Elementary reactivity at the nanometer scale: the abstraction of atoms from metal surfaces

Oihana Galparsoro[1,2,3], Rémi Pétuya[2,3], Fabio Busnengo[6], Cédric Crespos[2,3],
J. Iñaki Juaristi[4,5,1], Maite Alducin[5,1] and Pascal Larregaray[2,3]

[1] Donostia International Physics Center (DIPC), Donostia-San Sebastián, Spain
[2] Univ. Bordeaux, ISM, UMR5255, F-33400, Talence, France
[3] CNRS, ISM, UMR5255, F-33400, Talence, France
[4] Dep. de Física de Materiales, Facultad de Químicas, UPV/EHU, Donostia-San Sebastián, Spain
[5] Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Donostia-San Sebastián, Spain
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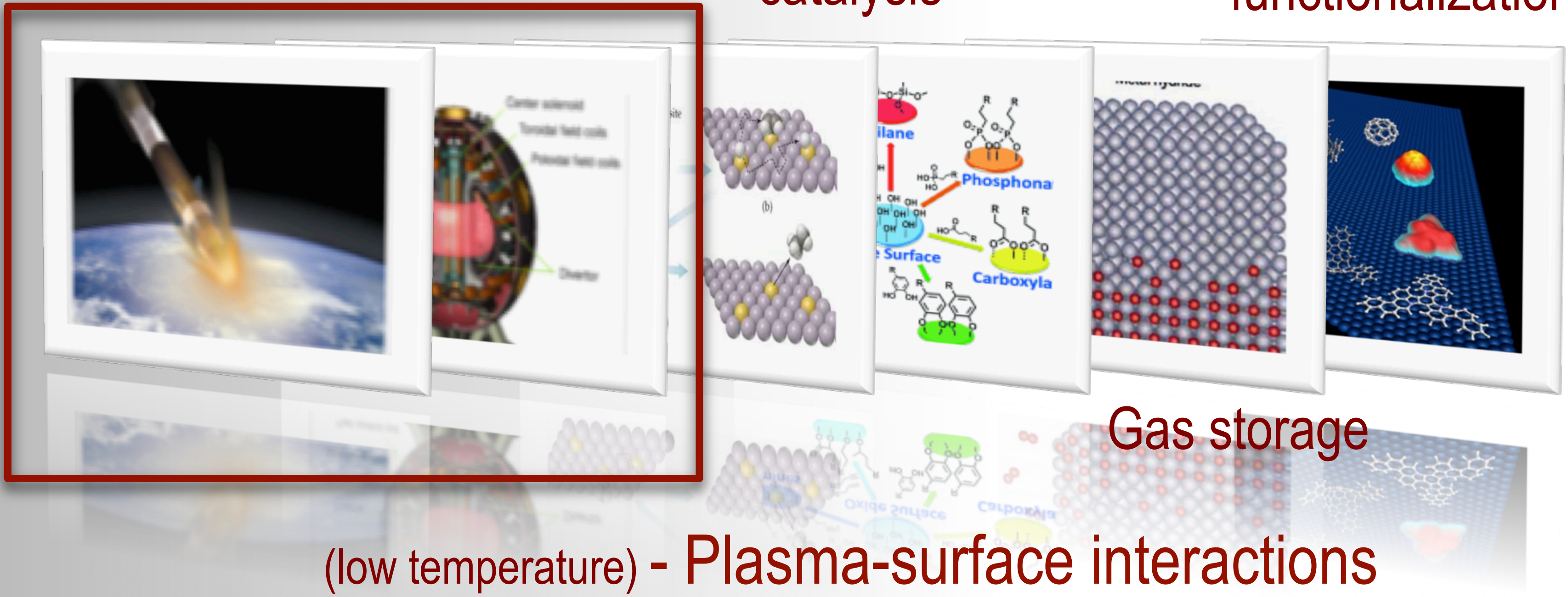
QuantumChemPhys joint Lab
http://www.quantumchemphys.org

