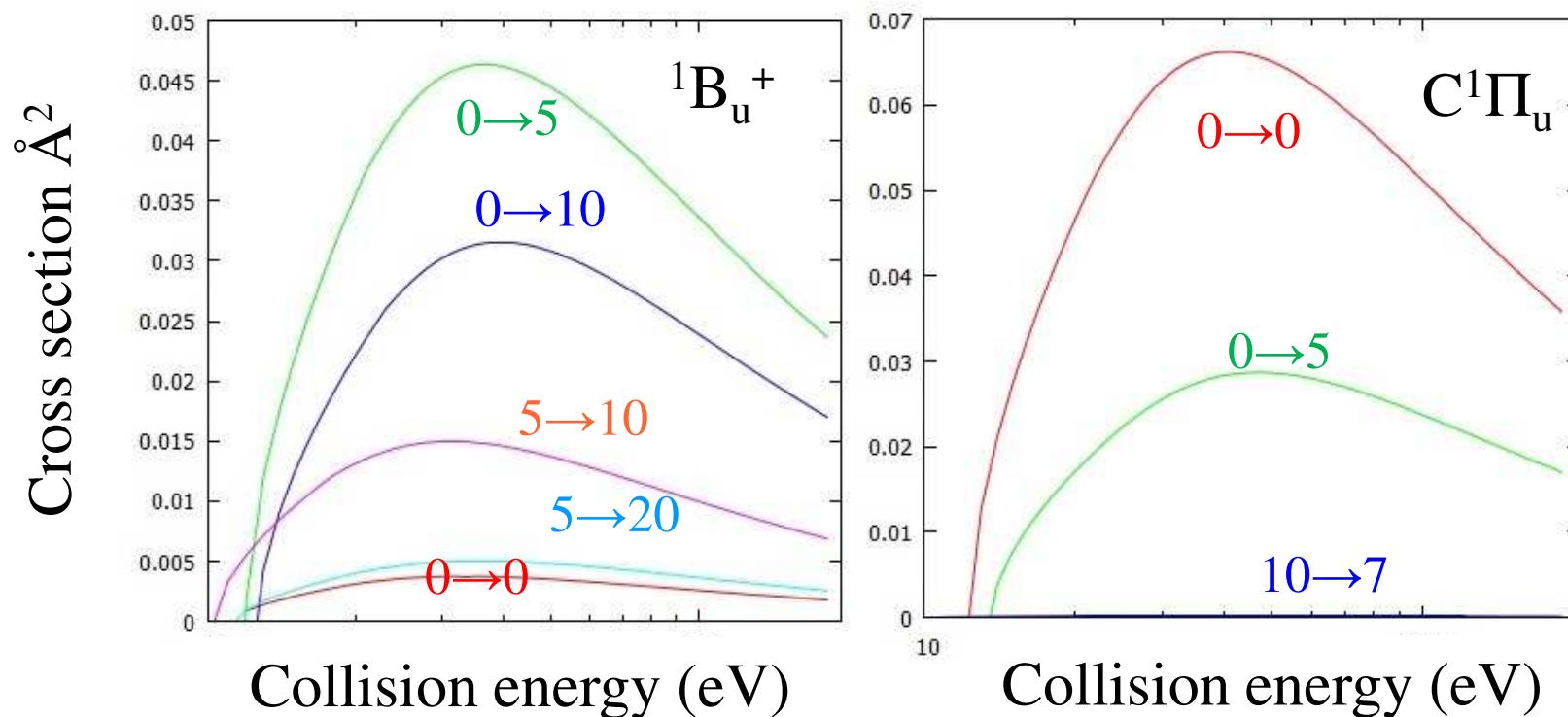
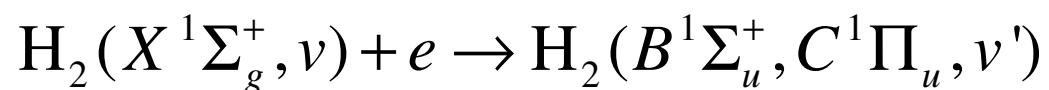


- ✓ state-to-state
- ✓ radiative processes

U. Fantz, D. Wunderlich, ADNDT (2006)



- ✓ state-to-state
- ✓ radiative processes
- ✓ energy profile cross section



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

The European Physical Journal D (2017), *Vibrational kinetics of electronically excited states in H<sub>2</sub> discharges*  
 Colonna, G., Pietanza, L. D., D'Ammando, G., Celiberto, R., Capitelli, M., & Laricchiuta, A.

✓ state-to-state

BE $f$  scaling

Tanaka et al. Reviews of Modern Physics (2016)  
Kim, J Chem Phys (2007)

✓ radiative processes

CCC approach

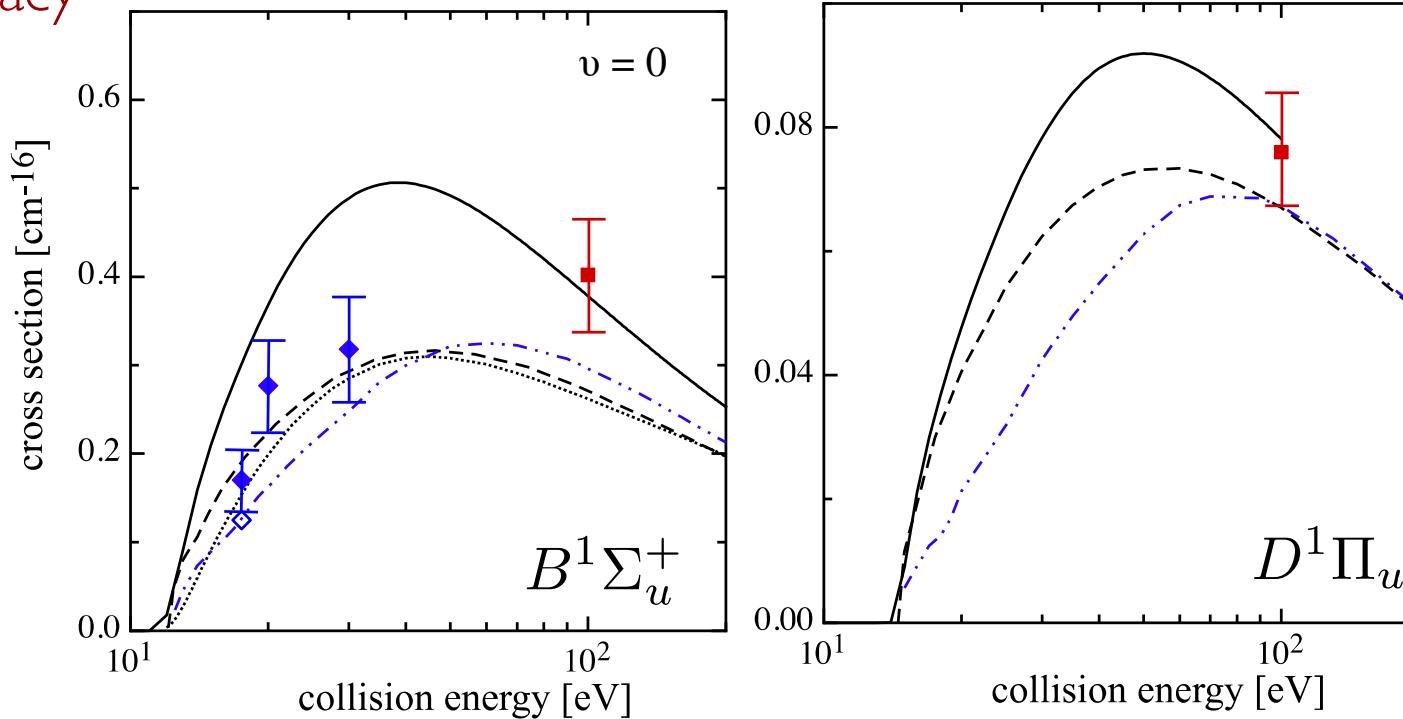
M.C. Zammit et al., Physical Review Letters (2016)

✓ energy profile cross sections

Ajello et al., Physical Review A (1984)

✓ accuracy

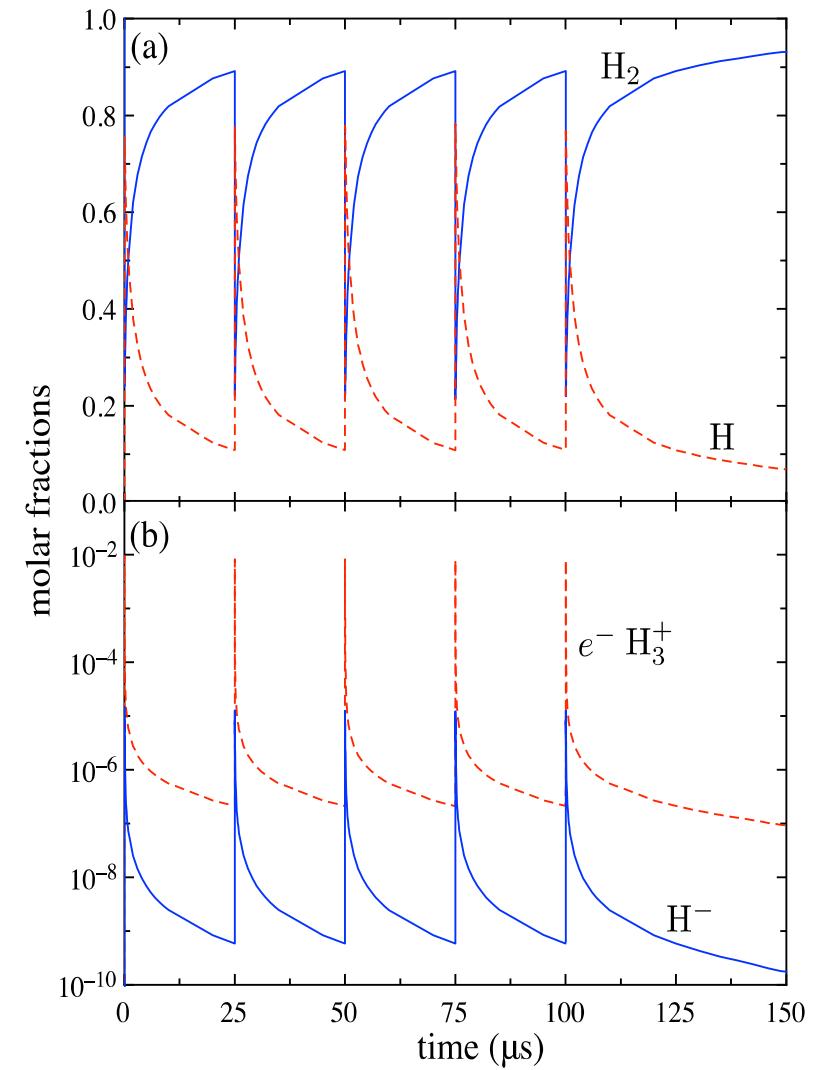
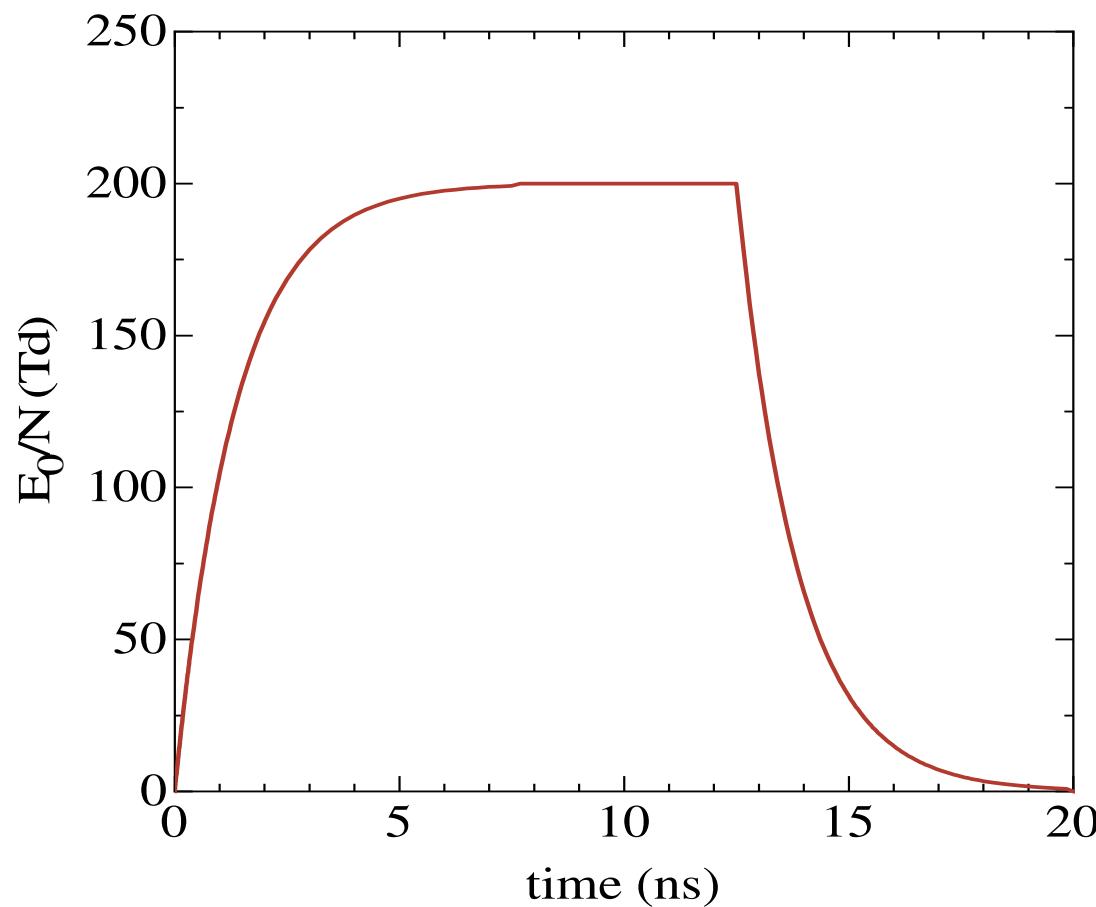
Wrkitch et al., Journal of Physics B (2002)



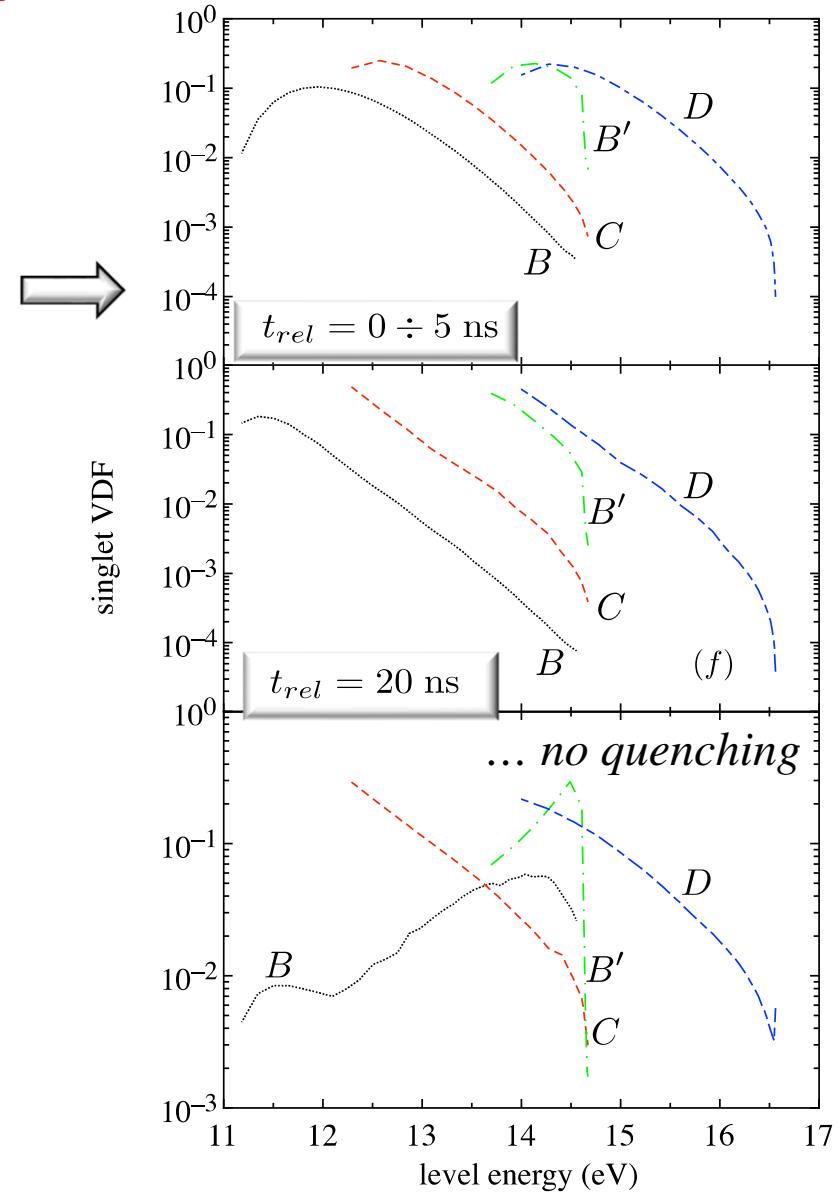
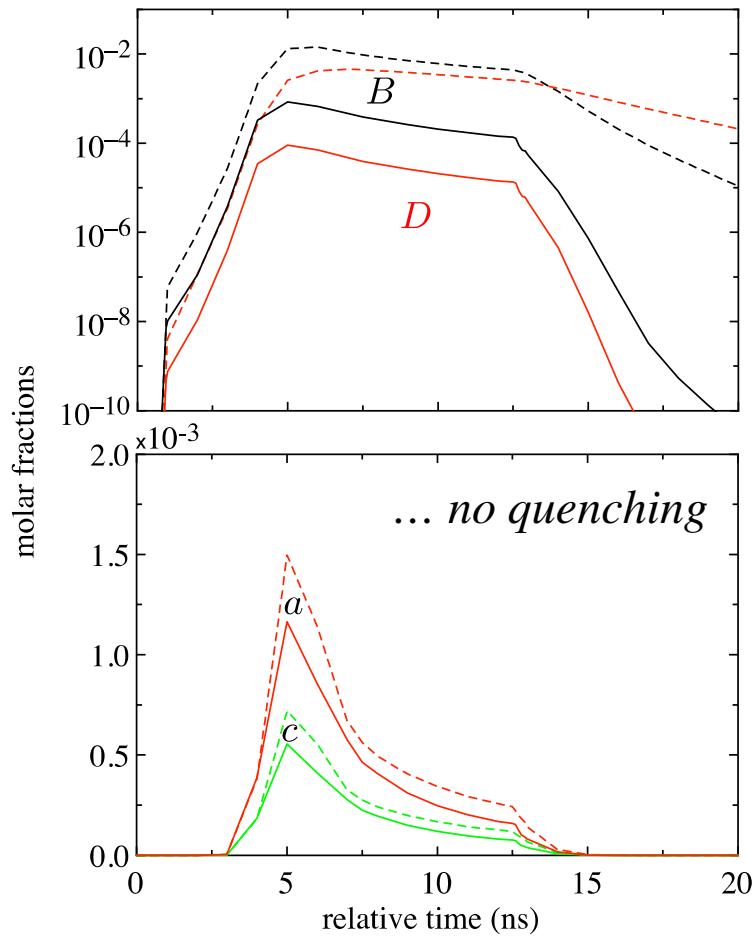
semiclassical IPM - R. Celiberto et al., ADNDT (2001)

The European Physical Journal D (2017), *Vibrational kinetics of electronically excited states in H<sub>2</sub> discharges*  
Colonna, G., Pietanza, L. D., D'Ammando, G., Celiberto, R., Capitelli, M., & Laricchiuta, A.

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

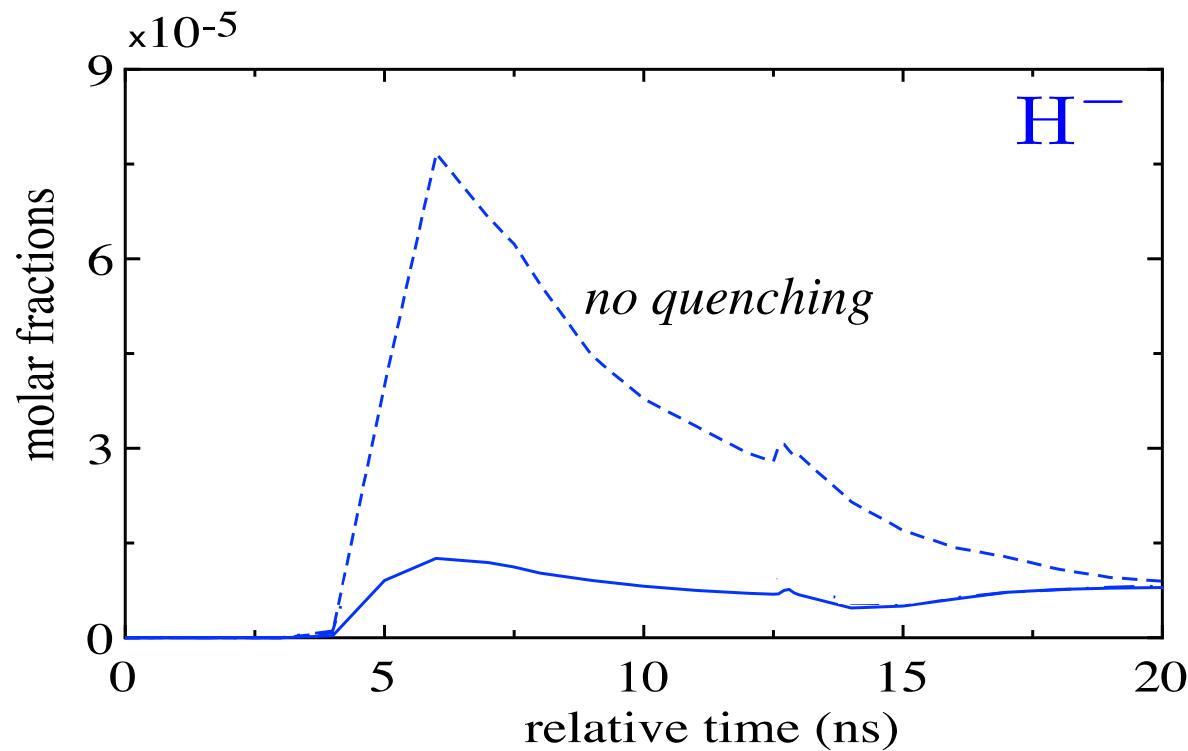


# Fast (ns-pulsed) discharges in hydrogen excited state concentration & singlets vibrational distributions



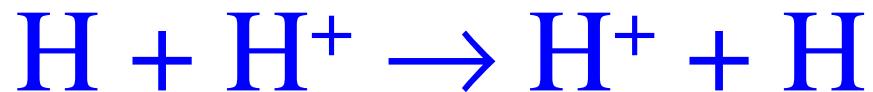
# Fast (ns-pulsed) discharges in hydrogen

## hydrogen negative ion concentration



## Dense plasmas

$$U = -\frac{e^{-r/\lambda_D}}{r} \quad \lambda_D = [k_B T_e / (4\pi n_e)]^{1/2}$$
 is the Debye length



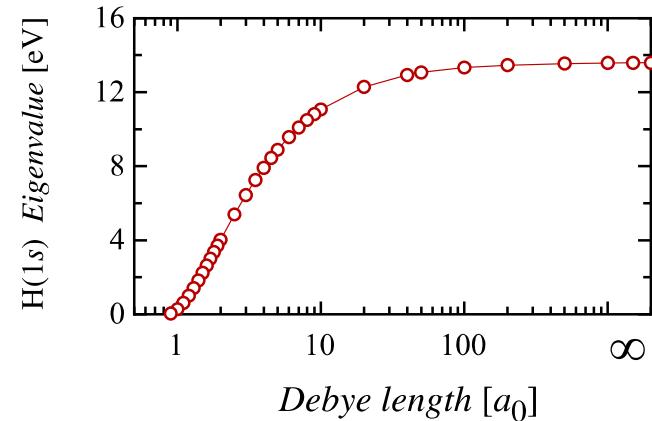
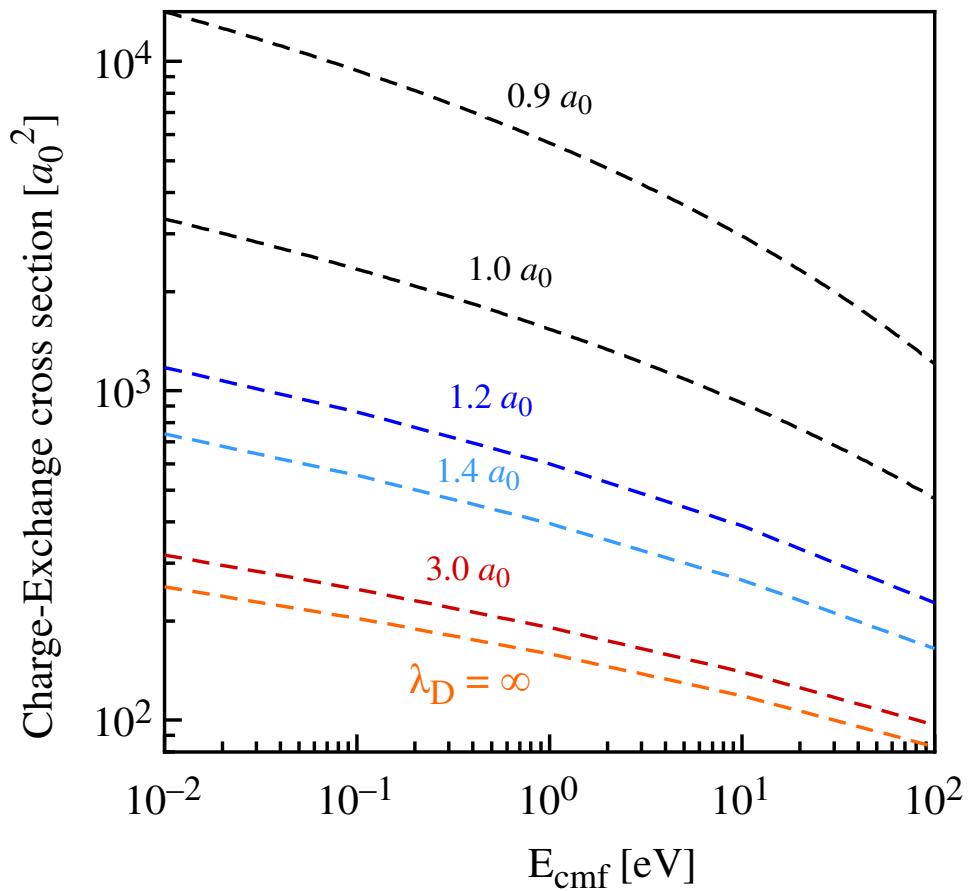
*Resonant charge exchange for H-H<sup>+</sup> in Debye plasmas*

A. Laricchiuta, G. Colonna, M. Capitelli, A. Kosarim, and B. M. Smirnov  
Eur. Phys. J. D (2017)

## $H^+ / H$ RESONANT CHARGE EXCHANGE in DEBYE PLASMAS

$s) + H^+$

### ASYMPTOTIC APPROACH

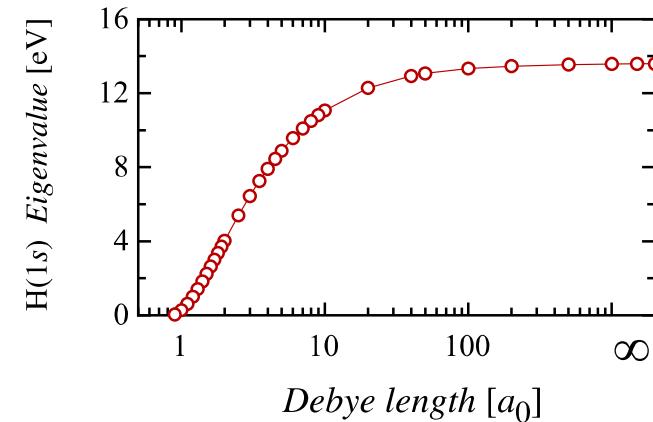
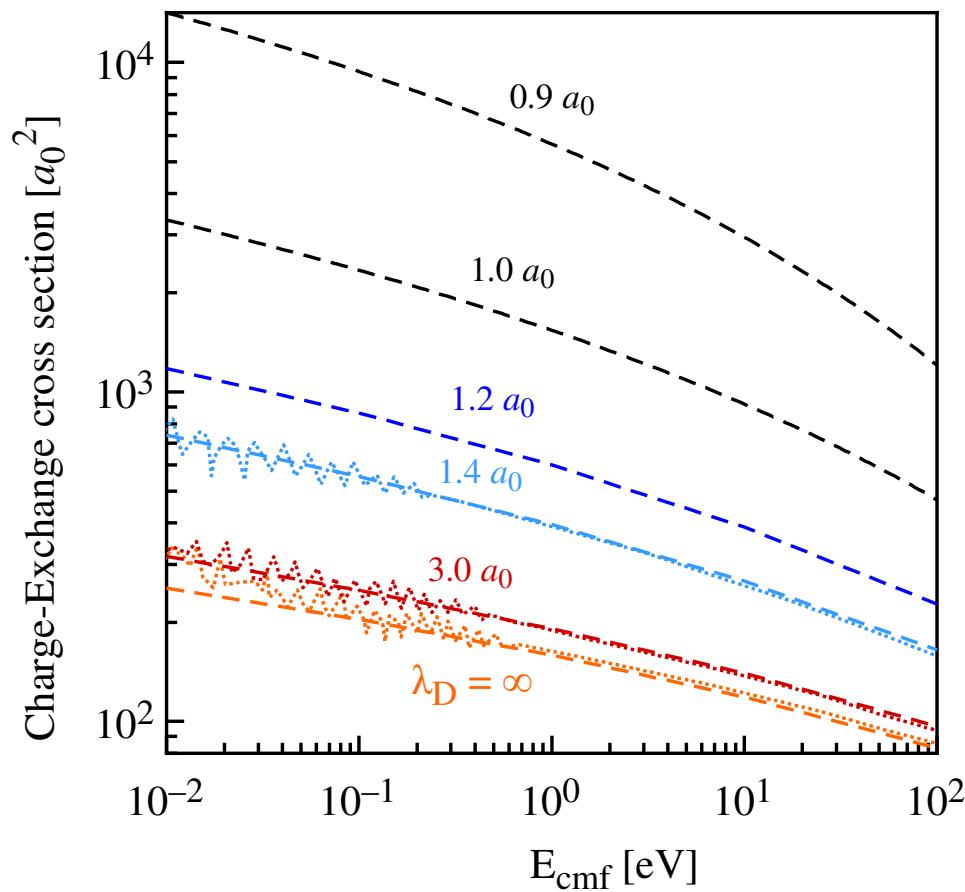


chiuta, A., Colonna, G., Capitelli, M., Kosarim, A., & Smirnov, B. M..  
Resonant charge exchange for  $H-H^+$  in Debye plasmas  
European Physical Journal D (2017).

$s) + H^+$

## H<sup>+</sup>/H RESONANT CHARGE EXCHANGE in DEBYE PLASMAS

### ASYMPTOTIC APPROACH vs QUANTUM



J.G. Wang, P.S. Krstic, R.K. Janev, J. Phys. B 43, (2010)

chiuta, A., Colonna, G., Capitelli, M., Kosarim, A., & Smirnov, B. M.

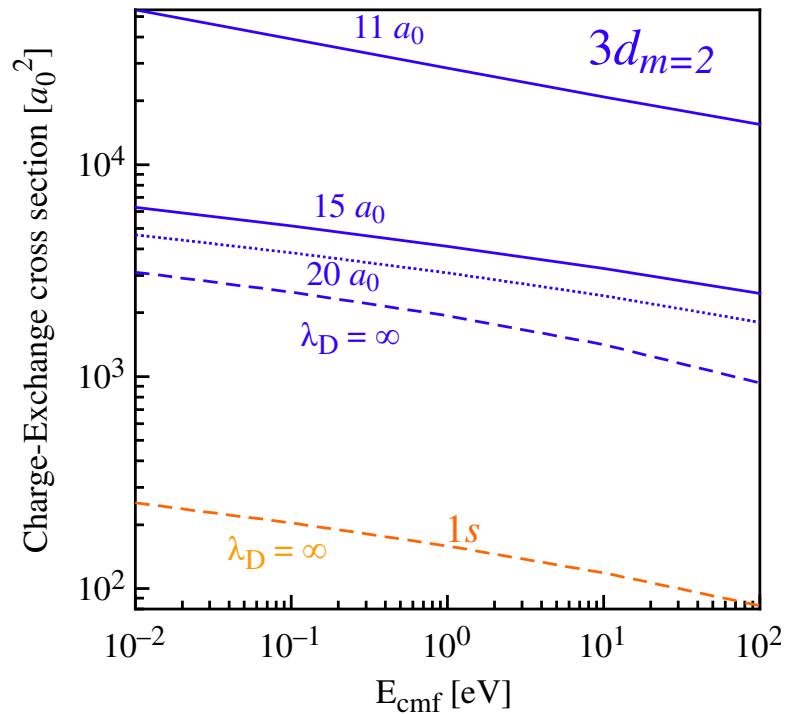
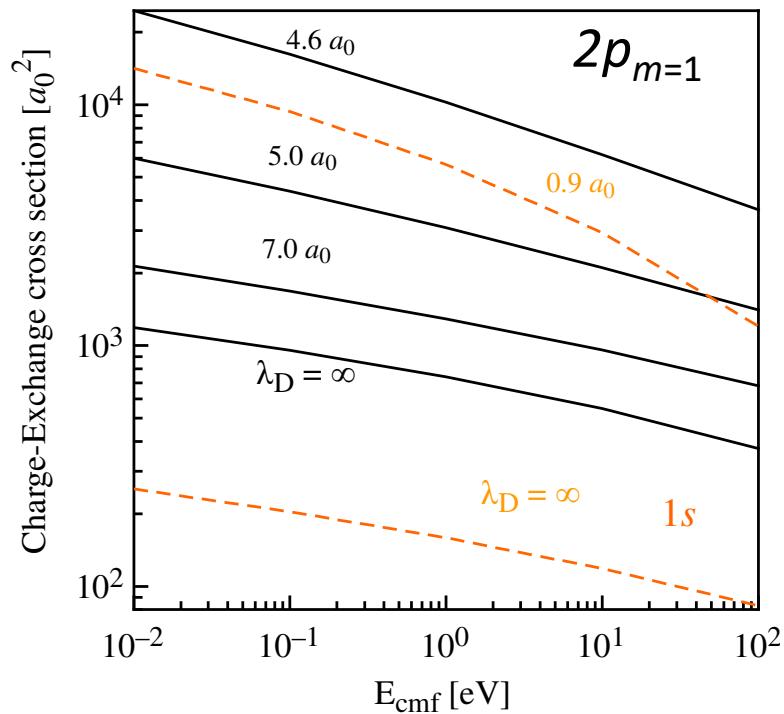
*Resonant charge exchange for H–H<sup>+</sup> in Debye plasmas*

European Physical Journal D (2017).

## $H^+/H$ RESONANT CHARGE EXCHANGE in DEBYE PLASMAS

$n = 2, 3) + H^+$

EXCITED STATES  $H^*$



chiuta, A., Colonna, G., Capitelli, M., Kosarim, A., & Smirnov, B. M..

*Resonant charge exchange for  $H-H^+$  in Debye plasmas*

European Physical Journal D (2017).