Introduction

Gas surface reactions



catalysis

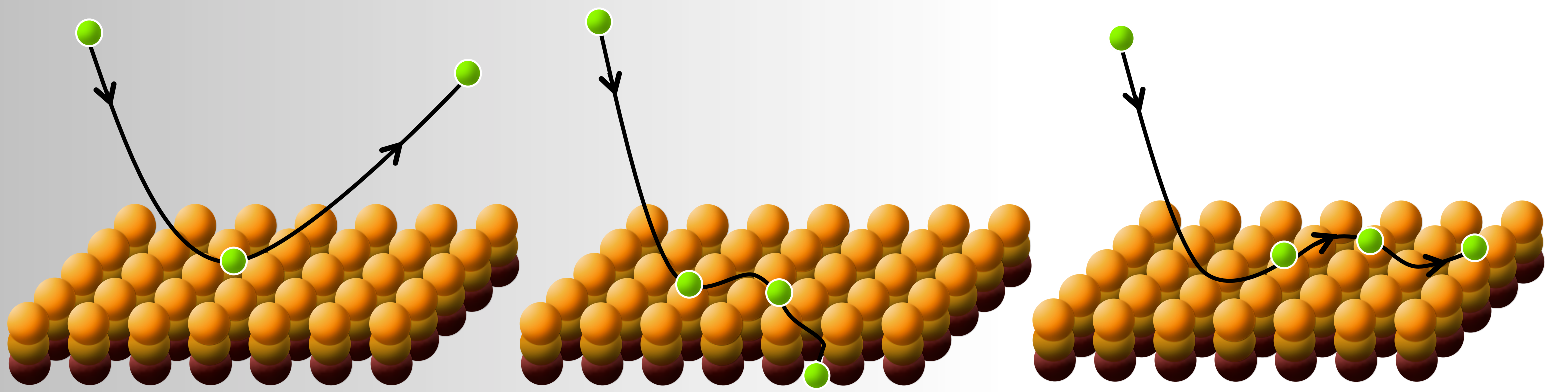
Surface functionalization

Gas storage

(low temperature) - Plasma-surface interactions

Introduction

An atom colliding with a clean surface



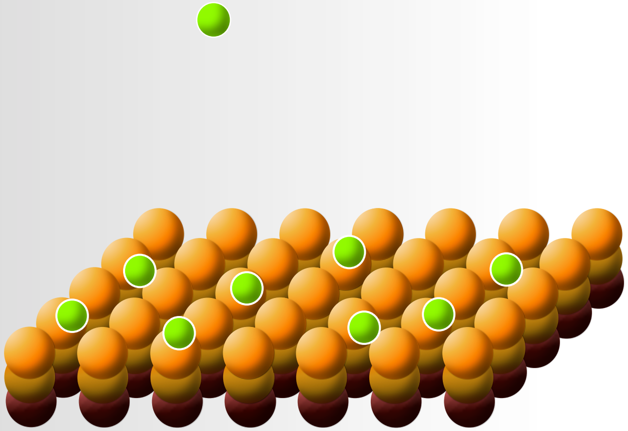
Reflection

Absorption

Adsorption

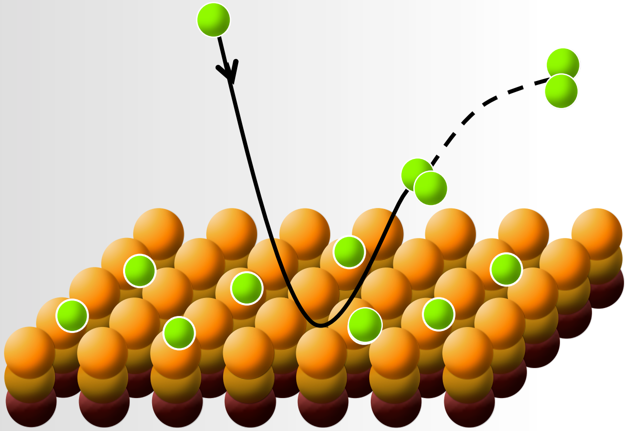
Introduction

An atom colliding with a covered surface



Introduction

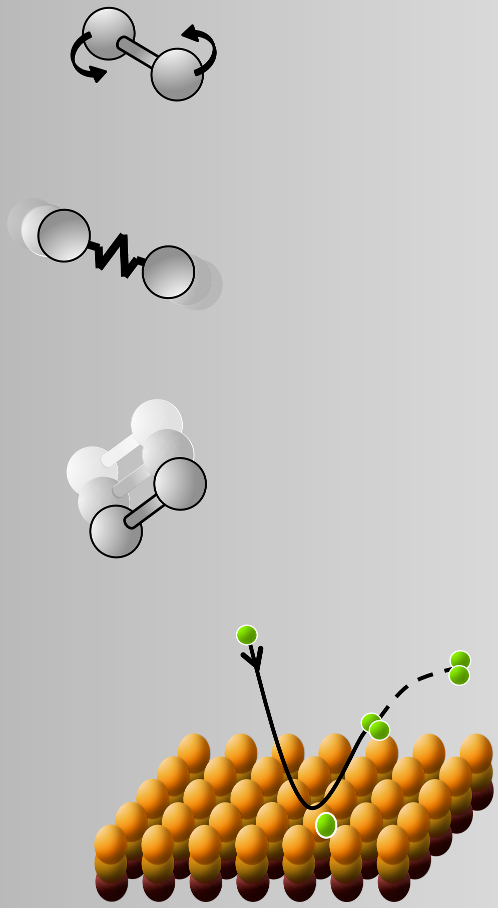
An atom colliding with a covered surface

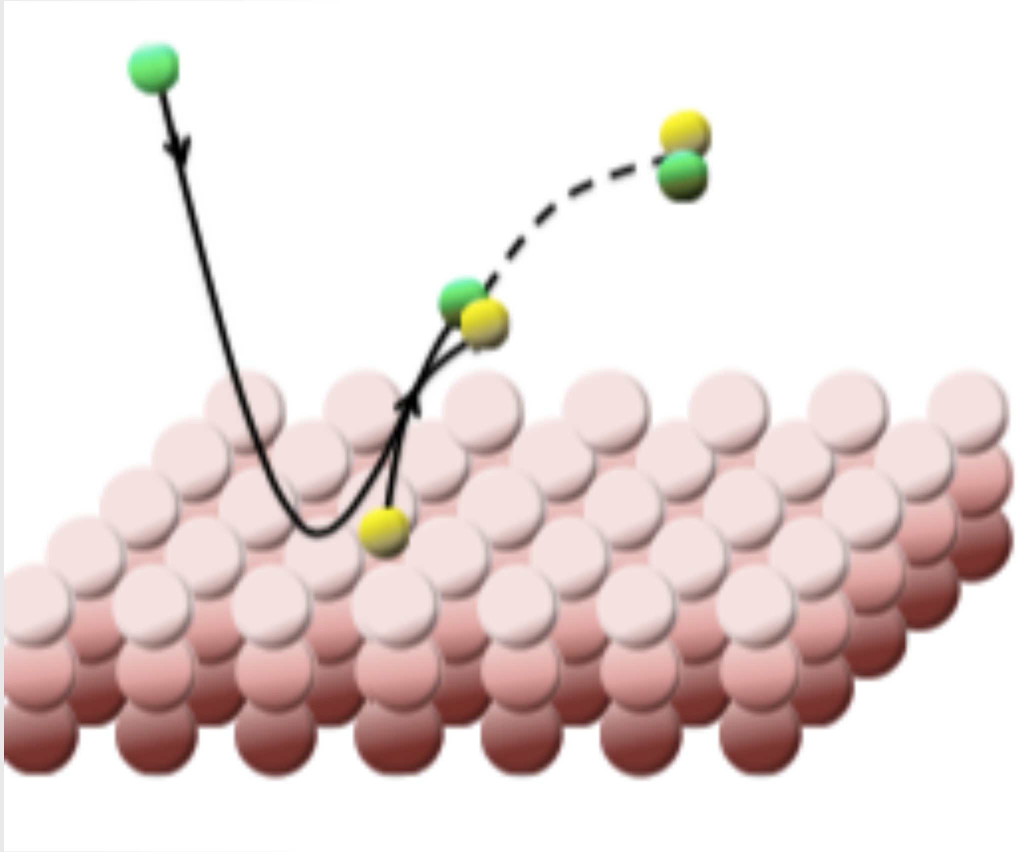


Abstraction or Recombination

Introduction

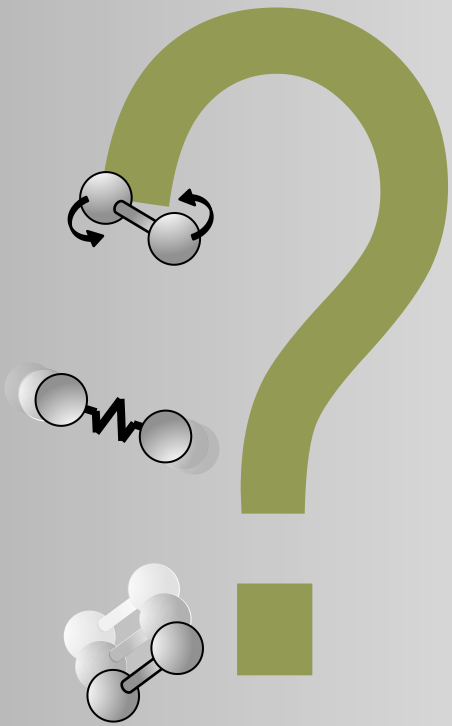
Eley-Rideal mechanism

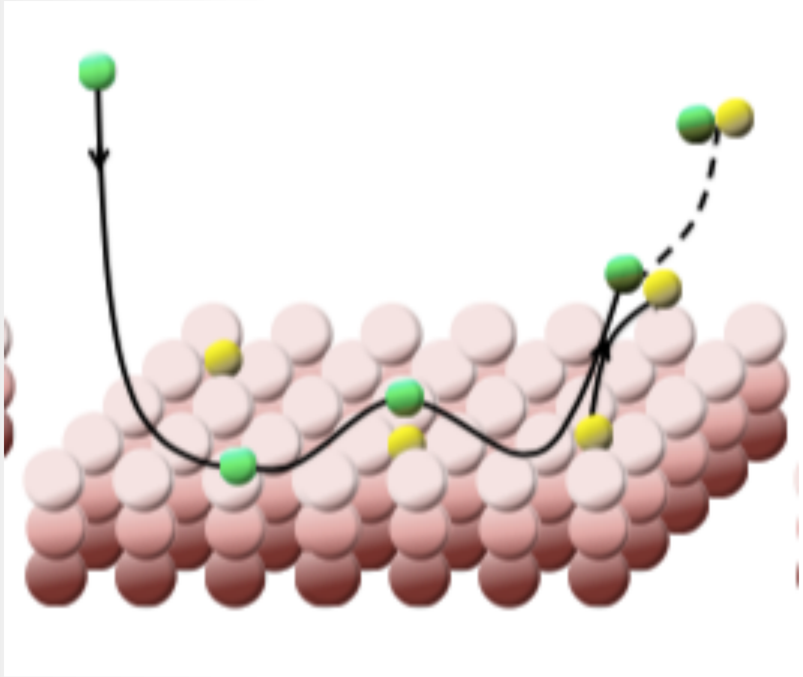




Introduction

Primary Hot-Atom (HA) mechanism





Introduction

H_2 and N_2 recombination on W(100) and W(110):