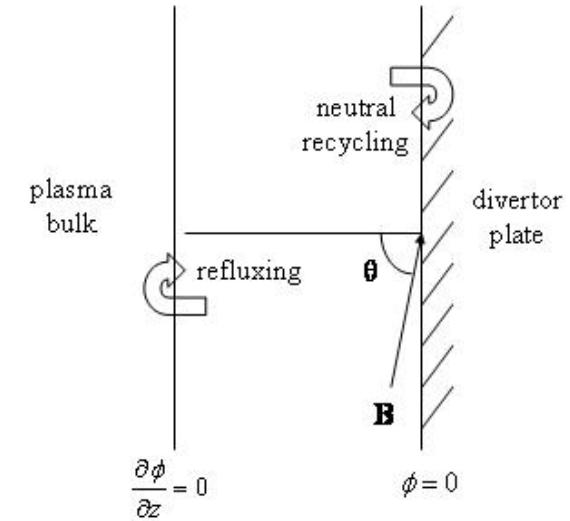
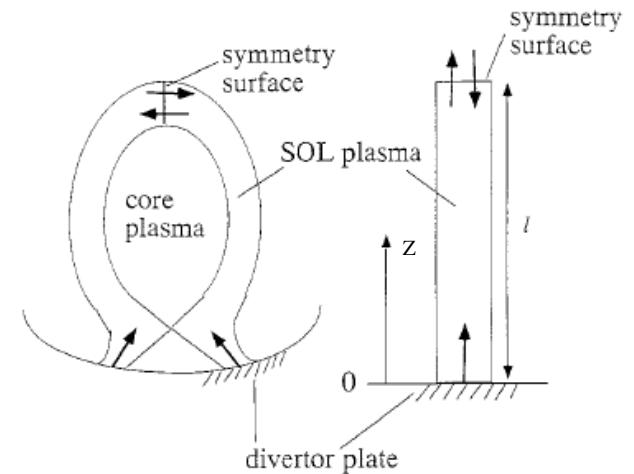
# Kinetic and divertor modeling

F. Taccogna, P. Minelli, D. Bruno, S. Longo, R. Schneider  
Chem. Phys. (2012)

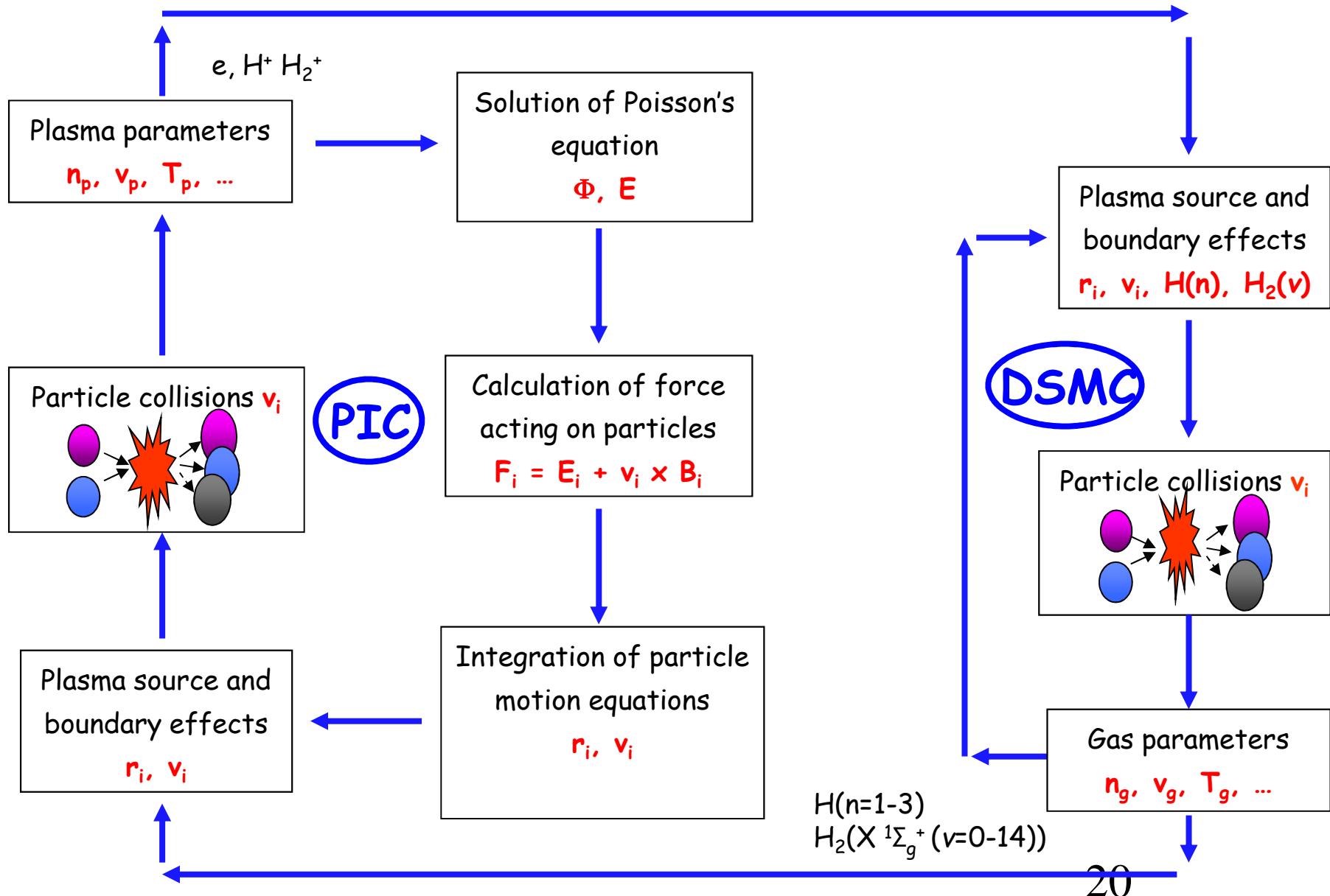
# Reduction of the Divertor Region to 1 Dimension



- o Input data:  
(detached divertor plasma condition)
  - e/H<sup>+</sup> density:  $n_p = 10^{21} \text{ m}^{-3}$
  - e/H<sup>+</sup> Temperature :  $T_p = 5 \text{ eV}$
  - $B = 1 \text{ Tesla}$ ;  $\theta = 85^\circ$
- o Simulation domain:  $l = 0.3 \text{ mm}$
- o Every Particle carries:
  - species: e, H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, H; H, H<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)
  - axial position, velocities: ( $z, v_x, v_y, v_z$ )
  - quantities averaged over x,y (uniformity)
  - quantum energy levels:
    - electronic: n=1s-3s for H
    - vibrational:  $v=0-14$  for H<sub>2</sub>
- o Collision Methodology:
  - Plasma-Plasma (e+H<sub>2</sub><sup>+</sup>/H+H<sup>+</sup>/H+e)
  - Plasma-Neutral
  - Neutral-Neutral relaxation (Vt/VT/VV)
- o Boundary module:
  - H<sub>2</sub>(v) wall relaxation-dissociation
  - H wall recombinative desorption (ER/LH) -> H<sub>2</sub>(v) vibrational excitation (A-V)
  - H<sup>+</sup>/H<sub>2</sub><sup>+</sup>/ wall Auger neutralization -> H<sub>2</sub>(v) vibrational excitation (s-V)

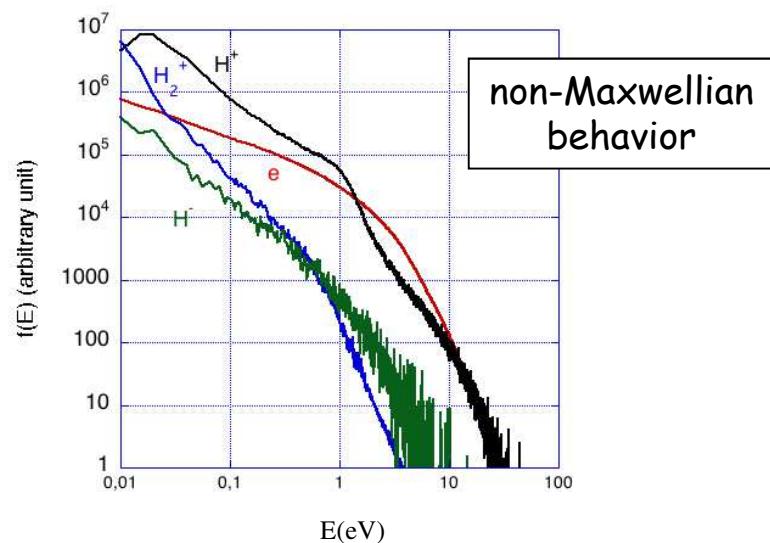
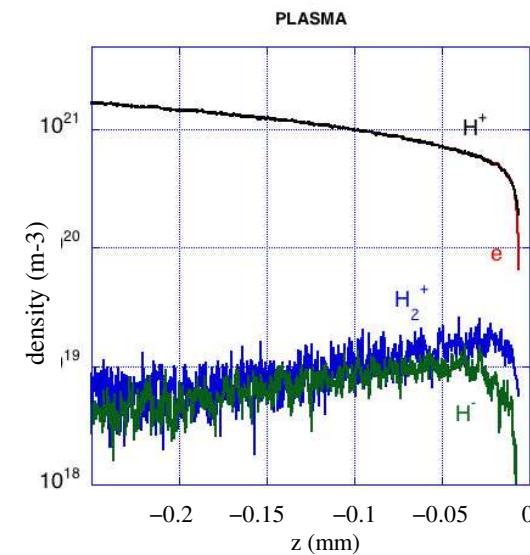
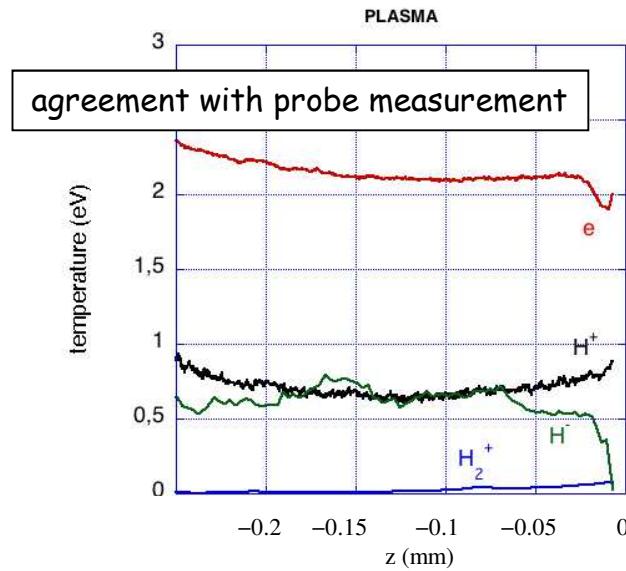
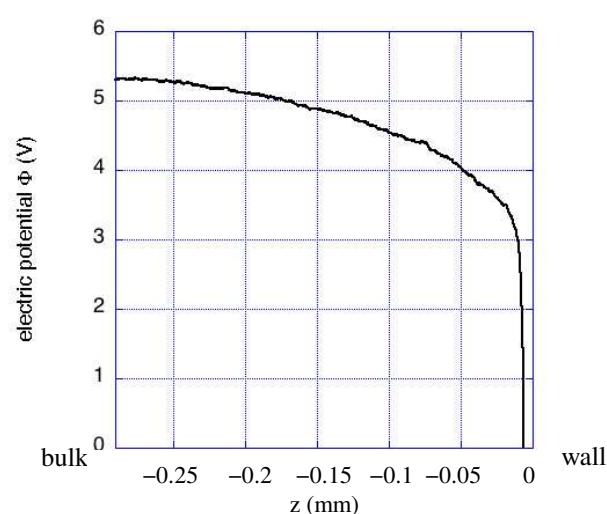


# Particle-in-Cell / Direct Simulation Monte Carlo Model of Plasma-Gas Coupling in the Divertor Region (PIC-DSMC)

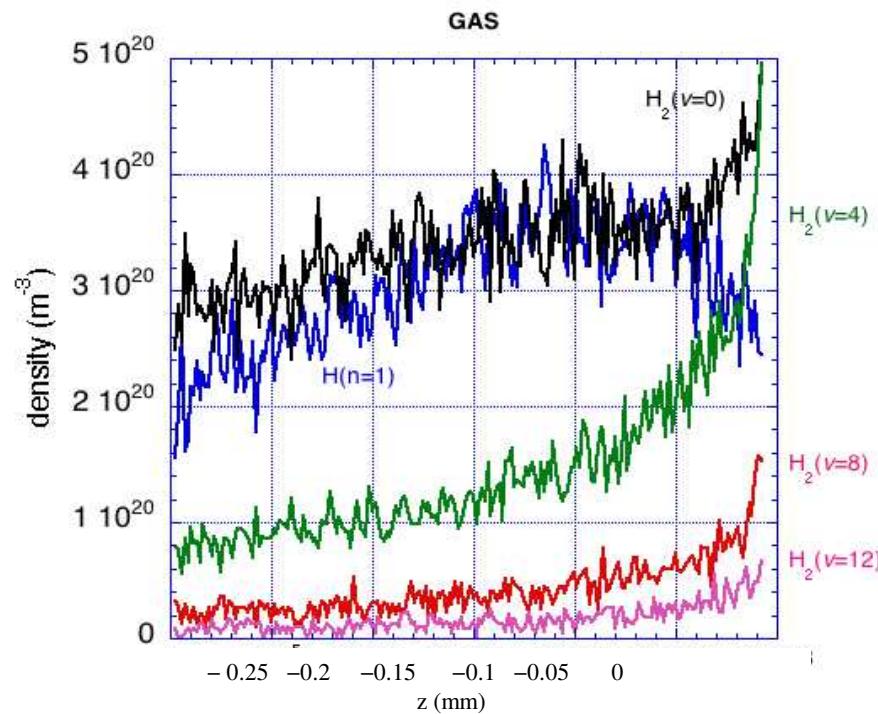




# Results: Plasma



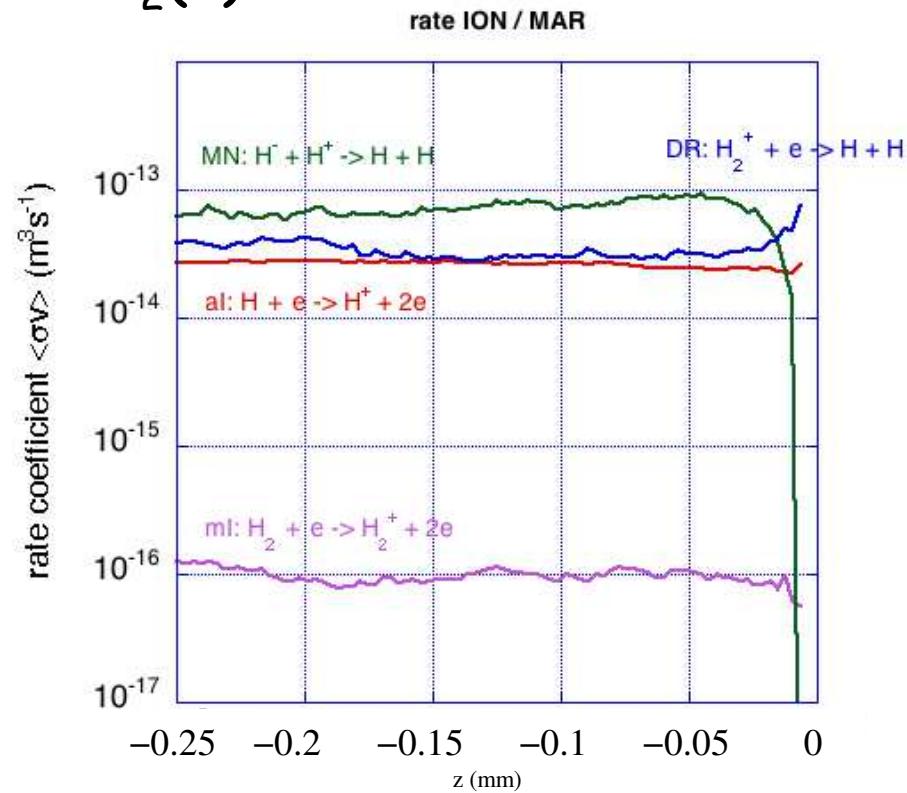
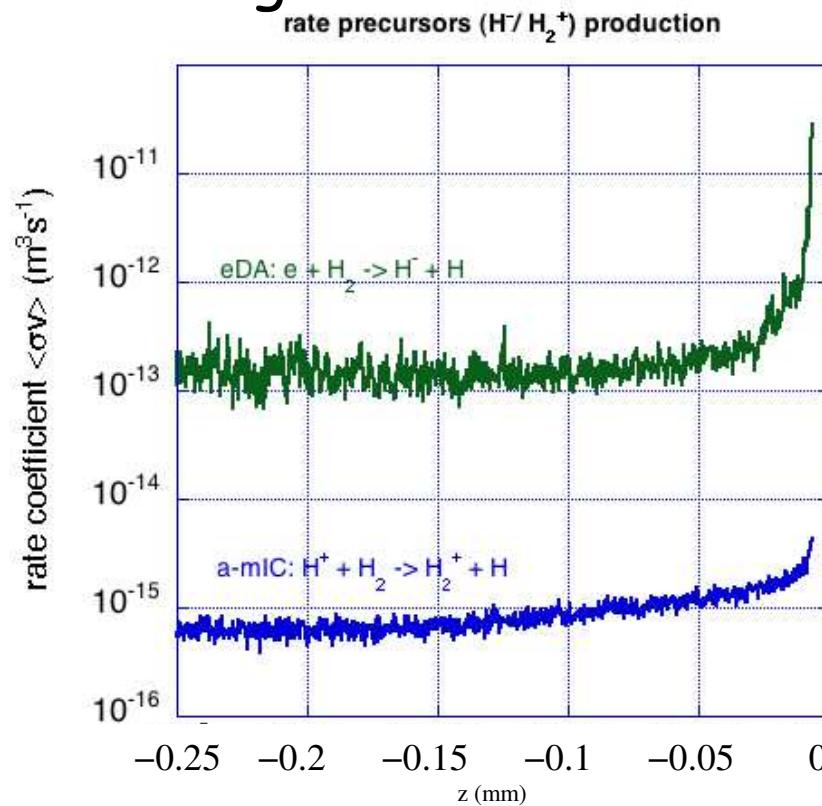
# Results: Gas