THE JOURNAL OF CHEMICAL PHYSICS **137**, 064709 (2012)

Dynamical reaction pathways in Eley-Rideal recombination of nitrogen from W(100)

E. Quintas-Sánchez,[1,2,3] P. Larrégaray,[2,3,a)] C. Crespos,[2,3] L. Martin-Gondre,[4,5] J. Rubayo-Soneira,[1] and J.-C. Rayez[2,3]

THE JOURNAL OF CHEMICAL PHYSICS **138**, 024706 (2013)

Surface temperature effects on the dynamics of N_2 Eley-Rideal recombination on W(100)

E. Quintas-Sánchez,[1,2] C. Crespos,[2,a)] P. Larrégaray,[2] J-C. Rayez,[2] L. Martin-Gondre,[3]

THE JOURNAL OF PHYSICAL CHEMISTRY C

Scattering of Atomic Hydrogen Off a H-Covered W(110) Surface: Atom versus Eley–Rideal Abstraction Dynamics

R. Pétuya,[†,‡] P. Larrégaray,[*,†,‡] C. Crespos,[†,‡] P. Aurel,[†,‡] H. F. Busnengo,[§] and A. E. Martínez[§]

Article

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THE JOURNAL OF PHYSICAL CHEMISTRY C

Influence of Surface Symmetry on the Onset of Nitrogen Eley–Rideal Recombination on Tungsten

E. Quintas-Sánchez,[†,‡,§] P. Larrégaray,[*,‡,§] and C. Crespos[‡,§]

Article

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THE JOURNAL OF PHYSICAL CHEMISTRY C

Comparative Theoretical Study of H_2 Eley–Rideal Recombination Dynamics on W(100) and W(110)

R. Pétuya,[†,‡] C. Crespos,[*,†,‡] E. Quintas-Sanchez,[†,‡,§] and P. Larrégaray[†,‡]

Article

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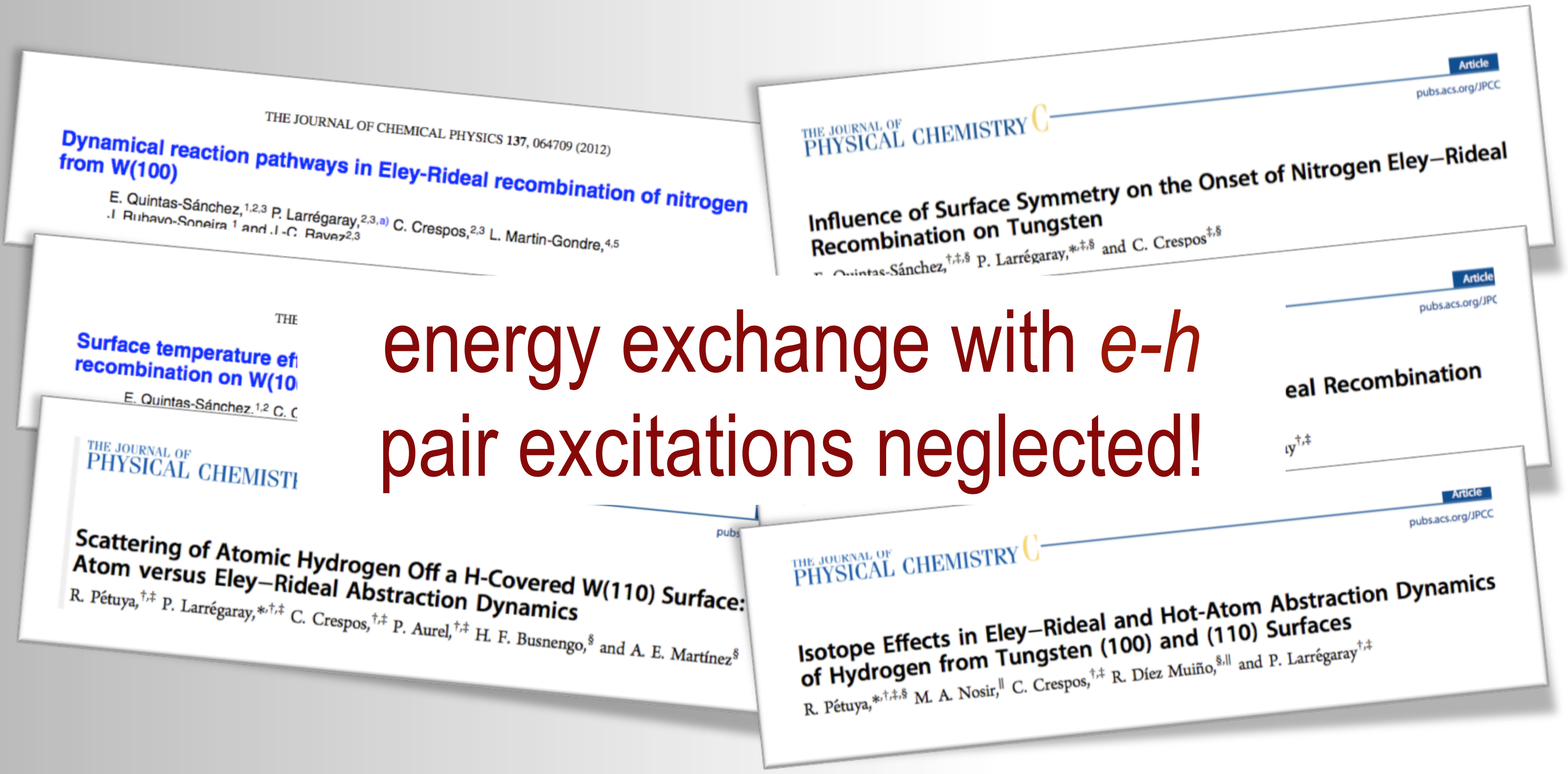
THE JOURNAL OF PHYSICAL CHEMISTRY C

Isotope Effects in Eley–Rideal and Hot-Atom Abstraction Dynamics of Hydrogen from Tungsten (100) and (110) Surfaces

R. Pétuya,[*,†,‡,§] M. A. Nosir,[‖] C. Crespos,[†,‡] R. Díez Muiño,[§,‖] and P. Larrégaray[†,‡]

Introduction

H_2 and N_2 recombination on W(100) and W(110):



THE JOURNAL OF CHEMICAL PHYSICS 137, 064709 (2012)

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THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Surface temperature ef
recombination on W(10

E. Quintas-Sánchez,[1,2] C. C

Article

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eal Recombination

THE JOURNAL OF PHYSICAL CHEMISTI

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THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Isotope Effects in Eley–Rideal and Hot-Atom Abstraction Dynamics of Hydrogen from Tungsten (100) and (110) Surfaces

R. Pétuya,[*,†,‡,§] M. A. Nosir,[∥] C. Crespos,[†,‡] R. Díez Muiño,[§,∥] and P. Larrégaray[†,‡]

energy exchange with *e-h* pair excitations neglected!