## Results: MAR processes

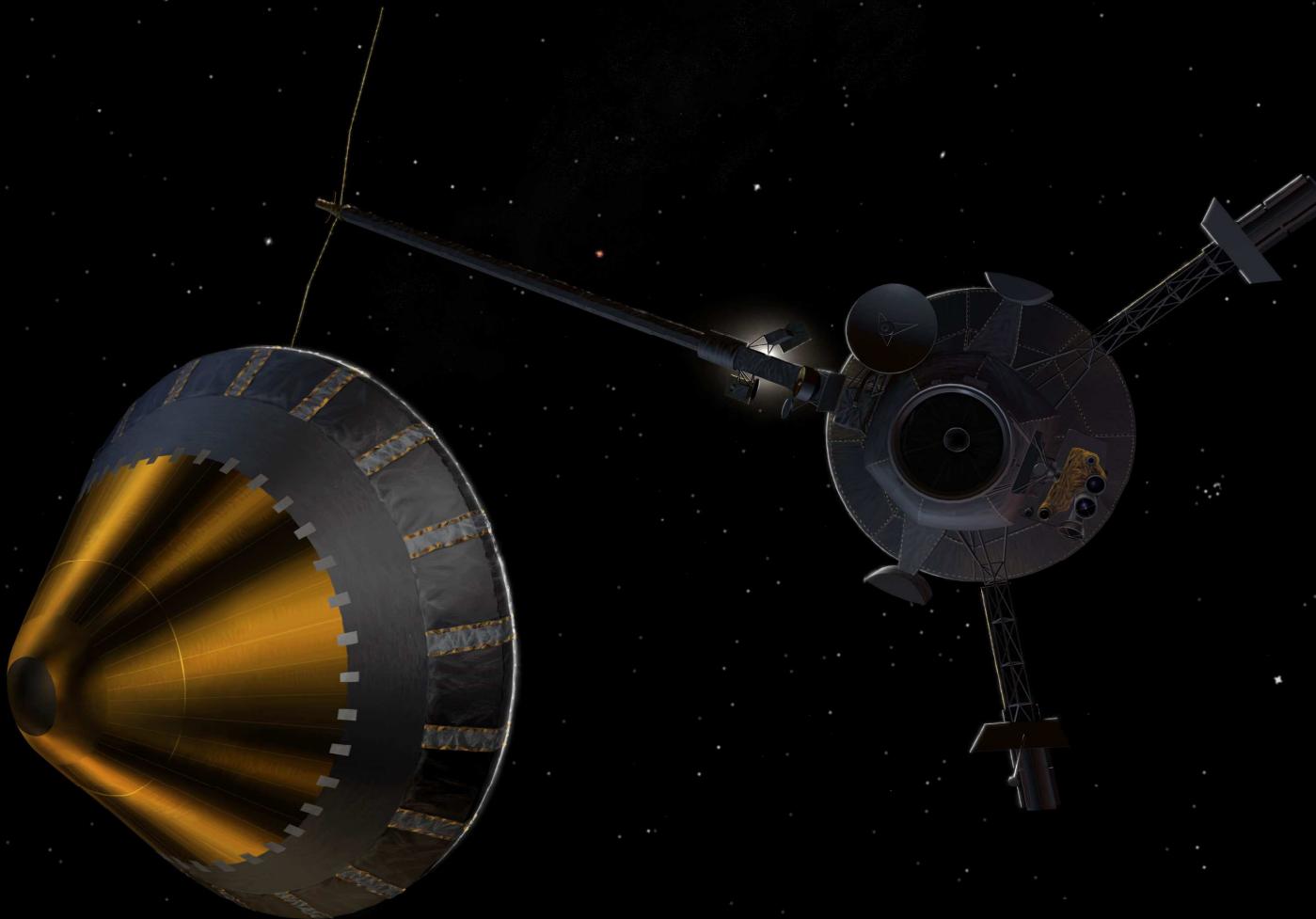


production of precursors peaks close to the wall  
due to high vibrational excitation  $H_2(v)$



- a)  $e + H_2(v) \rightarrow H + H^-$ ,  $H^- + H^+ \rightarrow H + H$
- b)  $H^+ + H_2(v) \rightarrow H + H_2^+$ ,  $H_2^+ + e \rightarrow H + H$

# Aerospace Sciences

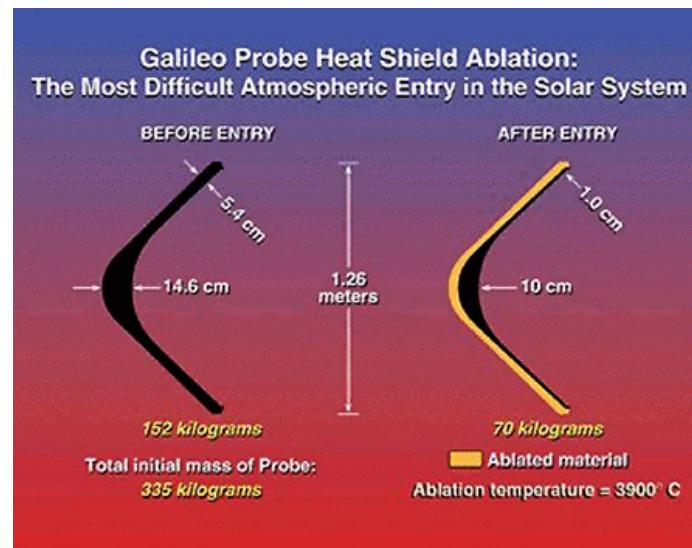


DON DAVIS 6/26/95



# Motivation

Planet	Speed (km/s)	Heat flux (kW/cm <sup>2</sup> )	Enthalpy (kJ/cm <sup>2</sup> )	Acceleration (g)
Jupiter	47.4	30	300	250
Saturn	26.9	1.3	257	
Uranus	22.3	5.1	32.8	



Modelling chemical kinetics and convective heating in giant planet entries  
P. Reynier, G. D'Ammendo, D. Bruno,  
Progress in Aerospace Sciences (2018)

The code couples the fluid-dynamics with the kinetic chemistry  
 (Jupiter atmosphere modeled: H<sub>2</sub>/He)

### Fluid-dynamics input data

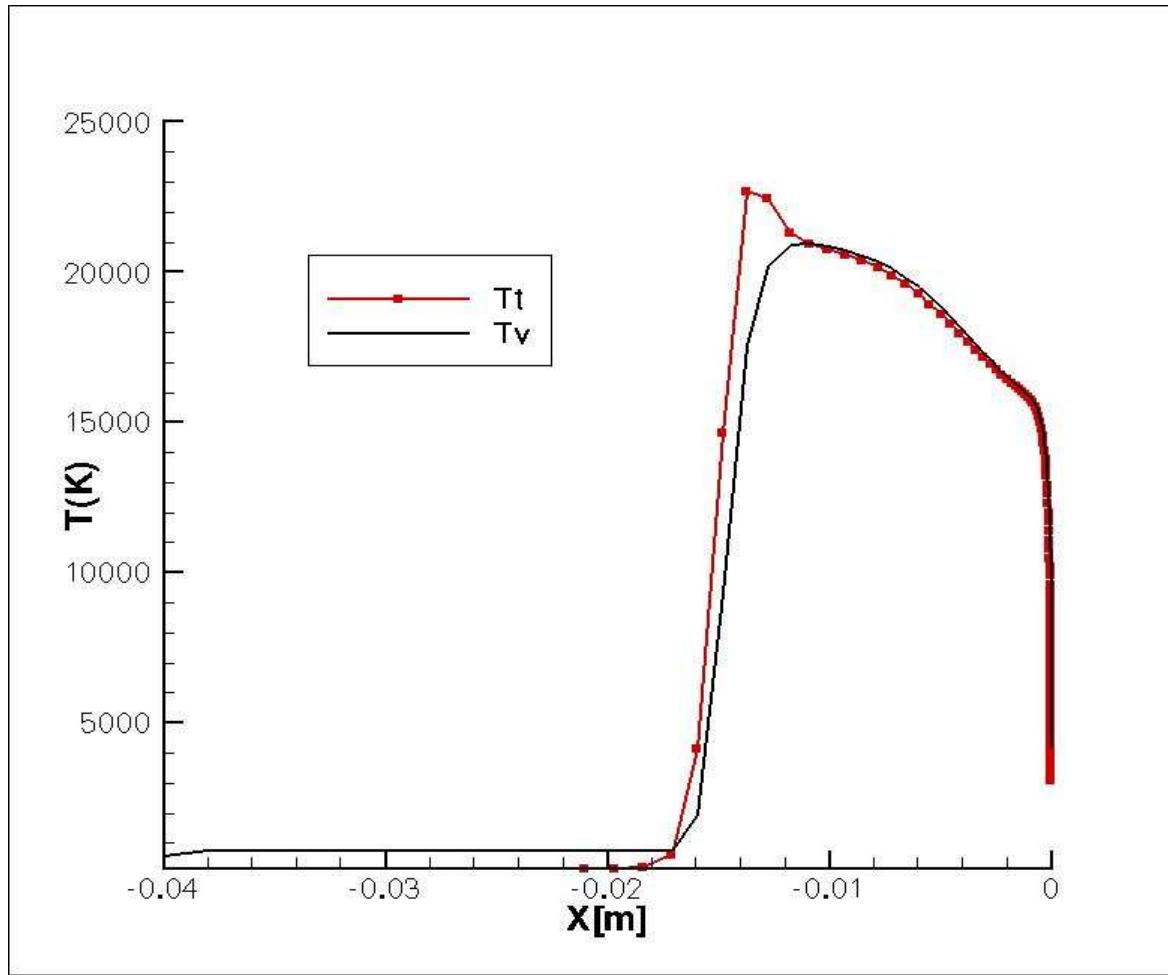
Flight data, i.e. probe velocity, gas density, gas temperature and pressure as a function of the altitude in the atmosphere.

### Chemical input data

Cross sections for all the processes included in the model.

#### Kinetic scheme

Processes	
$H + e^- = H^+ + e^- + e^-$	$H_2 + e^- = 2H + e^-$
$He + e^- = He^+ + e^- + e^-$	$H_2 + e^- = H_2^+ + 2e^-$
$H + H = H^+ + e^- + H$	$H_2 + e^- = H + H^+ + 2e^-$
$H + He = H^+ + e^- + He$	$H_2^+ + e^- = 2H^+ + 2e^-$
$H_2 + He = H + H + He$	$H_2^+ + e^- = H + H^+ + e^-$
$H_2 + H_2 = H + H + H_2$	$H_2^+ + e^- = 2H$
$H_2 + H = H + H + H$	$H + e^- = H^+ + 2e^-$
$H_2 + H^+ = H + H + H^+$	$He + e^- = He^+ + 2e^-$
$H_2 + e^- = H + H + e^-$	$H + H = H + H^+ + e^-$
$H_2^+ + e^- = H + H$	$He + He = He + He^+ + e^-$
	$H_2 + H_2 = 2H + H_2$
	$H_2 + H = 3H$
	$H_2 + He = 2H + He$



$T_t(K)$  = translational temperature along the stagnation line at 18 km of altitude;

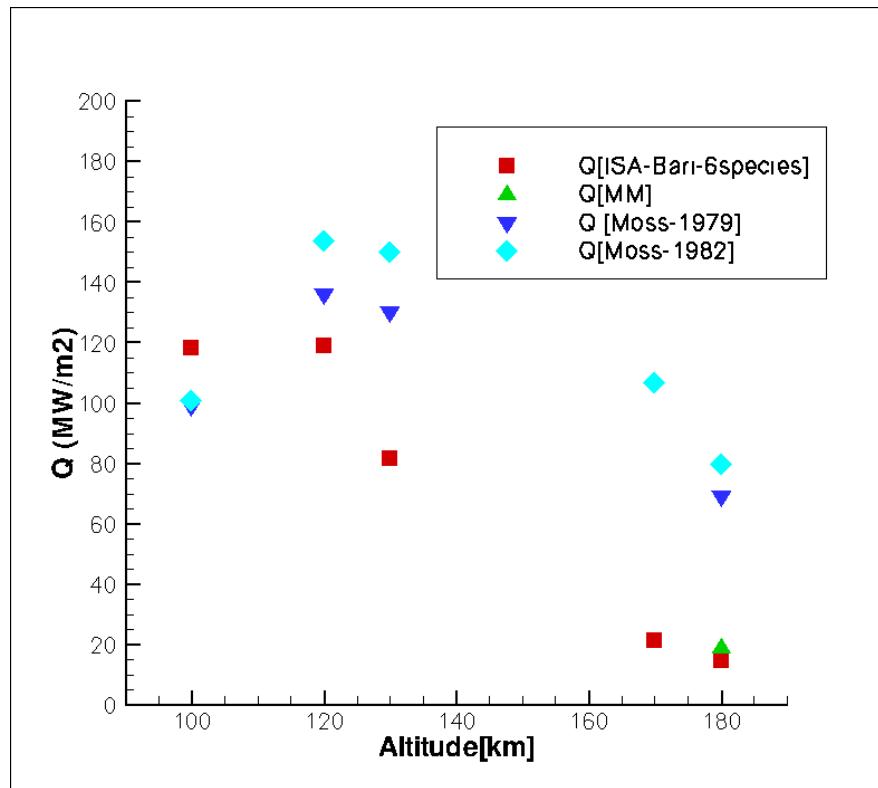
$T_v(K)$  = vibrational temperature;

$X(m)$  = distance from the pro-

[1] D. Bruno et al., Transport properties of high-temperature Jupiter atmosphere components, *Physics of Plasmas*, **17**(11) (2010) 112315.

[2] G. Palmer, D. Prabhu, B. A. Cruden, Aeroheating uncertainties in Uranus and Saturn entries by the Monte Carlo method, *Journal of Spacecraft and Rockets*, **51**(3) (2014) 801–814.

# Convective Heat Flux



Ph. Reynier, G. D'Ammando, D. Bruno, Review: Modelling chemical kinetics and convective heating in giant planet entries, *Progress in Aerospace Sciences* **96** (2018) 1-22.

## Elementary processes



Heavy particle collisions



Electron-molecule collisions

# *Collision processes of heavy particles*

Inelastic processes



Reactive processes



Dissociation



# *Collision processes of heavy particles*

Inelastic processes



Reactive processes



Dissociation

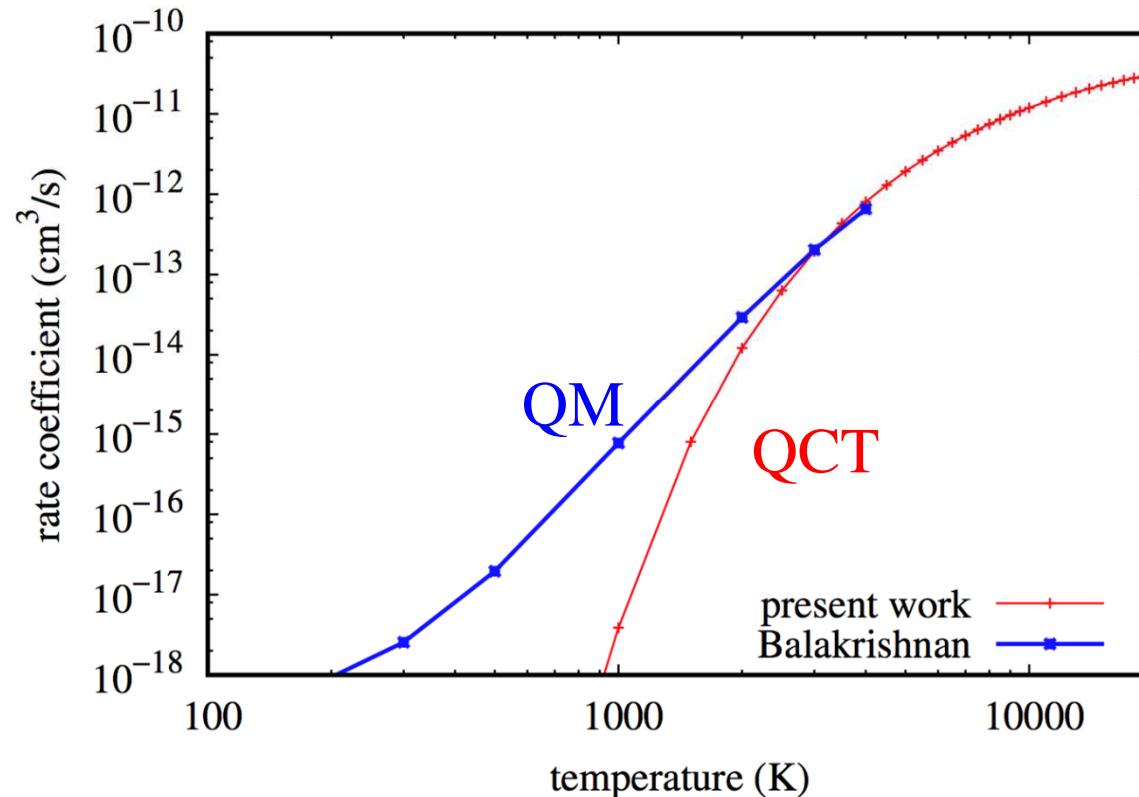


The general philosophy is to use approximated methods for cross section calculations to reduce the computational load

*Quasi-classical trajectory method*

# *Relaxation of He+H<sub>2</sub>*

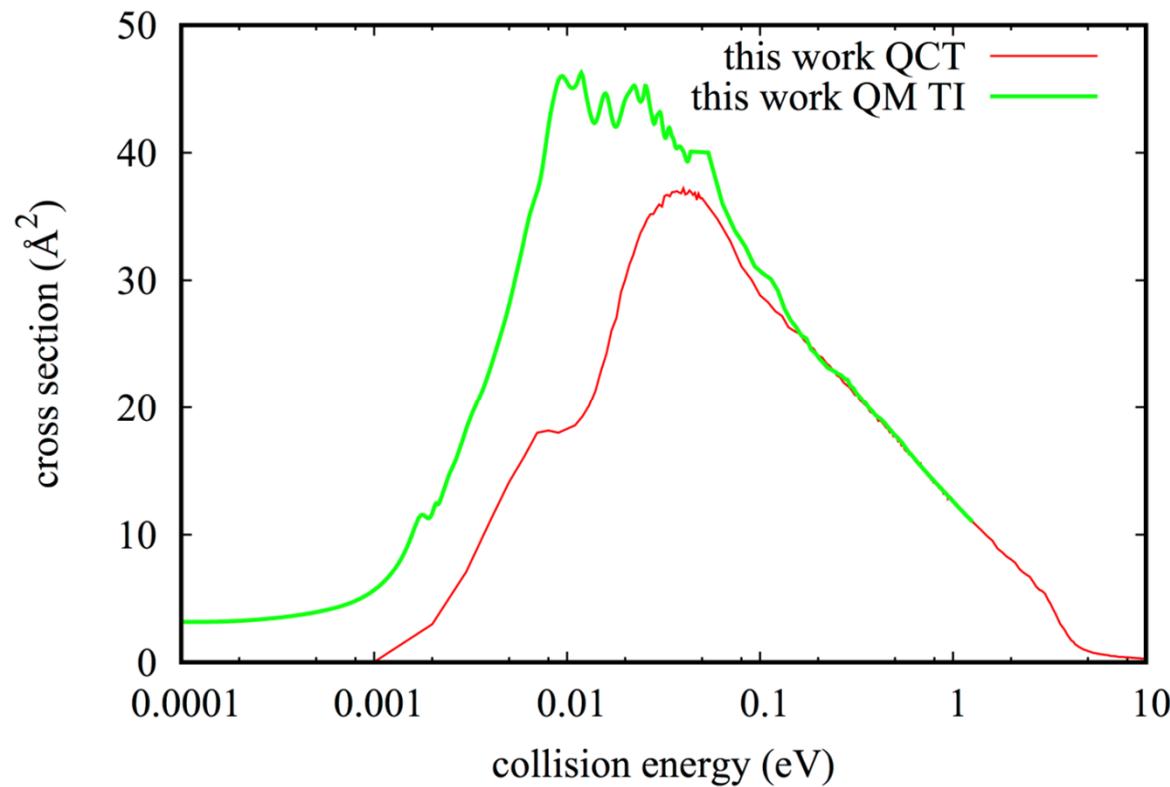
Comparison of QCT with QM Close Coupling calculations



- R. Celiberto, M. Capitelli, G. Colonna, G. D’Ammando, F. Esposito,  
R. Janev, V. Laporta, A. Laricchiuta, L. Pietanza, M. Rutigliano, and J. Wadehra, Atoms **5**, 18 (2017).  
N. Balakrishnan, M. Vieira, J. Babb, A. Dalgarno, R. Forrey, and S. Lepp, ApJ **524**, 1122 (1999).