Introduction

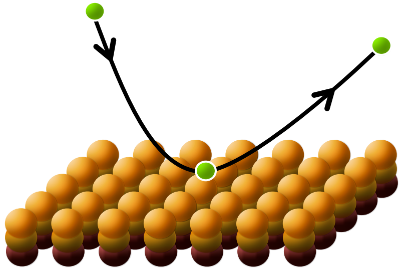
Experiments have provided convincing evidence that energy dissipation by the creation of e-h pairs is a significant effect in gas-surface dynamics:

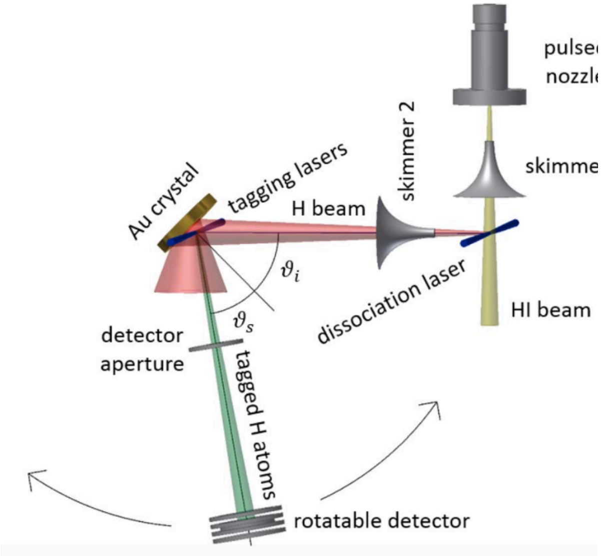
- Chemicurrents, chemiluminescene
- Translational inelasticity

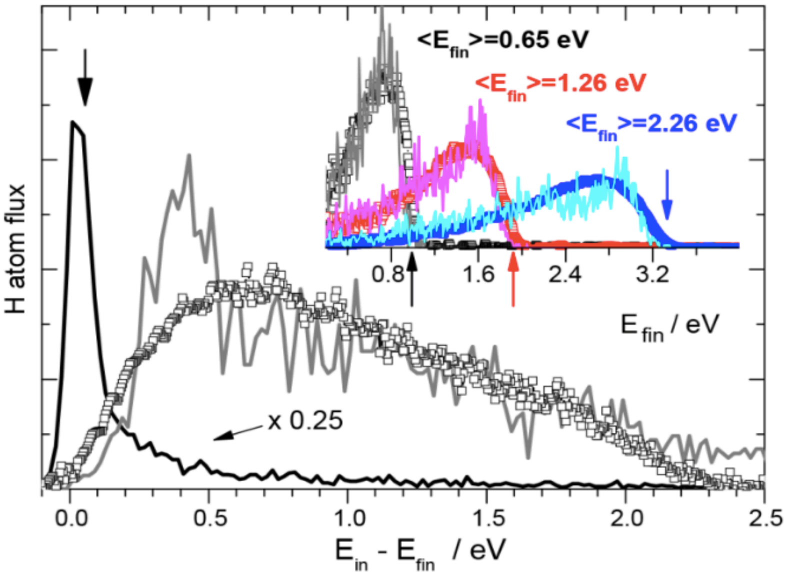

Sciencexpress

Electron-hole pair excitation determines the mechanism of hydrogen atom adsorption

Oliver Bünermann,[1,2,3*] Hongyan Jiang,[1] Yvonne Dorenkamp,[1] Alexander Kandratsenka,[1,2] Svenja Janke,[1,2] Daniel J. Auerbach,[1,2] Alec M. Wodtke[1,2,3]





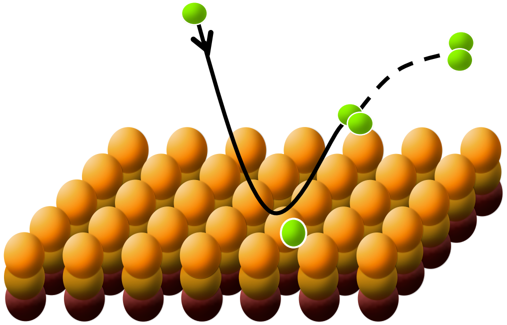


O. Bunermann et al.
***Sciencexpress**, nov. 2015*

$\Theta_i = 45°$
$\Theta_s = 45°$

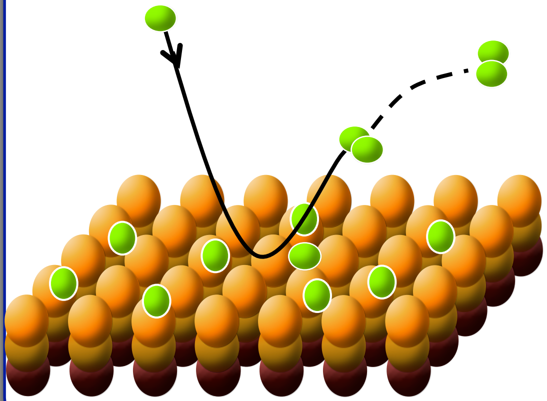
Methodology: Quasiclassical dynamics simulation

H_2 and N_2 recombination on W(100) and W(110)



- Eley-Rideal reaction in the single adsorbate limit:

  Energy dissipation effects



- H abstraction from H-covered W(100) and W(110):

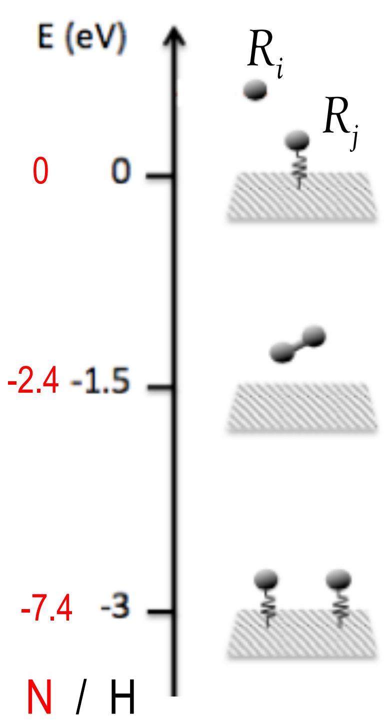
  Adiabatic and non-adiabatic dynamics

Methodology: Quasiclassical dynamics simulation

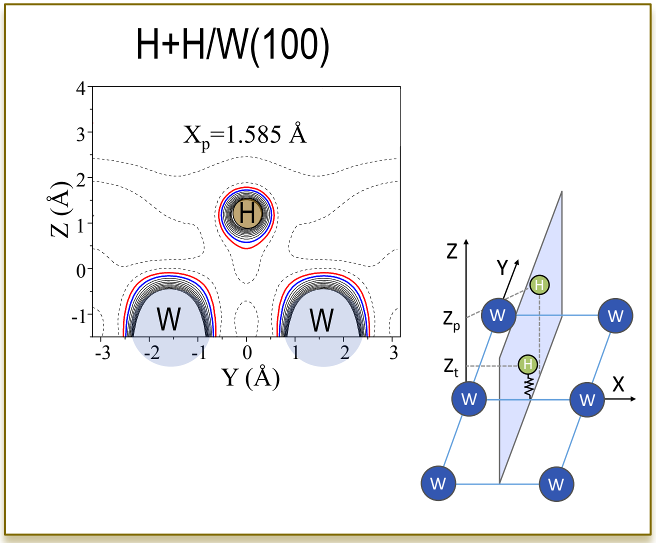
1. Adiabatic DFT-based multidimensional (6D) PES

1.1 Extended set of DFT (GGA) energy values (VASP, PW91): Static Surface approximation

1.2 Fitting method / Interpolation method



$$V_{6D}(\boldsymbol{R}_i, \boldsymbol{R}_j) = V^{3D}(\boldsymbol{R}_i) + V^{3D}(\boldsymbol{R}_j) + I^{6D}(\boldsymbol{R}_i, \boldsymbol{R}_j)$$