# *Reaction of $H+HeH^+\rightarrow He+H_2^+$*

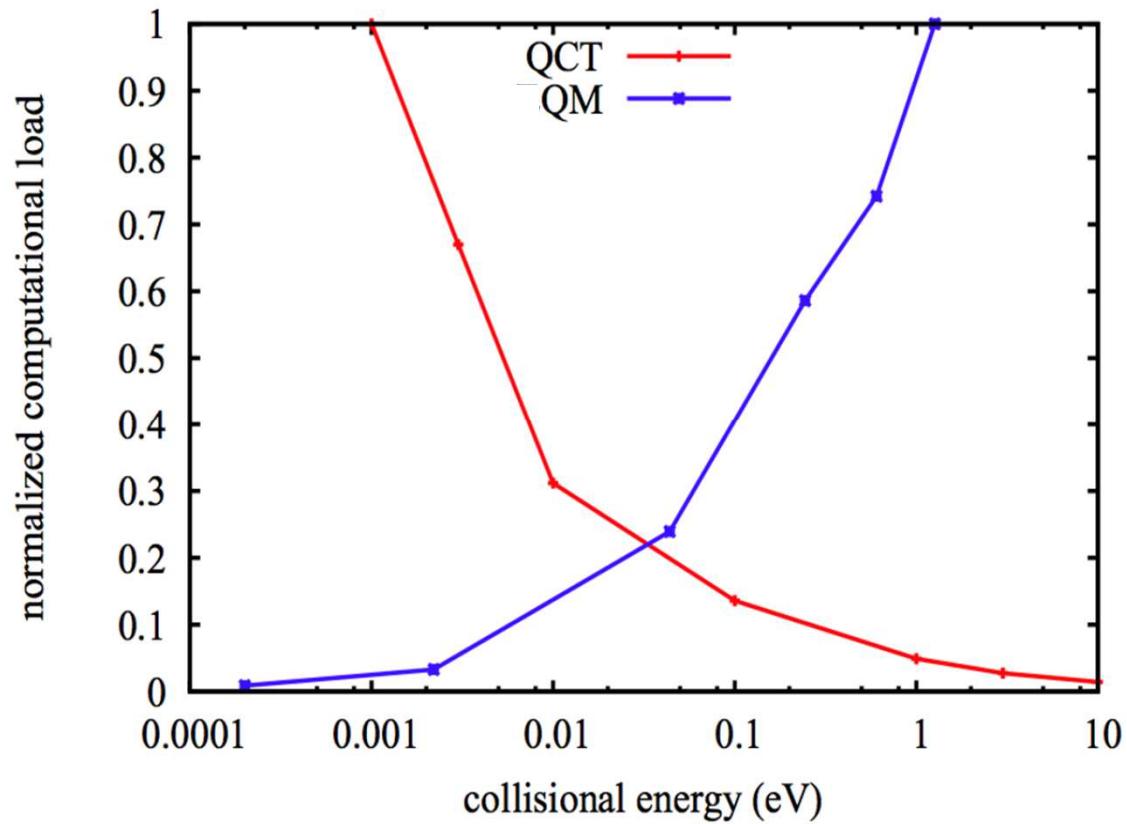
Comparison of QCT with accurate QM calculations



F. Esposito, C.M. Coppola, and D. De Fazio,  
JPCA **119**, 12615–12626 (2015).

# *Reaction of $H + HeH^+ \rightarrow He + H_2^+$*

Normalized computational load in QCT and QM calculations



F. Esposito, C.M. Coppola, and D. De Fazio,  
JPCA **119**, 12615–12626 (2015).

## Electron-molecule collisions



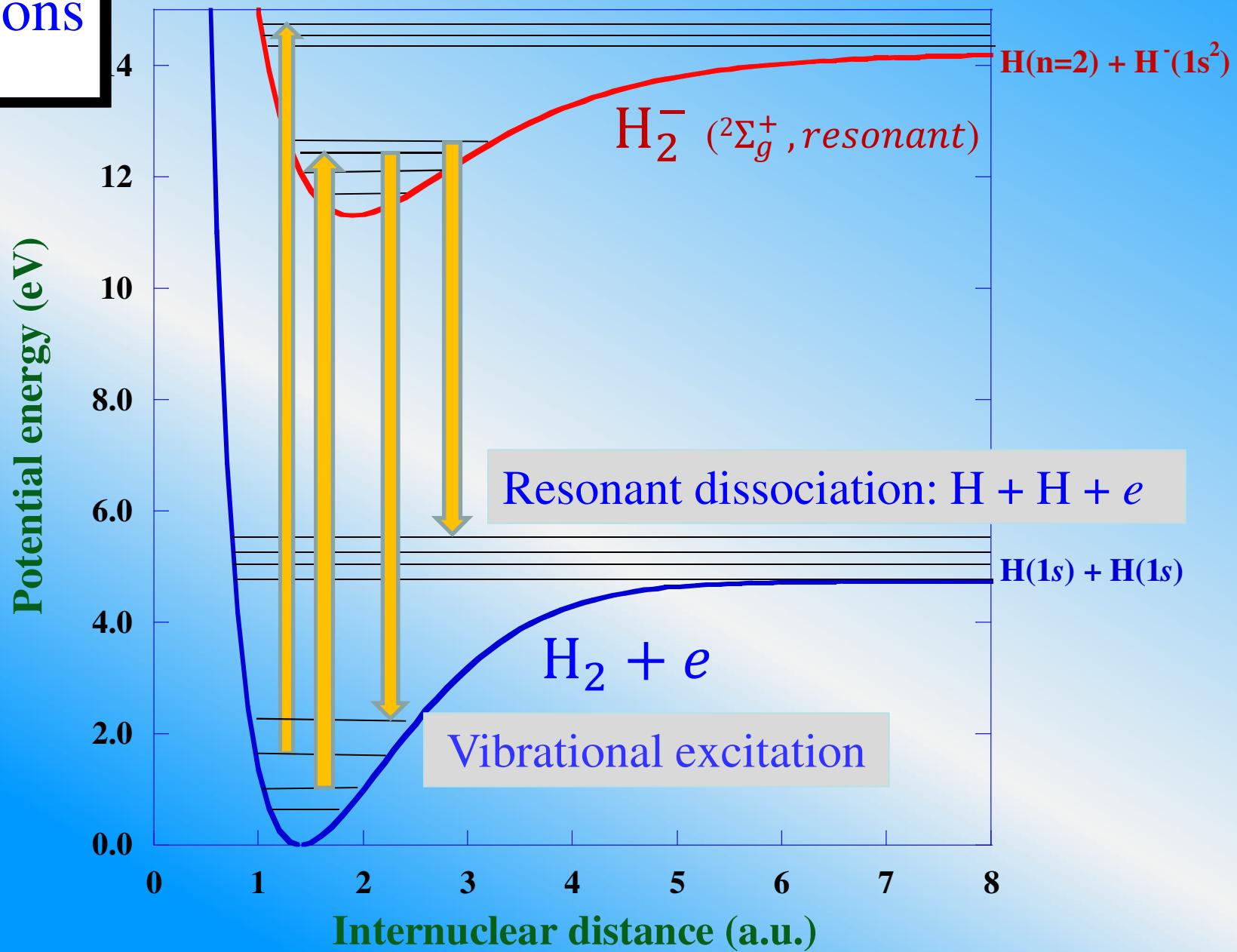
Resonant collisions



Non-resonant collisions

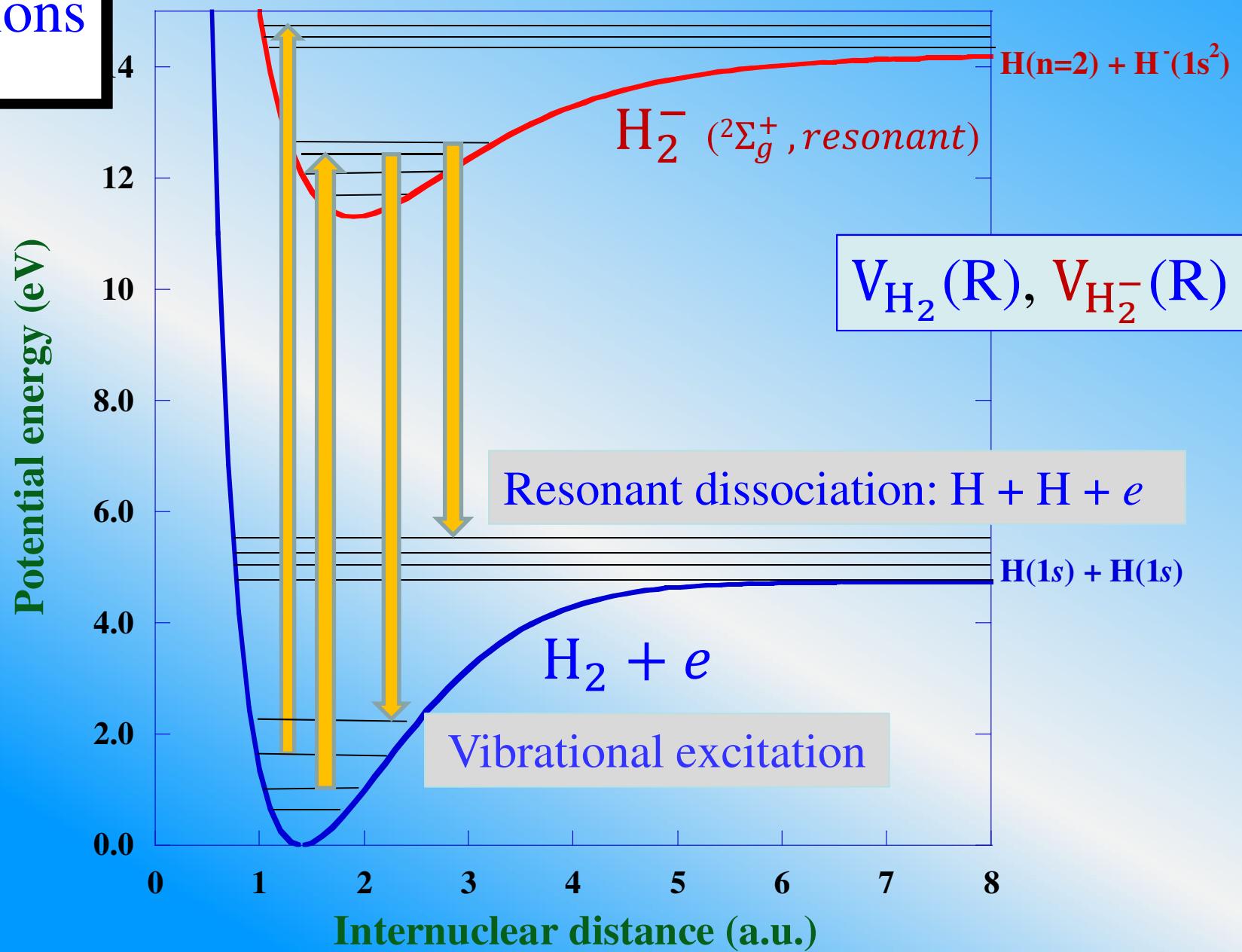
onant collisions

Dissociative attachment:  $\text{H} + \text{H}^-$



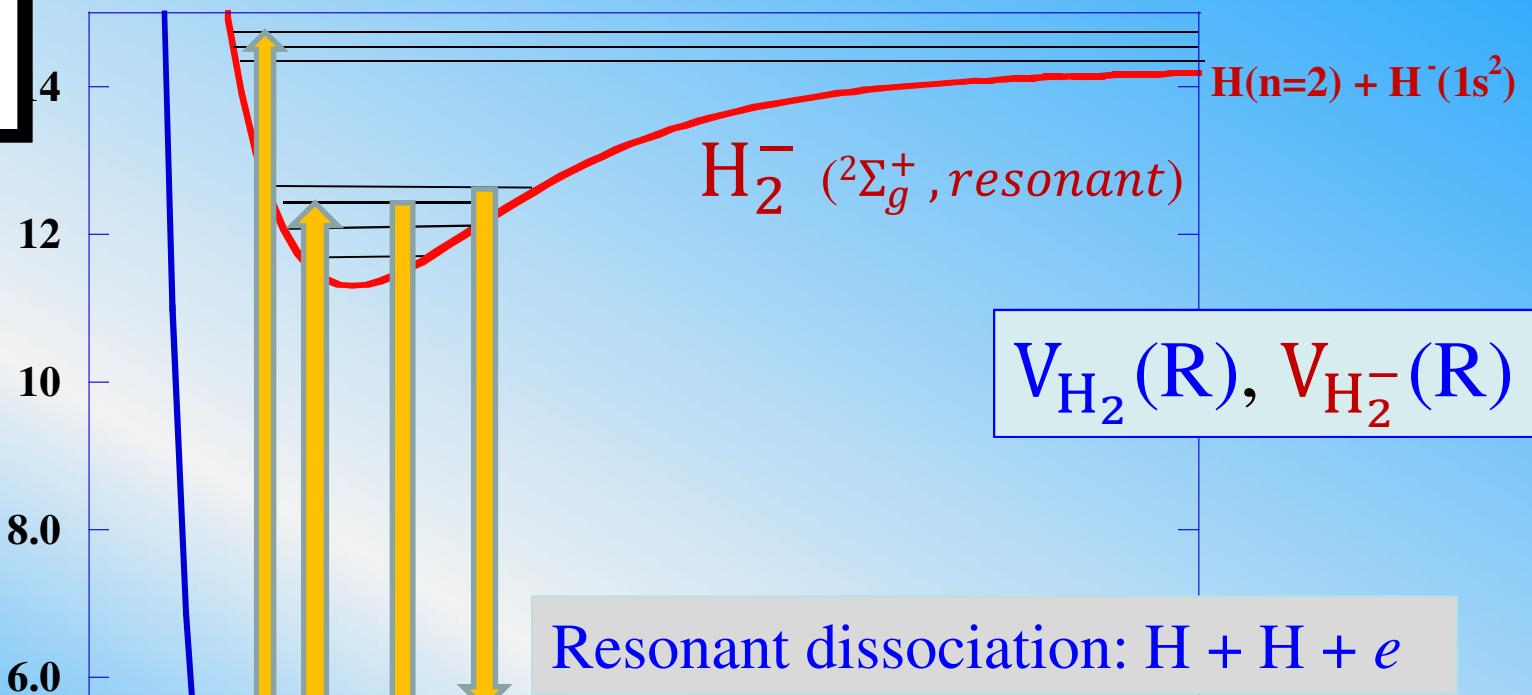
onant collisions

Dissociative attachment:  $\text{H} + \text{H}^-$



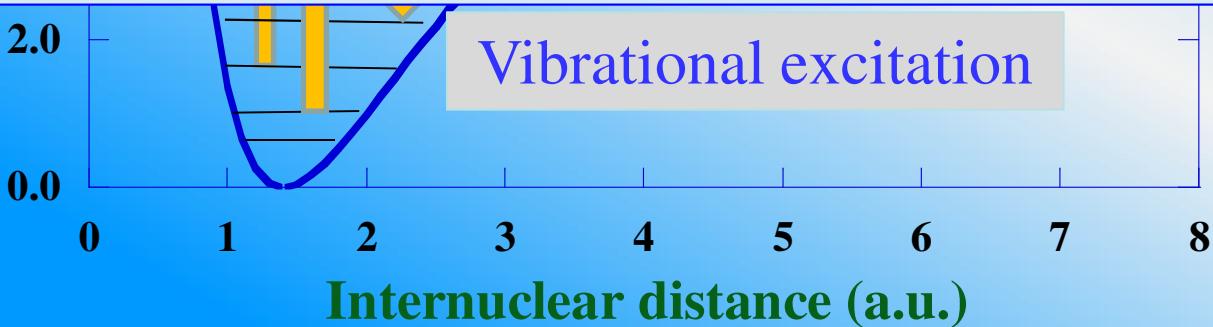
onant collisions

Dissociative attachment:  $\text{H} + \text{H}^-$



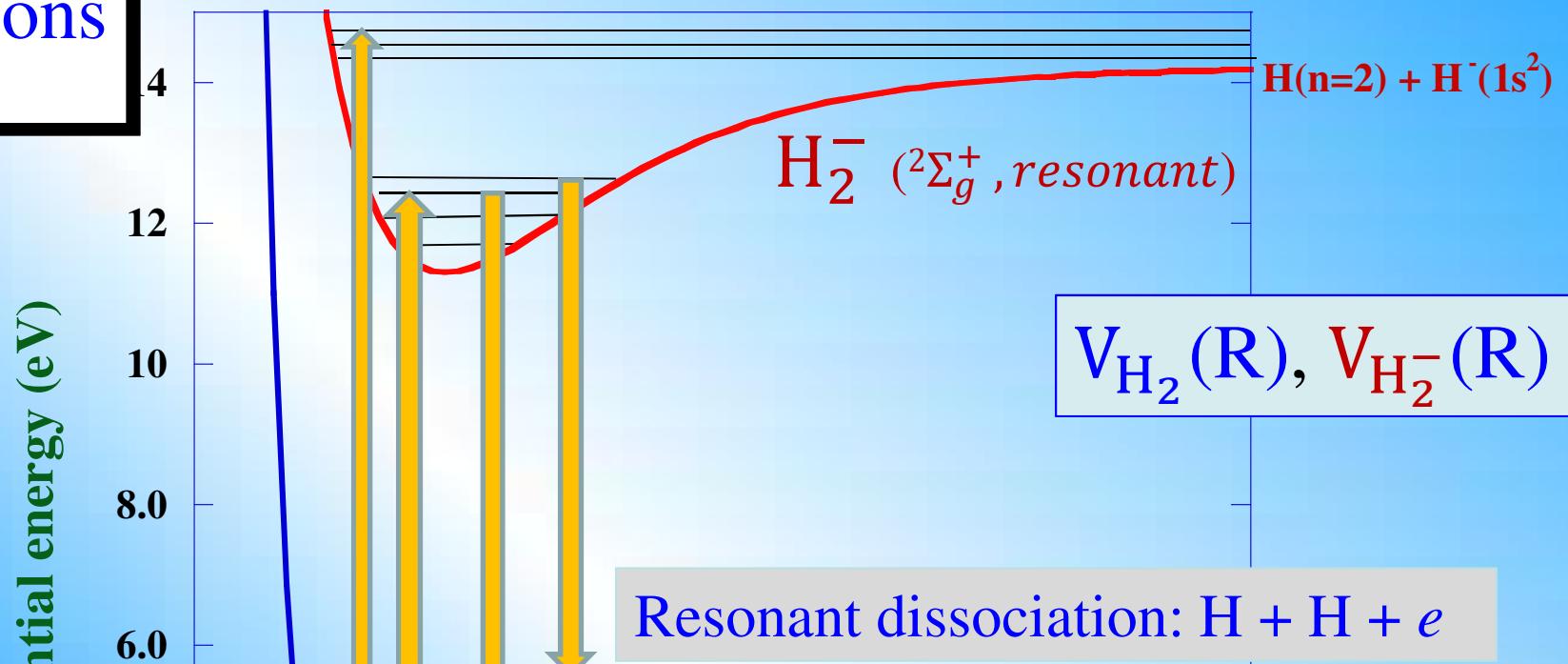
Resonant dissociation:  $\text{H} + \text{H} + e$