Born Oppenheimer Static Surface (**BOSS**) model

Methodology: Quasiclassical dynamics simulation

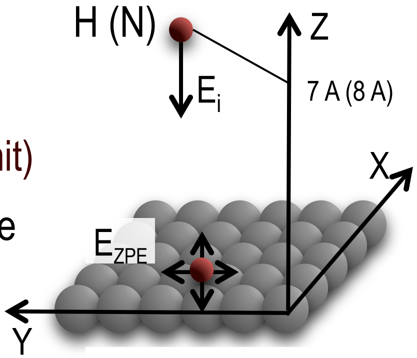
2. Classical equations of motion

$$M_i \frac{d^2\mathbf{R}_i}{dt^2} = -\nabla_i \underset{6D}{V}(\mathbf{R}_i - \mathbf{R}_s, \mathbf{R}_j - \mathbf{R}_s)$$

INITIAL CONDITIONS

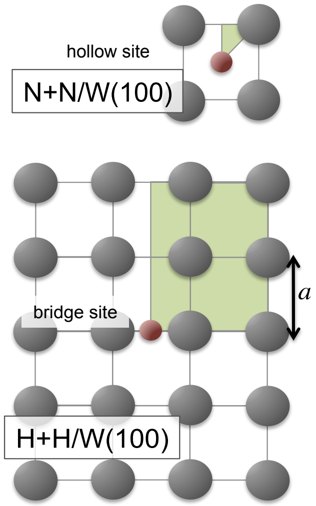
Single adsorbate (zero coverage limit)

- in the most stable adsorption site
- with ZPE

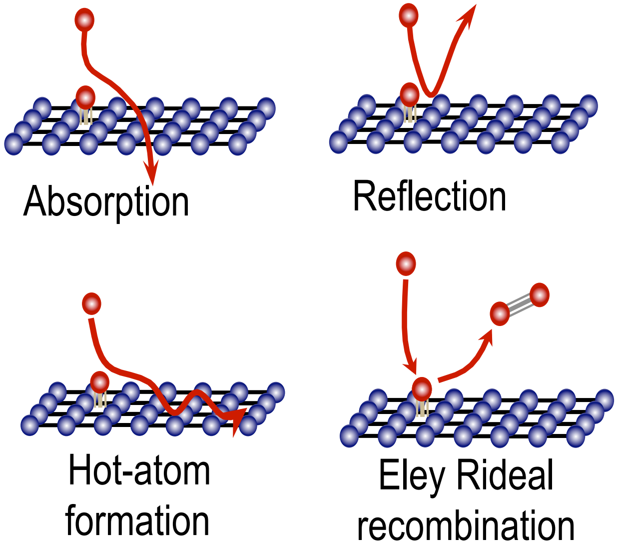


Normal incidence of the projectile

- various collision energy (0.25-5.0eV)
- Random sampling for initial position of the projectile

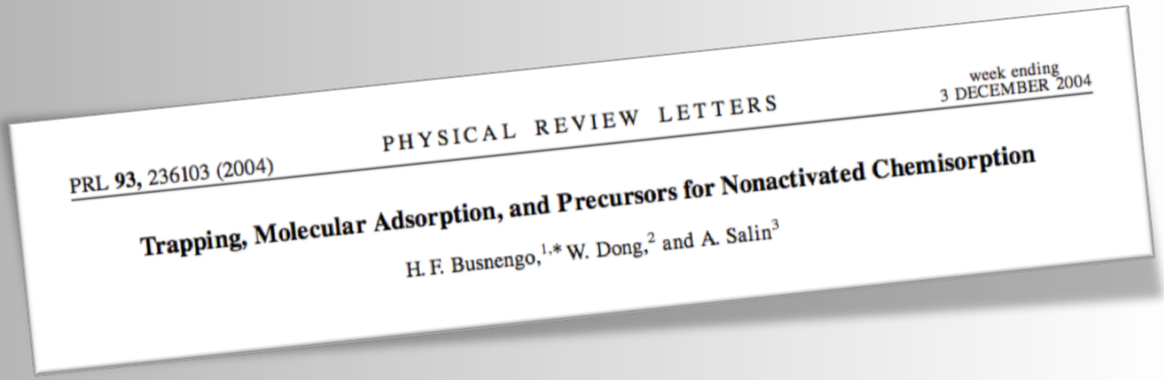


EXIT CHANNELS



Born Oppenheimer Static Surface(BOSS) model

Methodology: dissipation to phonons



PRL 93, 236103 (2004) PHYSICAL REVIEW LETTERS week ending 3 DECEMBER 2004

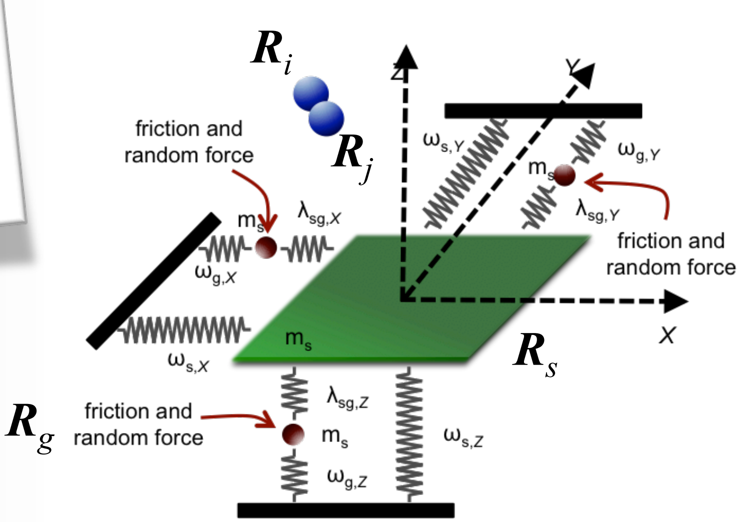
Trapping, Molecular Adsorption, and Precursors for Nonactivated Chemisorption

H. F. Busnengo,[1,*] W. Dong,[2] and A. Salin[3]

$$M_i \frac{d^2\mathbf{R}_i}{dt^2} = -\nabla_i V(\mathbf{R}_i - \mathbf{R}_s, \mathbf{R}_j - \mathbf{R}_s)$$

$$\frac{d^2\mathbf{R}_s}{dt^2} = -\frac{1}{m_s}\nabla_s V^{6D}(\mathbf{R}_i - \mathbf{R}_s, \mathbf{R}_j - \mathbf{R}_s) - \hat{\omega}_s^2\mathbf{R}_s + \hat{\lambda}_{gs}\mathbf{R}_g$$

$$\frac{d^2\mathbf{R}_g}{dt^2} = -\hat{\omega}_g^2\mathbf{R}_g + \hat{\lambda}_{gs}\mathbf{R}_s - \hat{\gamma}_g\frac{d\mathbf{R}_g}{dt} + \frac{1}{m_s}\mathbf{F}_r(t)$$



S. A. Adelman, JCP 71, 4471 (1979)
J. Tully, JCP 73,1975 (1980)
H. F. Busnengo *et al.* PRB 72, 125411 (2005)

Generalized Langevin Oscillator (GLO) model

Methodology: dissipation to e-h pairs

PRL 100, 116102 (2008)

PHYSICAL REVIEW LETTERS

week ending
21 MARCH 2008

Role of Electron-Hole Pair Excitations in the Dissociative Adsorption of Diatomic Molecules on Metal Surfaces

J. I. Juaristi,[1,2,3] M. Alducin,[2,3] R. Díez Muiño,[2,3] H. F. Busnengo,[4] and A. Salin[3]

a friction force acting in each atom

$$M_i \frac{d^2\mathbf{R}_i}{dt^2} = -\nabla_i V(\mathbf{R}_i, \mathbf{R}_j) - \eta(\mathbf{R}_i)\frac{d\mathbf{R}_i}{dt}$$