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V^-(R) + \frac{i}{2} \Gamma(R) - E \right) \xi(R) = -\mathcal{V}_{\epsilon_i}(R) \chi_{\nu_i}(R)$$



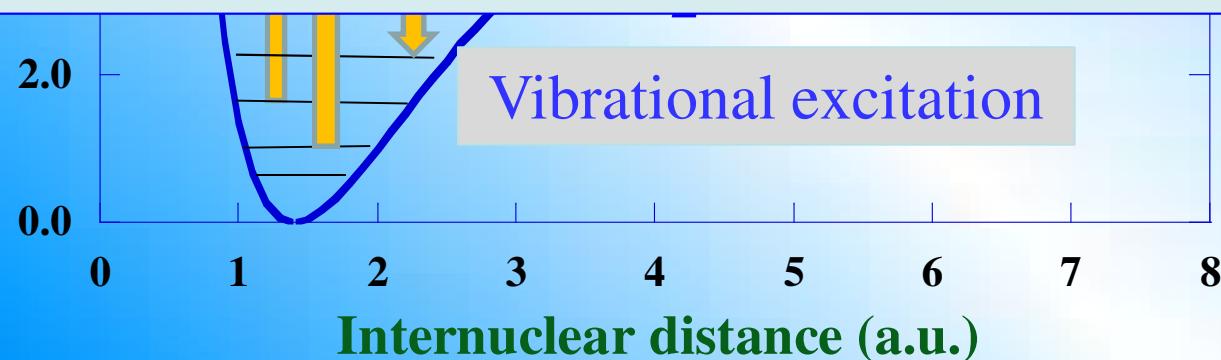
onant collisions

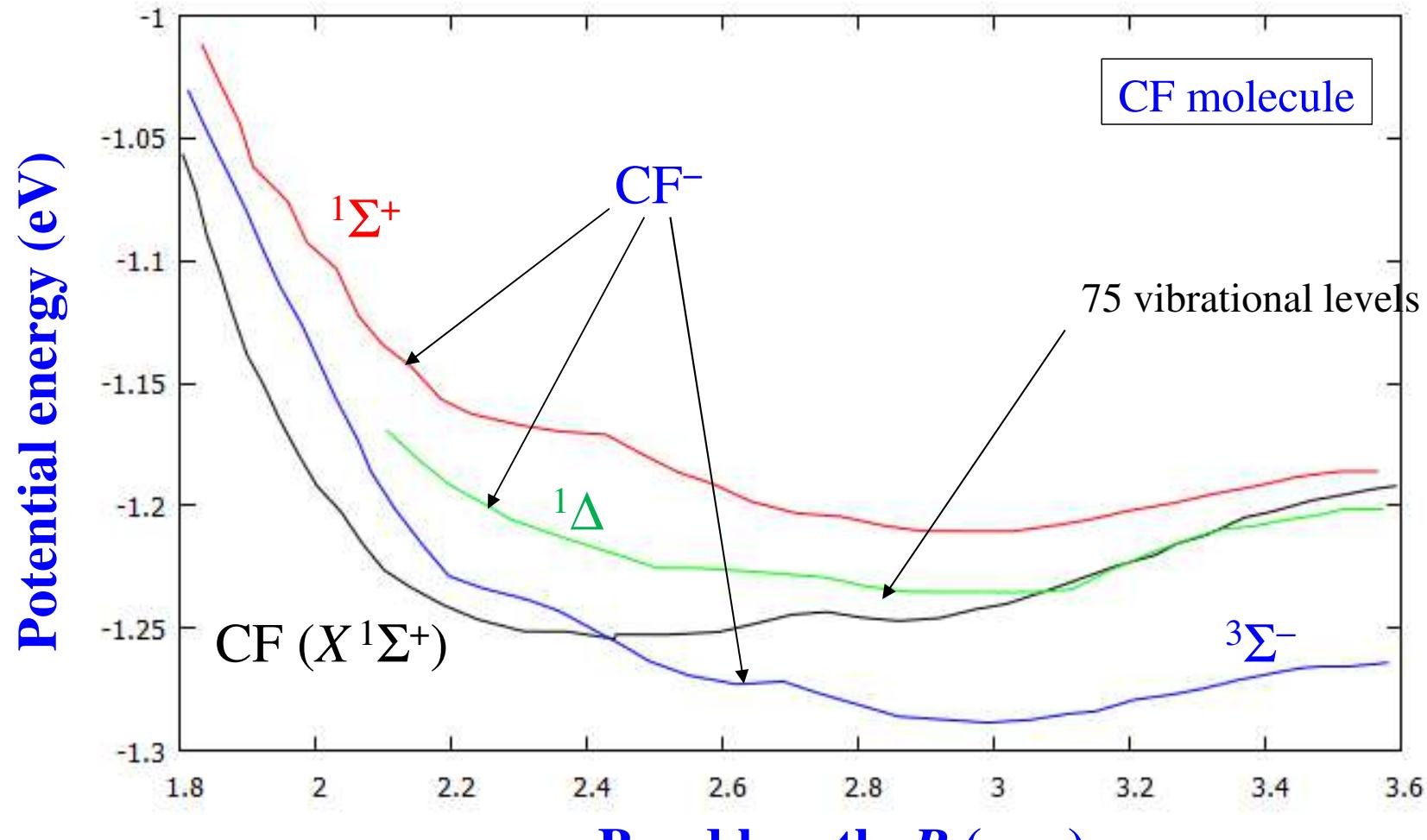
Dissociative attachment:  $\text{H} + \text{H}^-$



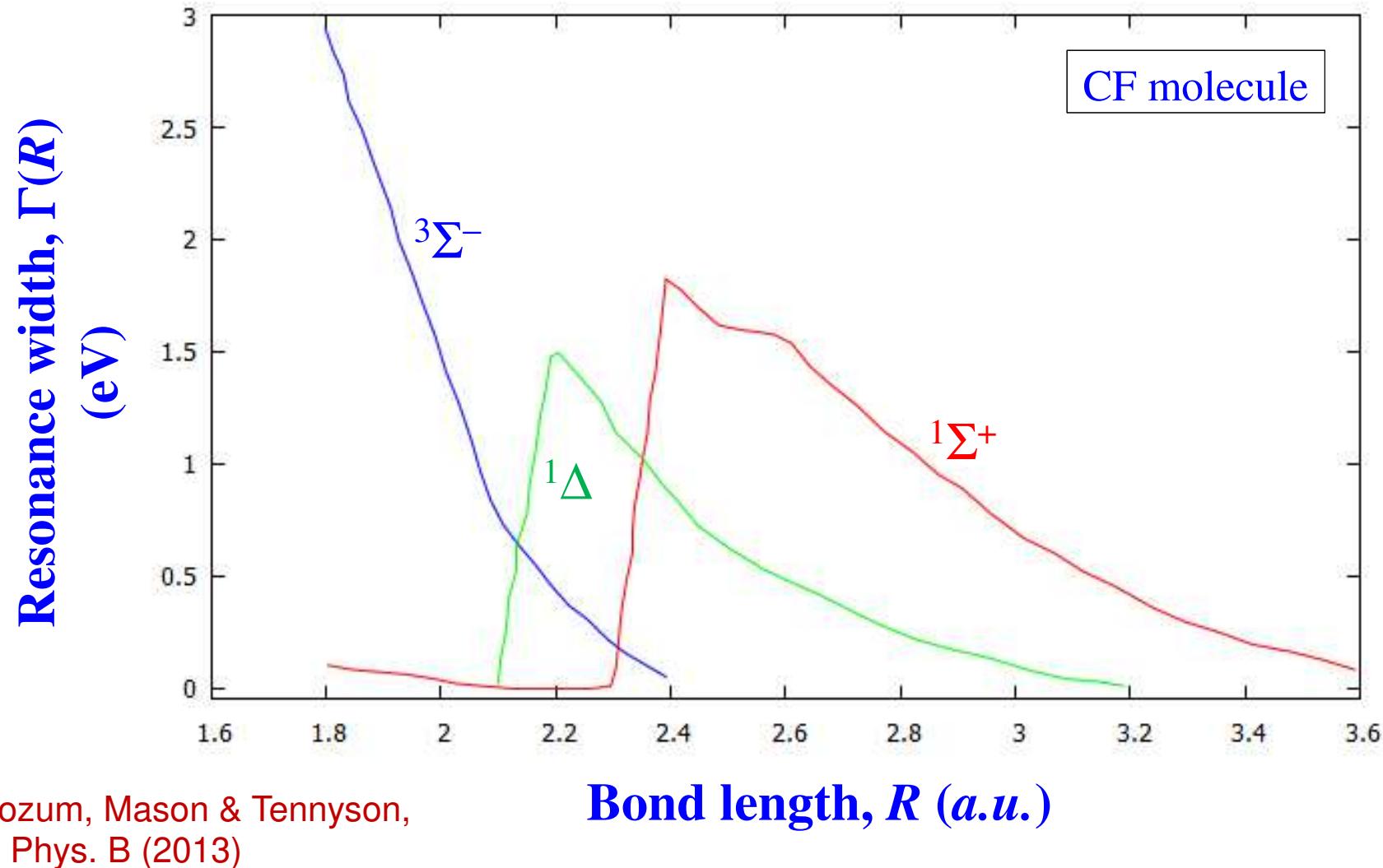
Resonant dissociation:  $\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H} + e$

CO, NO, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, He<sub>2</sub><sup>+</sup>, BeH, BeH<sup>+</sup>

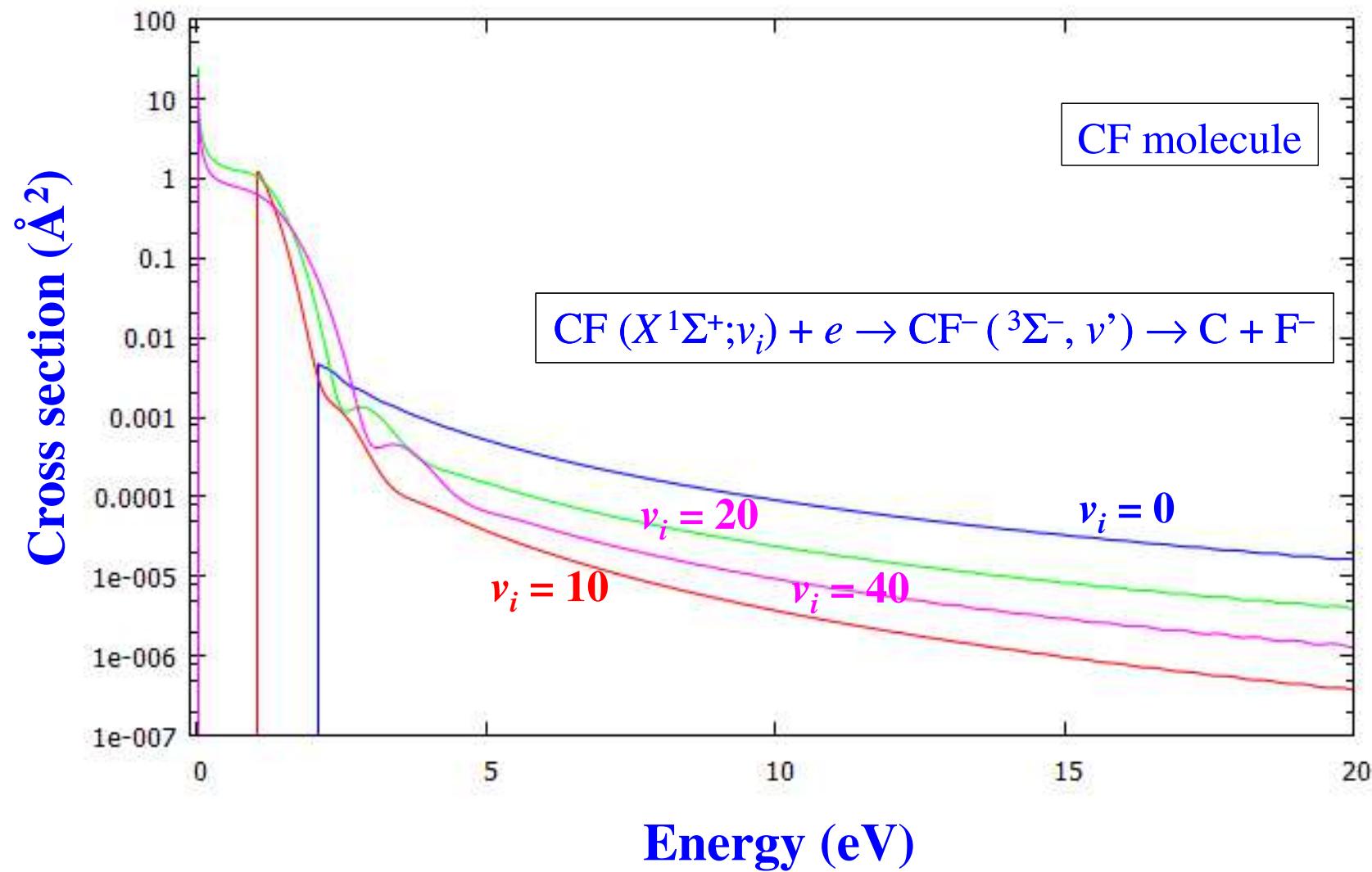




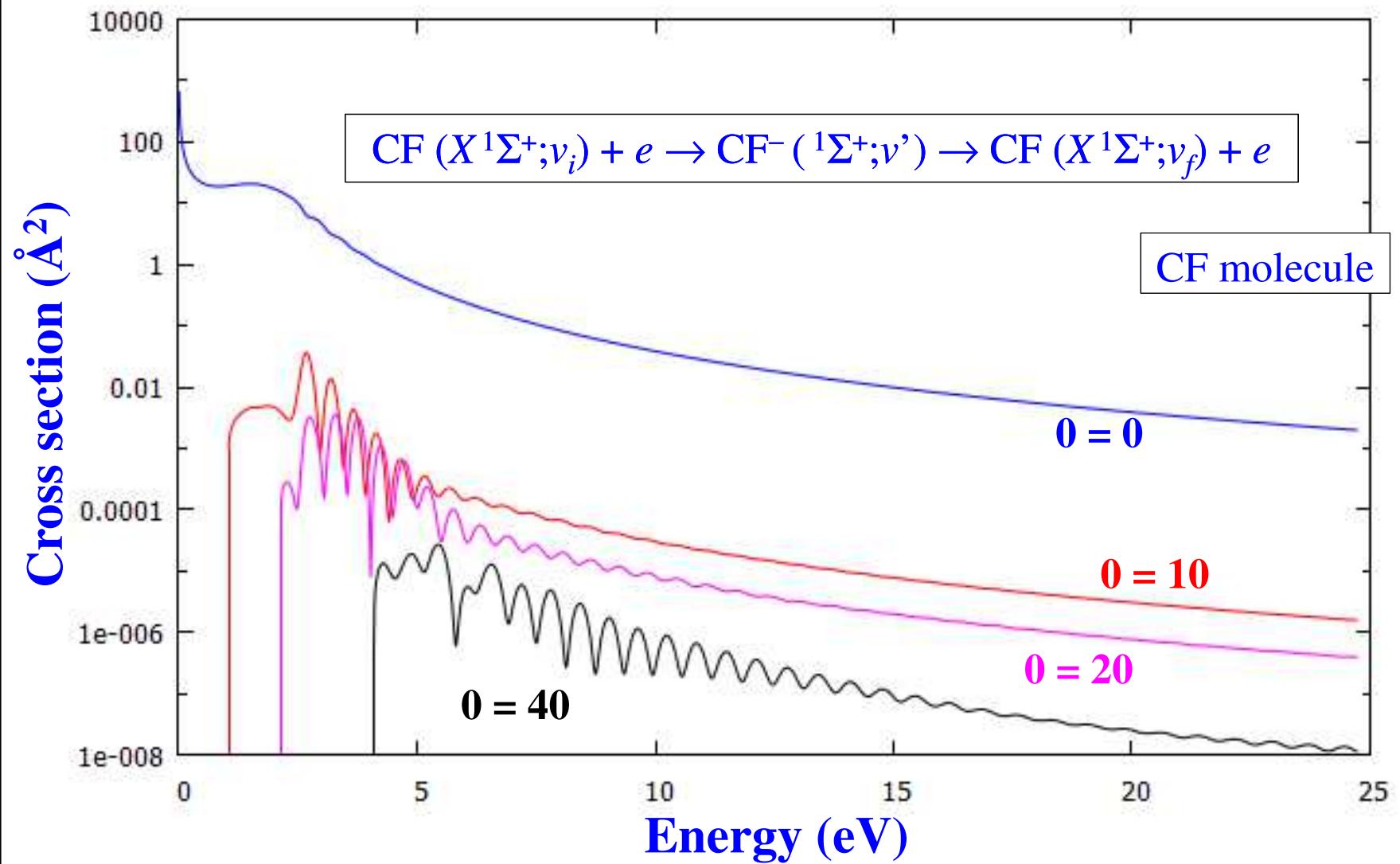
Rozum, Mason & Tennyson,  
J. Phys. B (2013)