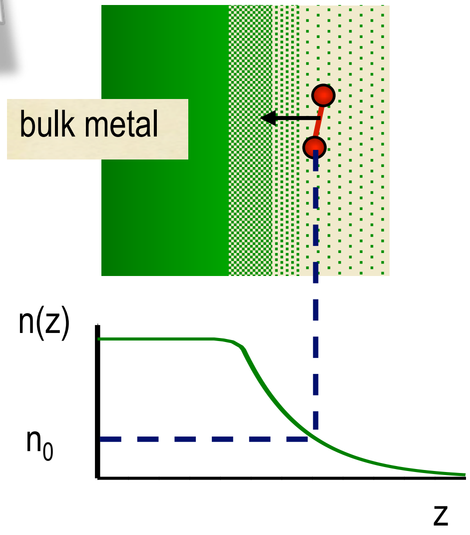
Friction coefficient of an atom in a FEG

$$\eta(\mathbf{R}_i) = n_0(\mathbf{R}_i)\ \ k_F\ \sigma_{tr}(k_F)$$

FEG electron density

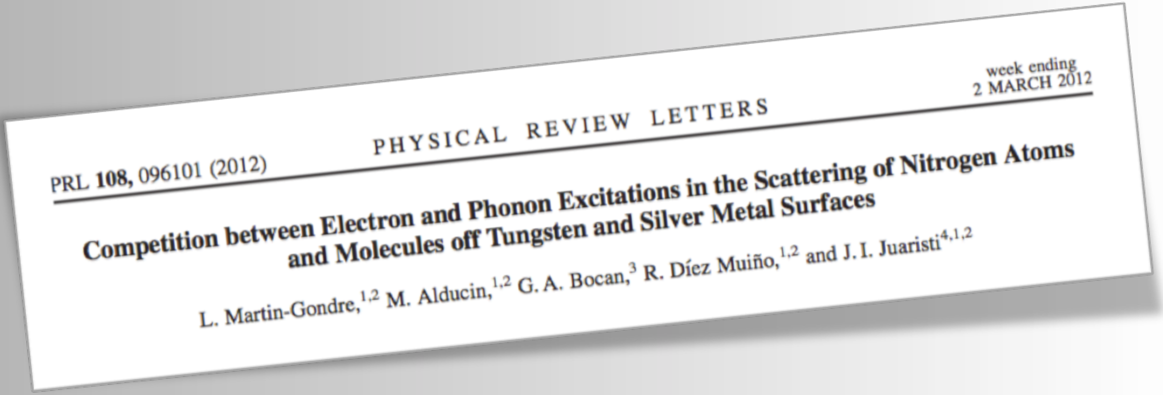
FEG Fermi momentum

Transport cross section of the electrons scattered by the atom



Local density friction approximation (LDFA) model

Methodology: dissipation to e-h pairs



PRL **108,** 096101 (2012) PHYSICAL REVIEW LETTERS week ending 2 MARCH 2012

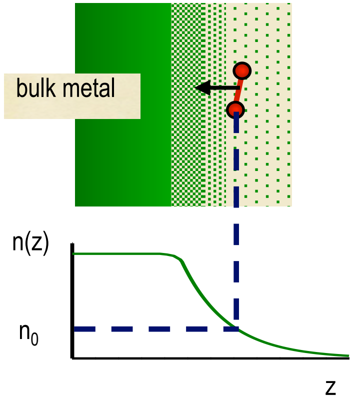
Competition between Electron and Phonon Excitations in the Scattering of Nitrogen Atoms and Molecules off Tungsten and Silver Metal Surfaces

L. Martin-Gondre,[1,2] M. Alducin,[1,2] G. A. Bocan,[3] R. Díez Muiño,[1,2] and J. I. Juaristi[4,1,2]

$$M_i\frac{d^2\mathbf{R}_i}{dt^2} = -\nabla_i V(\mathbf{R}_i-\mathbf{R}_s,\mathbf{R}_j-\mathbf{R}_s) - \boxed{\eta((\mathbf{R}_i-\mathbf{R}_s)\frac{d\mathbf{R}_i}{dt}}$$

$$\frac{d^2\mathbf{R}_s}{dt^2} = -\frac{1}{m_s}\nabla_s V^{6D}(\mathbf{R}_i-\mathbf{R}_s,\mathbf{R}_j-\mathbf{R}_s) - \hat{\omega}_s^2\mathbf{R}_s + \hat{\lambda}_{gs}\mathbf{R}_g$$

$$\frac{d^2\mathbf{R}_g}{dt^2} = -\hat{\omega}_g^2\mathbf{R}_g + \hat{\lambda}_{gs}\mathbf{R}_s - \hat{\gamma}_g\frac{d\mathbf{R}_g}{dt} + \frac{1}{m_s}\mathbf{F}_r(t)$$



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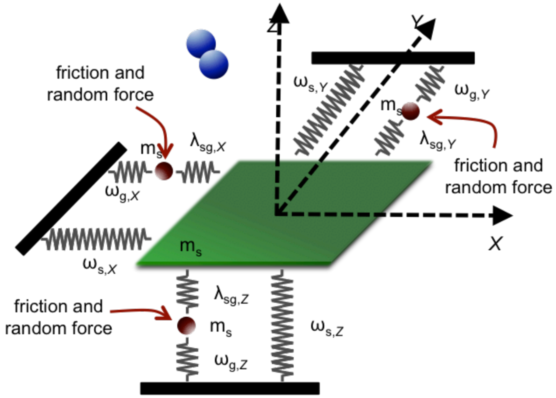
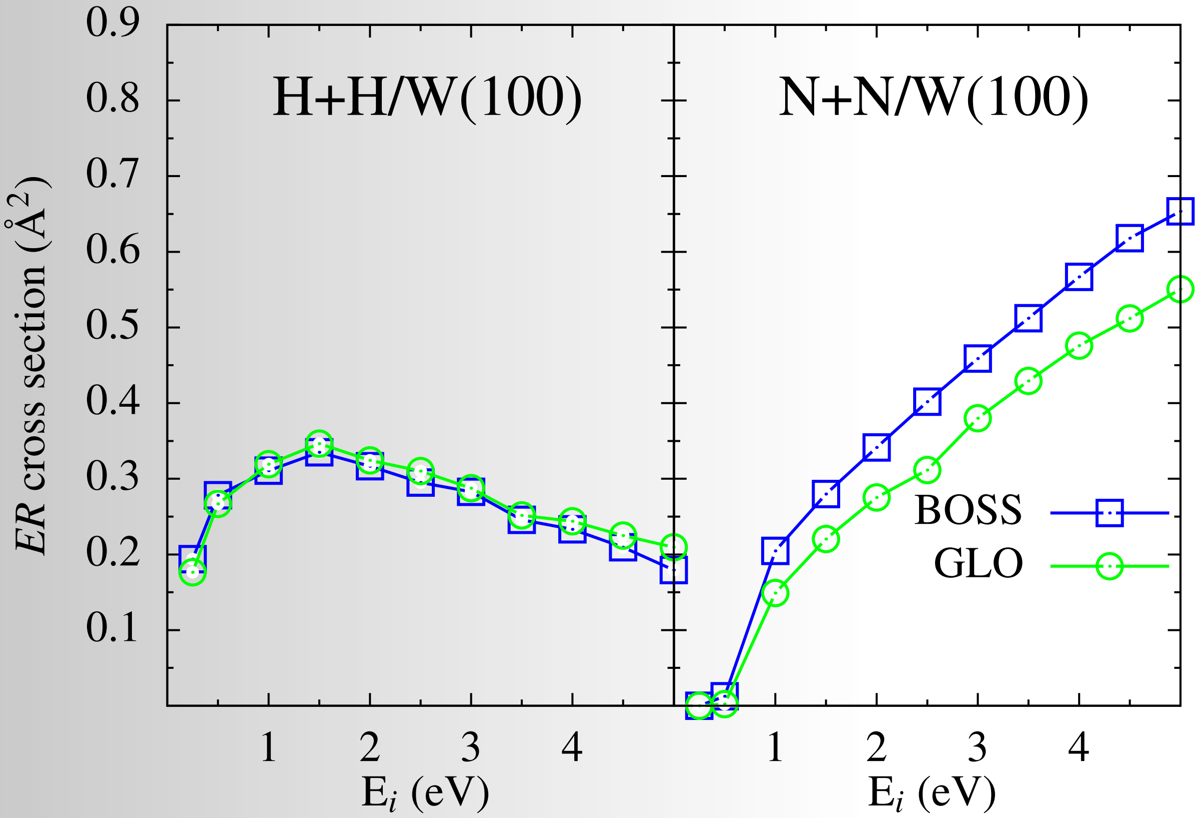