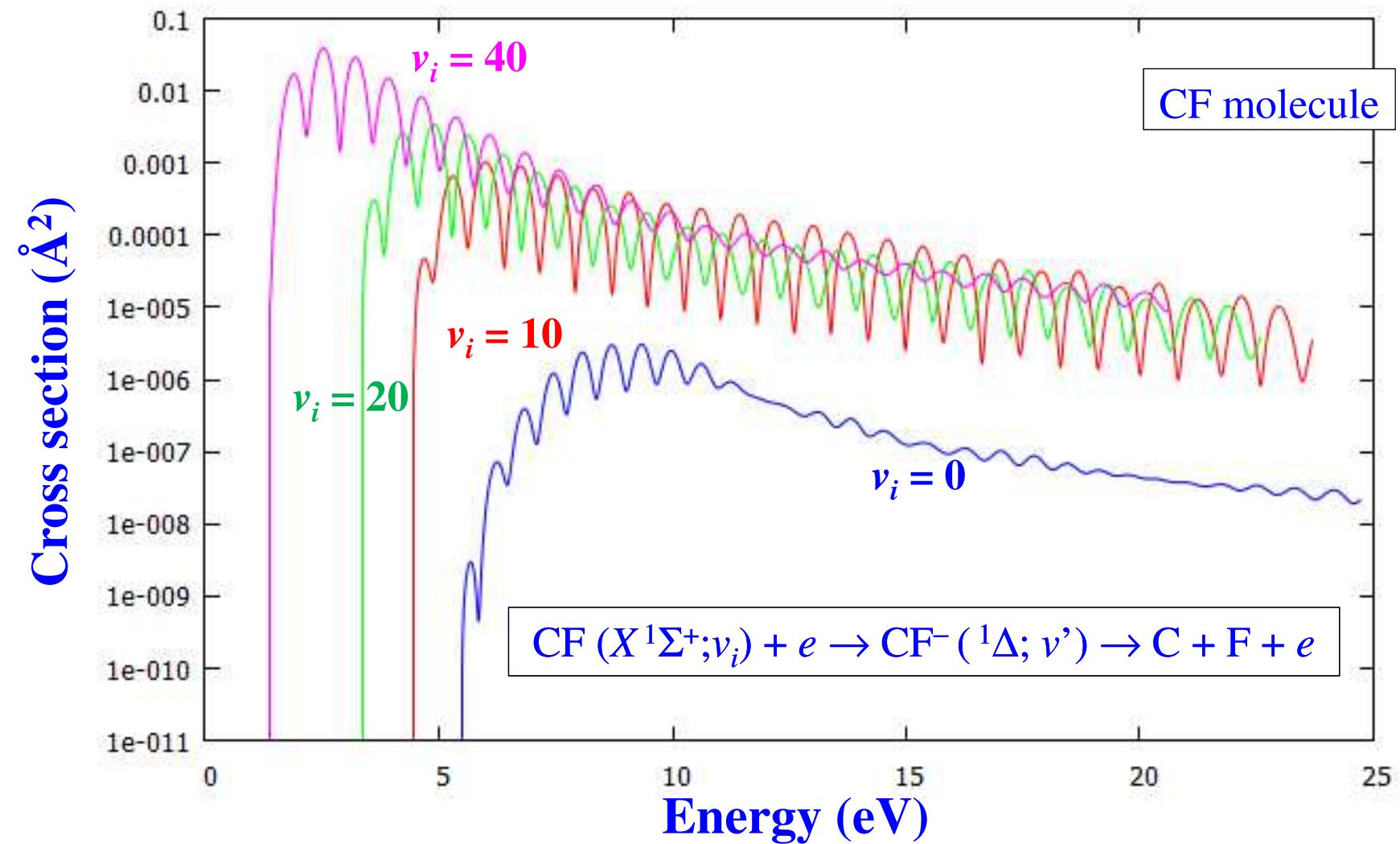
## Dissociative attachment



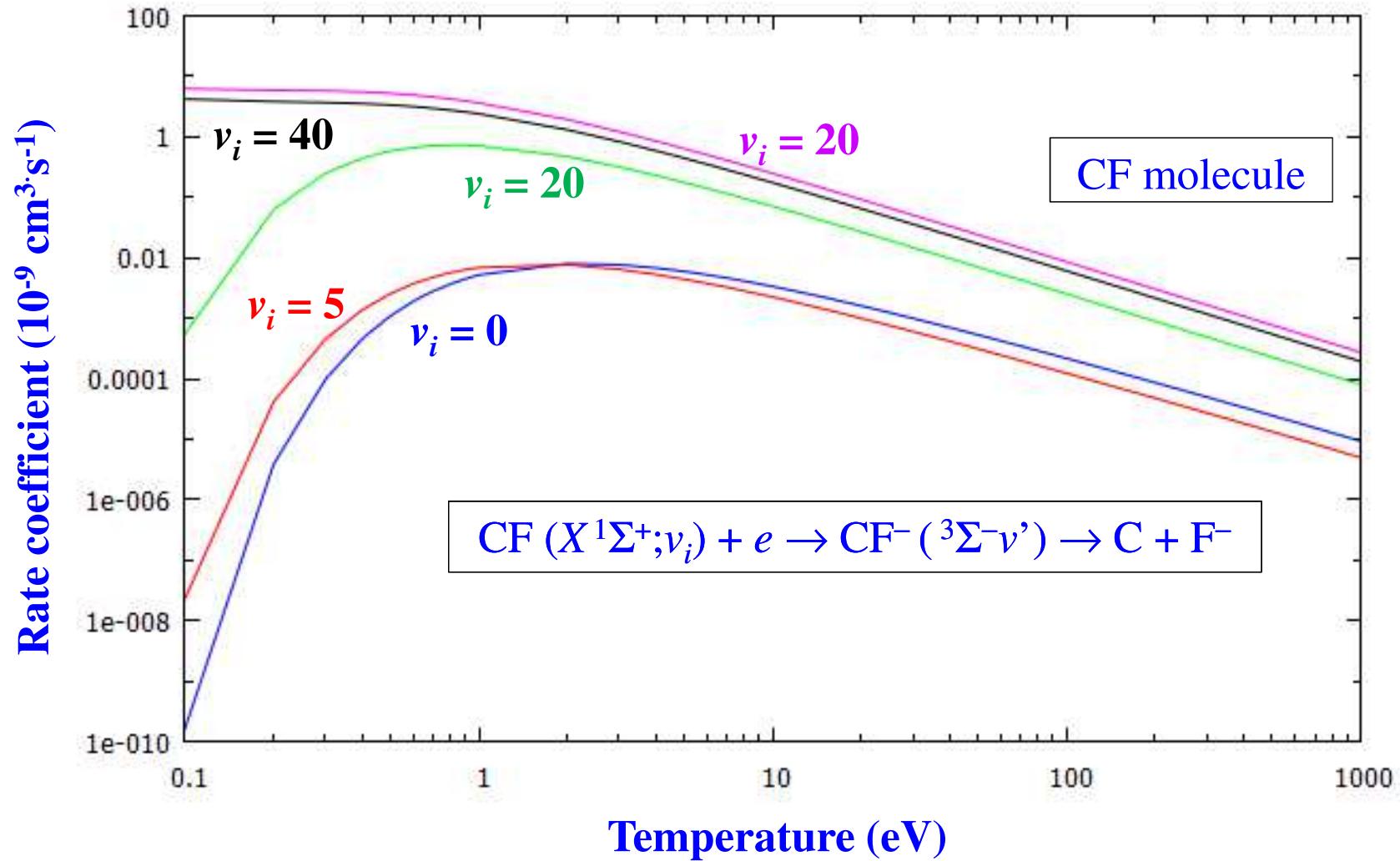
## Resonant vibrational excitation



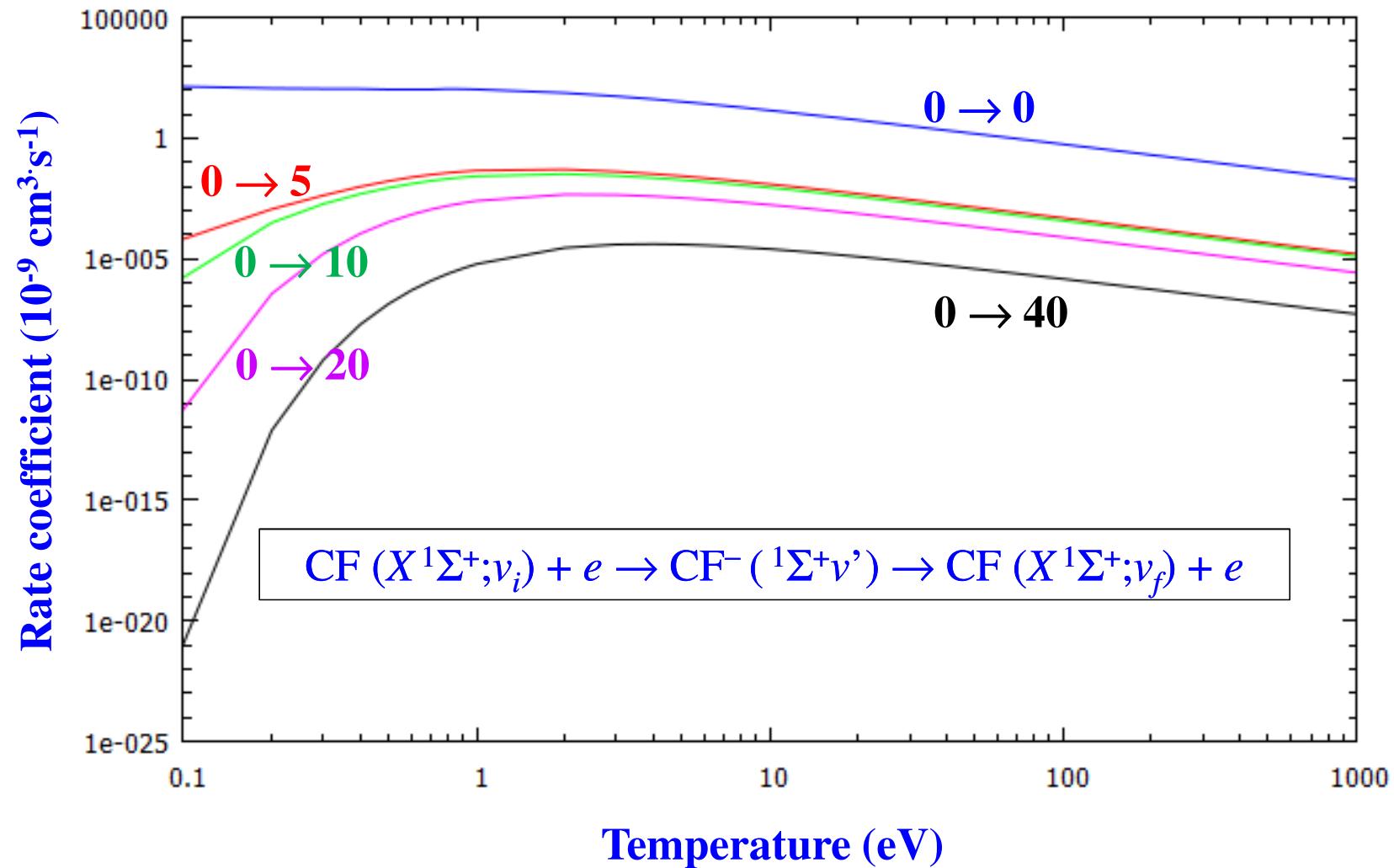
## Dissociative excitation



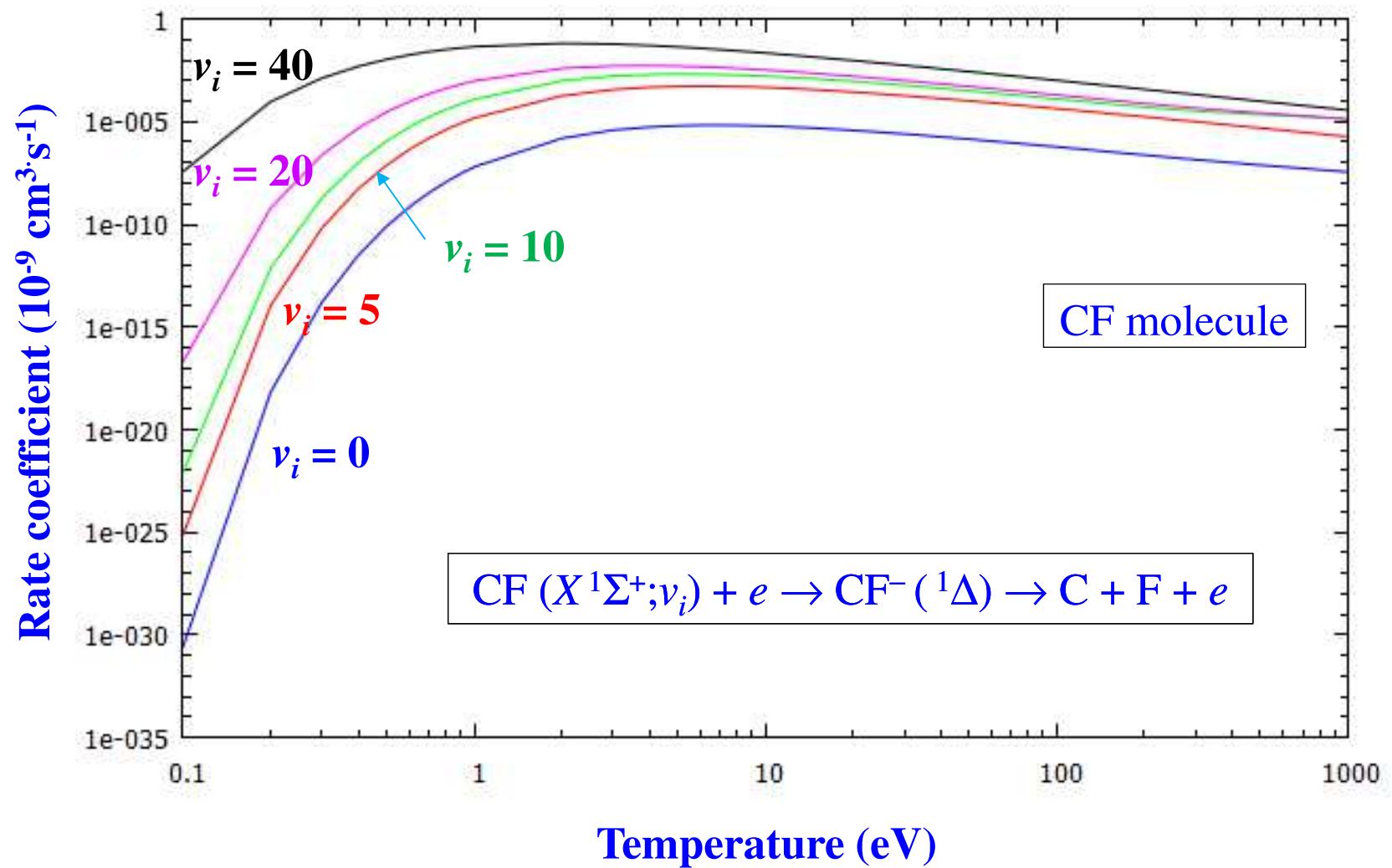
## Dissociative attachment



## Resonant vibrational excitation



## Dissociative excitation





(R. Celiberto, R.K. Janev and D. Reiter, 2009)



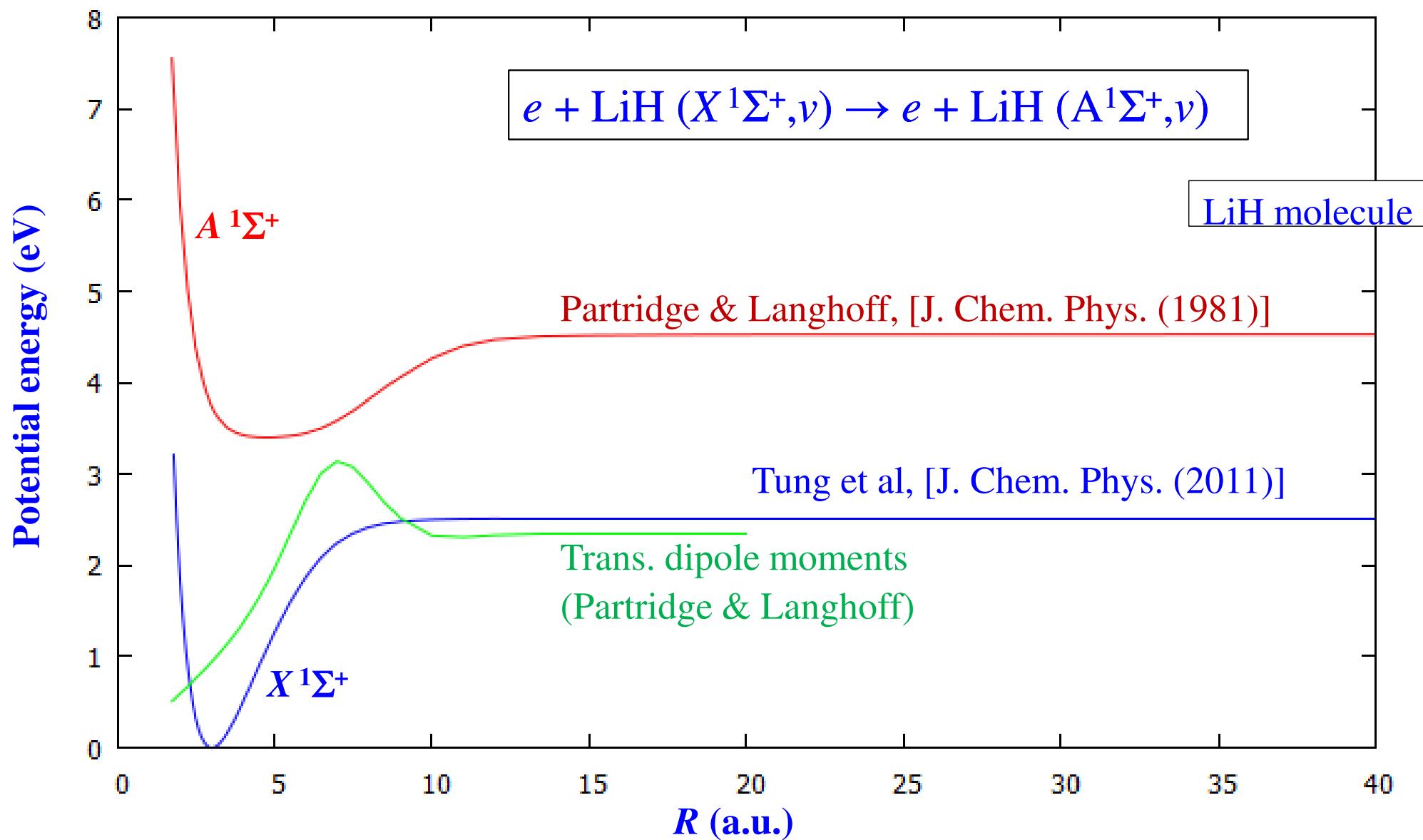
(R. Celiberto, R.K. Janev and D. Reiter, 2012)

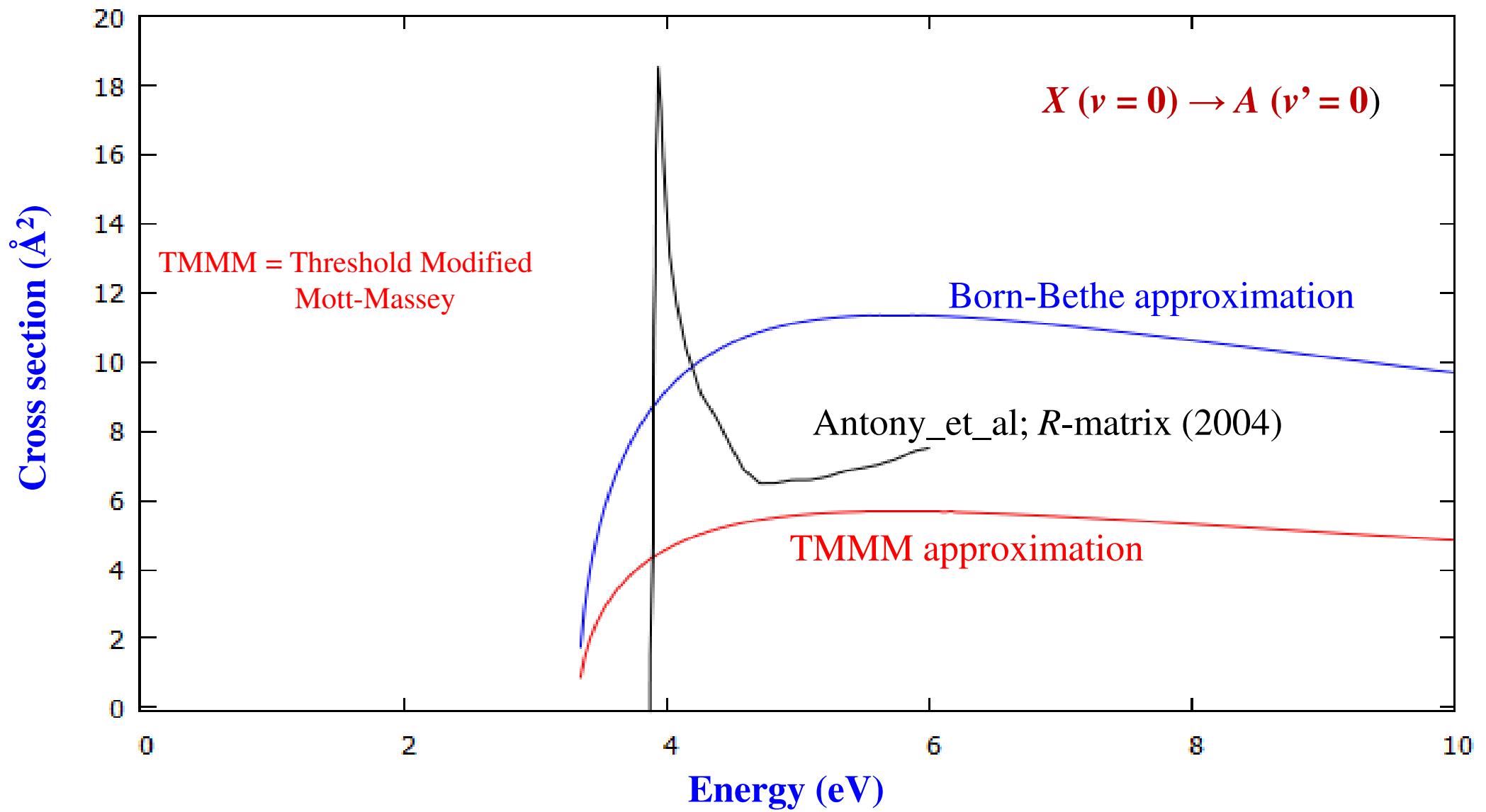


(R. Celiberto, K.L. Baluja and R.K. Janev, 2013)



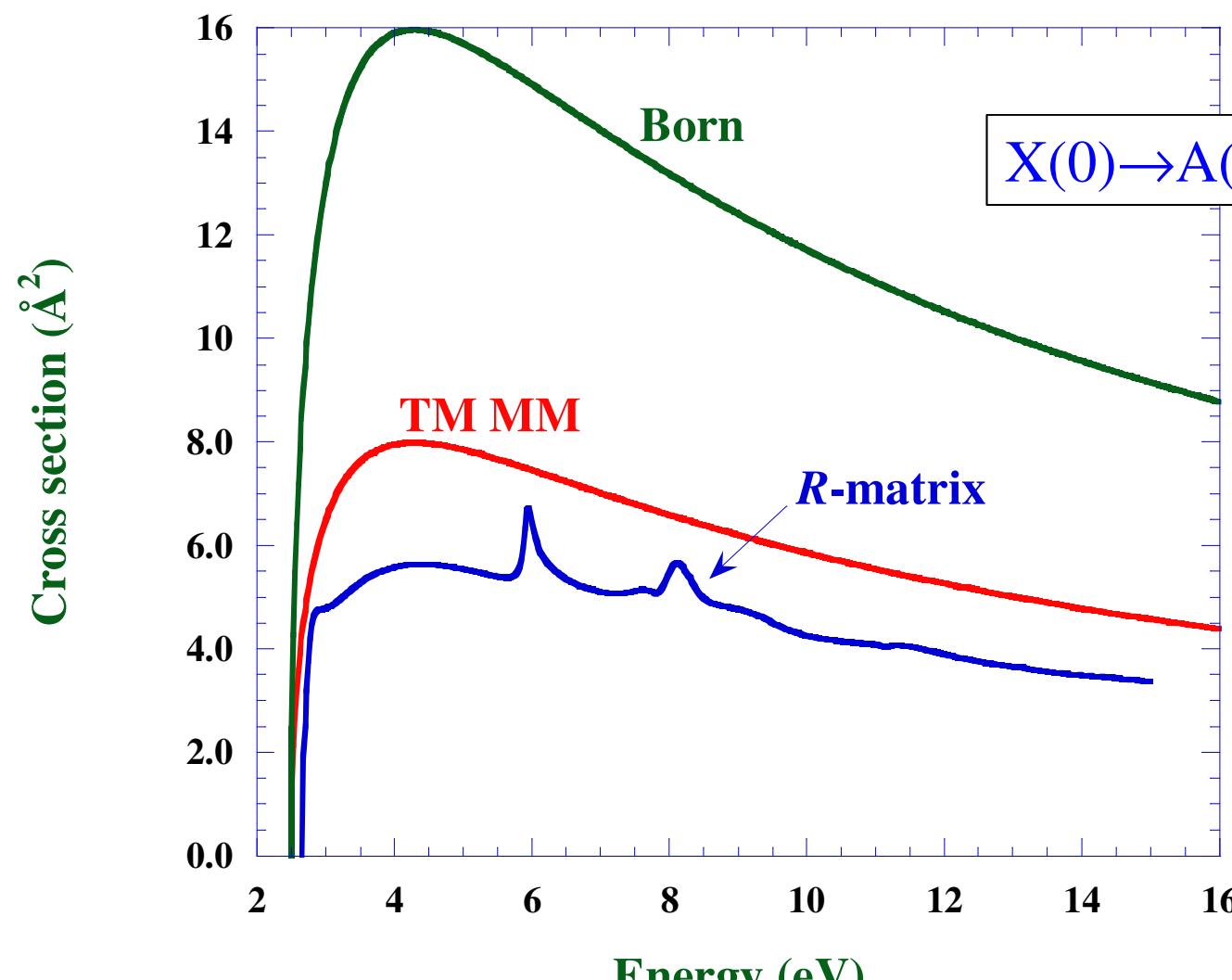
(R. Celiberto, K.L. Baluja, R.K. Janev and V. Laporta, 2015)



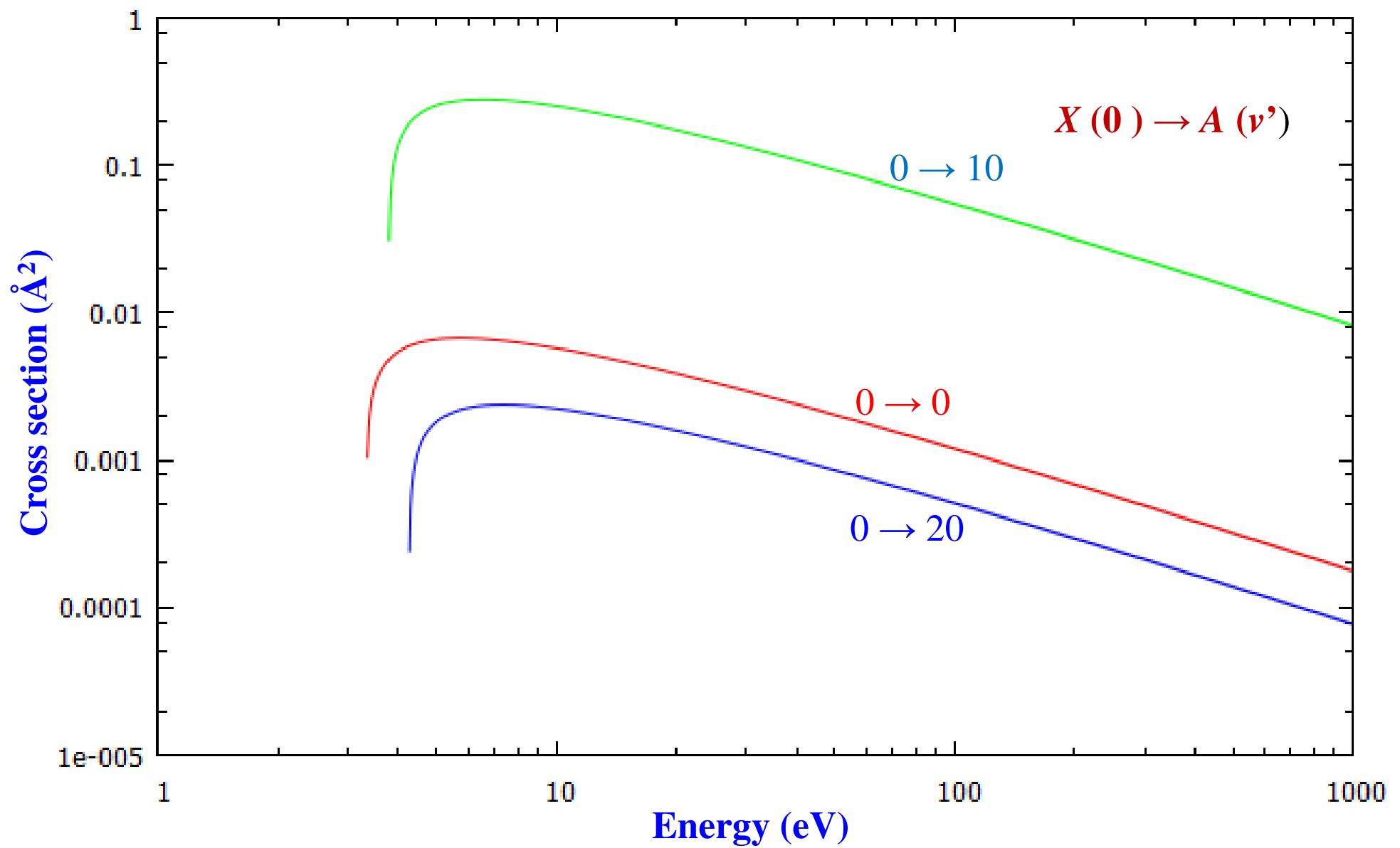


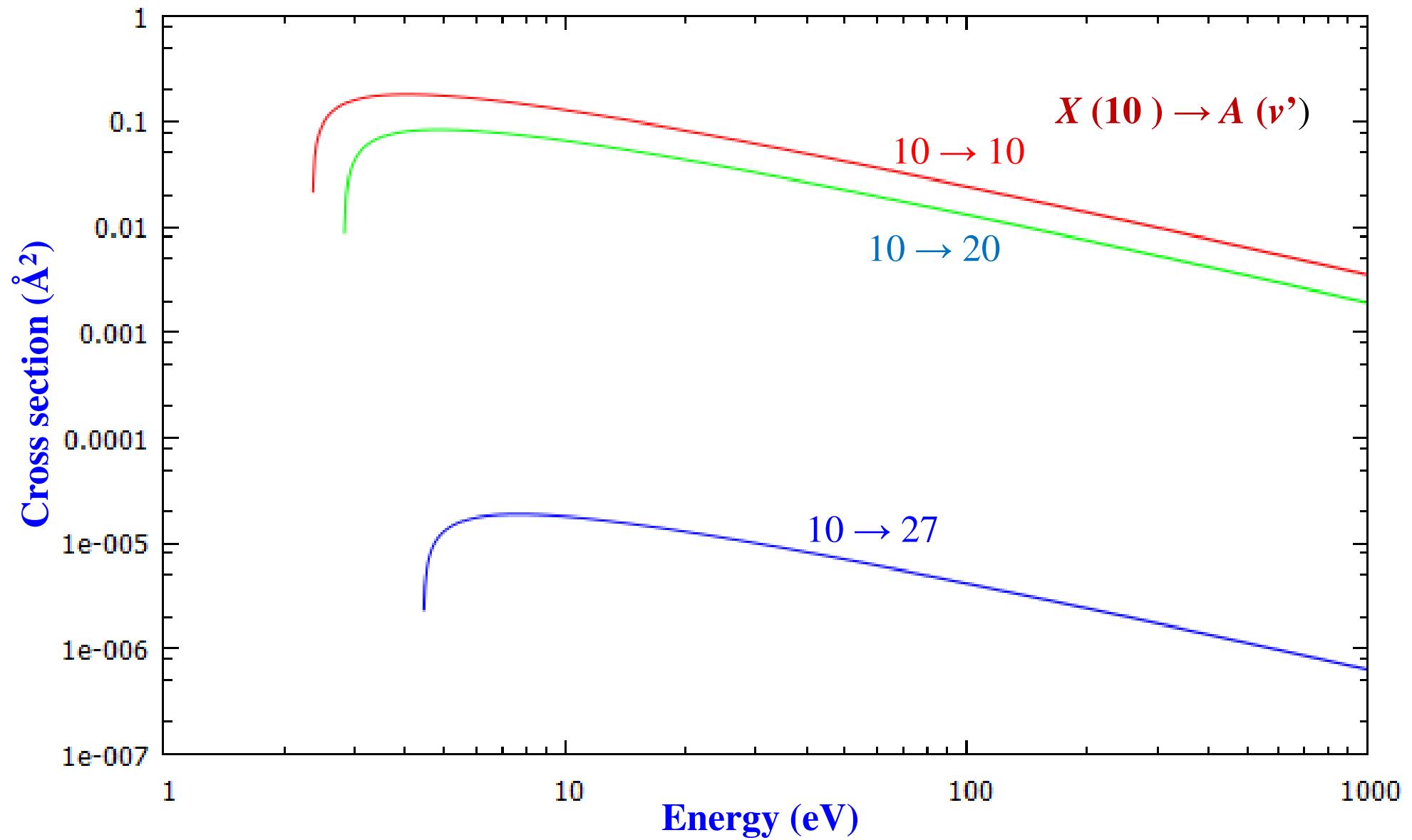
BeH

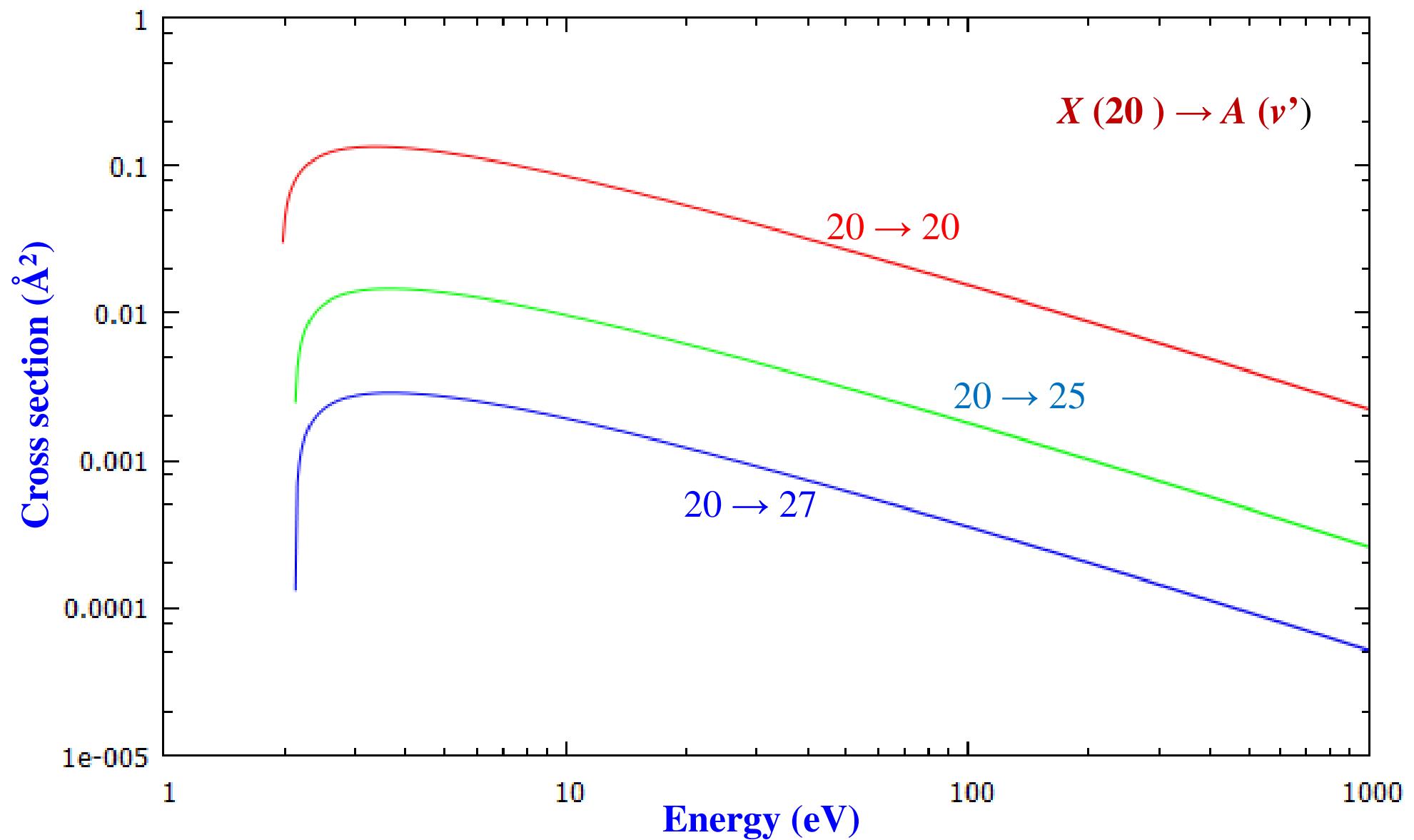
$X(0) \rightarrow A(0)$



R Celiberto,  
K L Baluja  
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