LDFA-GLO model

Results

Eley-Rideal reaction in the single adsorbate limit:

Energy dissipation effects



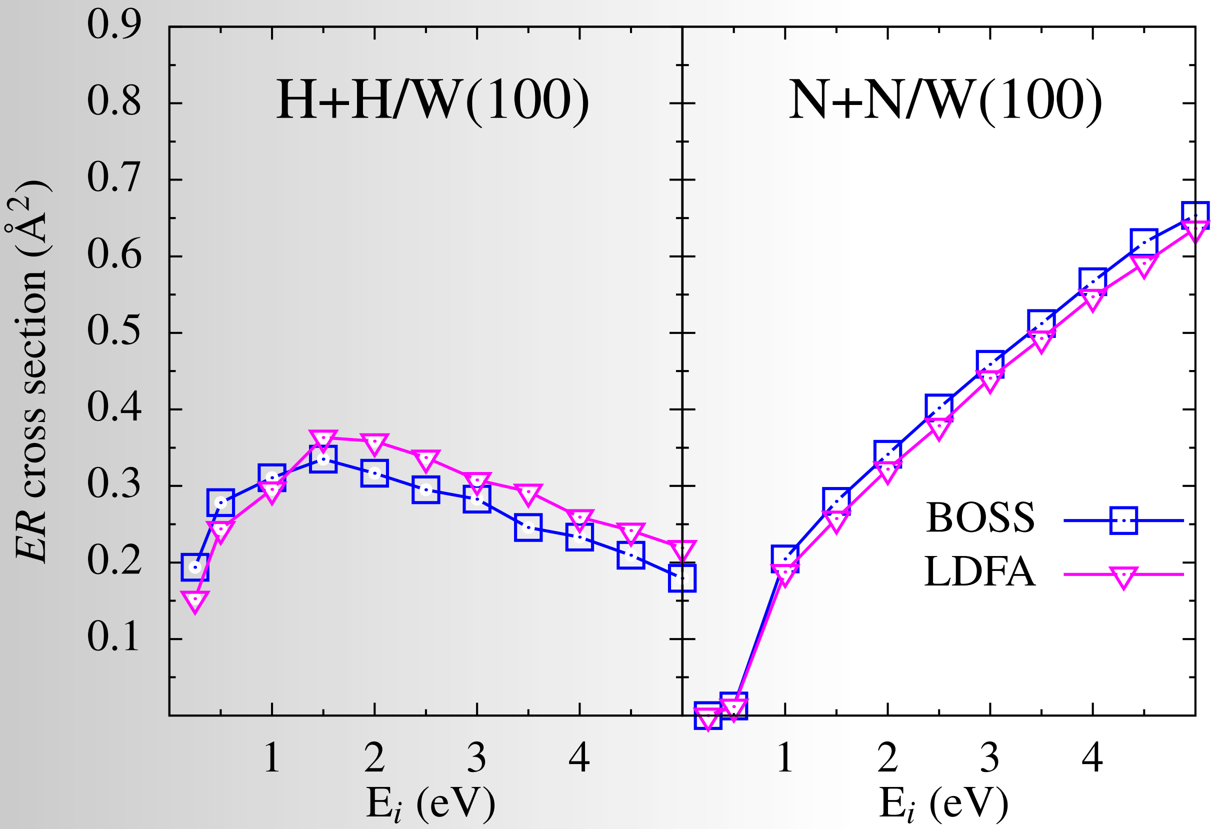
Dissipation to phonons

Only relevant for N abstraction

Results

Eley-Rideal reaction in the single adsorbate limit:

Energy dissipation effects

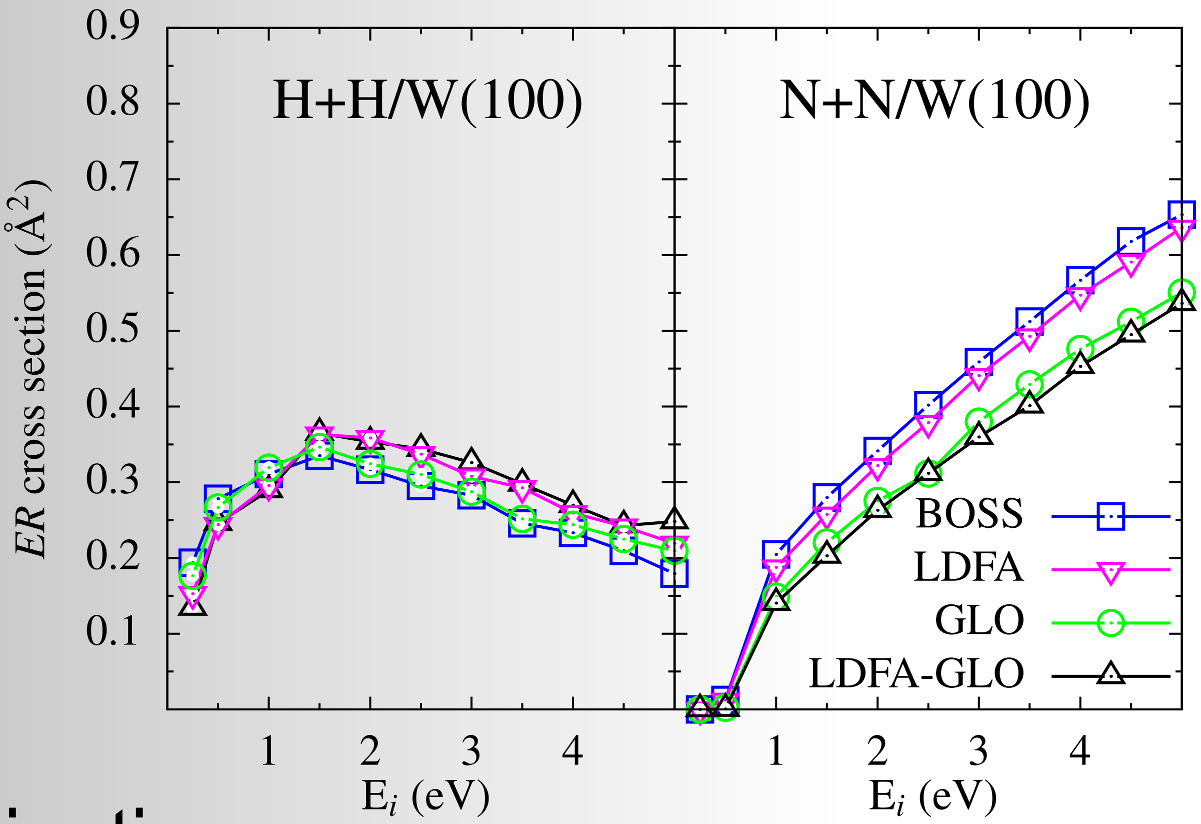


Dissipation to e-h pairs

Low influence on cross sections

Results

Eley-Rideal reaction in the single adsorbate limit:
Energy dissipation effects

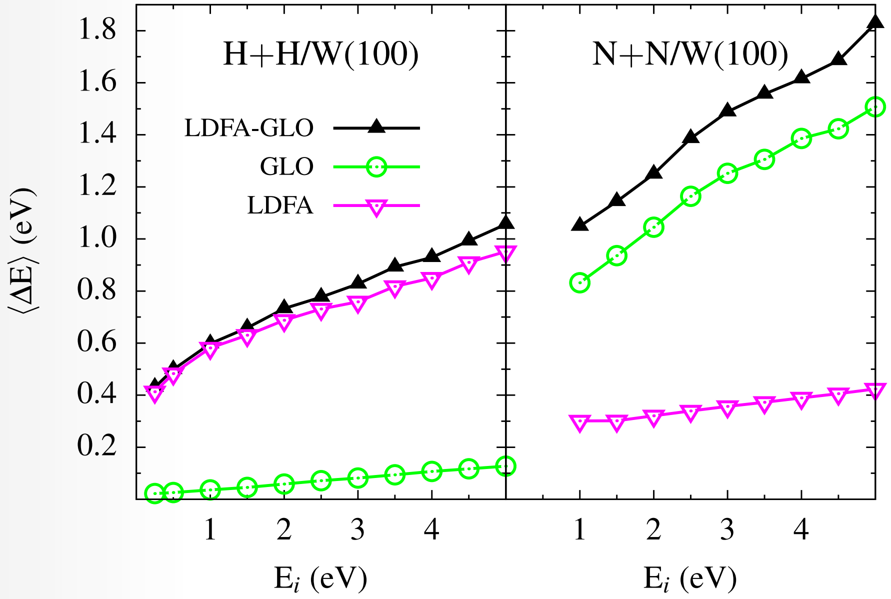


Total Dissipation

Results

Eley-Rideal reaction in the single adsorbate limit:
Energy dissipation effects

$$\begin{array}{ccc} -\ \langle\Delta E_N\rangle & \approx & 2\ \langle\Delta E_H\rangle \\ \uparrow & & \uparrow \\ \langle\Delta E_{ph}\rangle & & \langle\Delta E_{eh}\rangle \\ + & & + \\ \langle\Delta E_{eh}\rangle & & \cancel{\langle\Delta E_{ph}\rangle} \end{array}$$



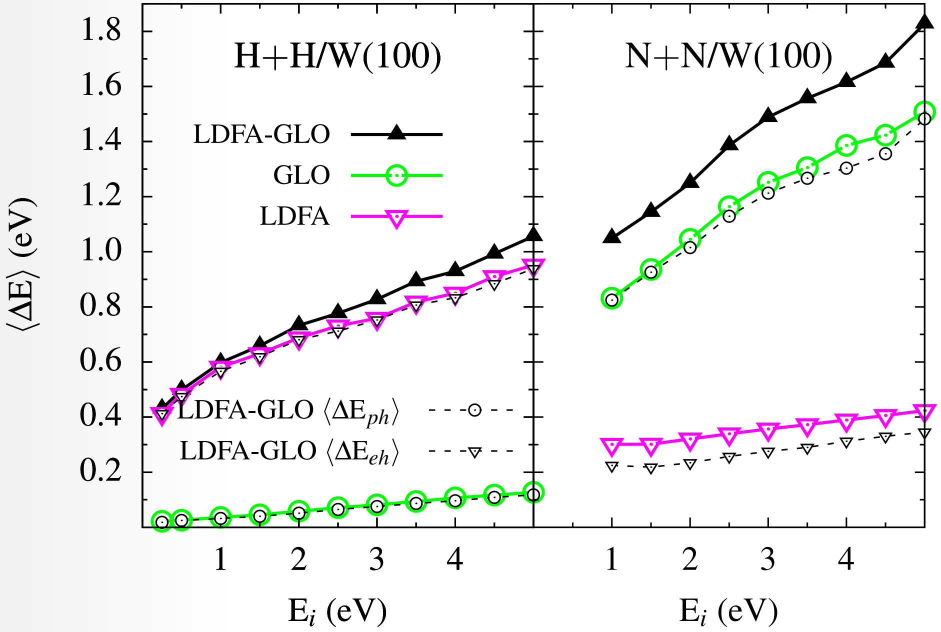
Results

Eley-Rideal reaction in the single adsorbate limit:

Energy dissipation effects

- $$\underset{\langle \Delta E_{eh} \rangle}{\underset{+}{\underset{\langle \Delta E_{ph} \rangle}{\underset{\uparrow}{\langle \Delta E_N \rangle}}}} \approx 2 \underset{\cancel{\langle \Delta E_{ph} \rangle}}{\underset{+}{\underset{\langle \Delta E_{eh} \rangle}{\underset{\uparrow}{\langle \Delta E_H \rangle}}}}$$
- N_2 : $\langle \Delta E_{eh} \rangle$ (LDFA) > $\langle \Delta E_{eh} \rangle$ (LDFA-GLO)

$$\Delta \mathrm{E}_{eh} = \sum_{i,n} \eta(\mathbf{R}_i) \left(\frac{d\mathbf{R}_i}{dt} \right)^2 \Delta t_n$$

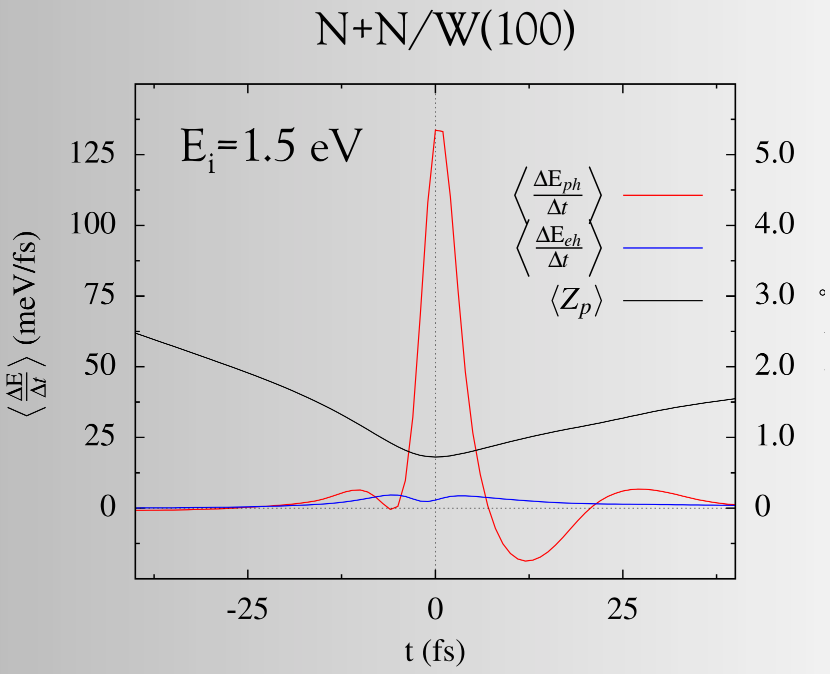


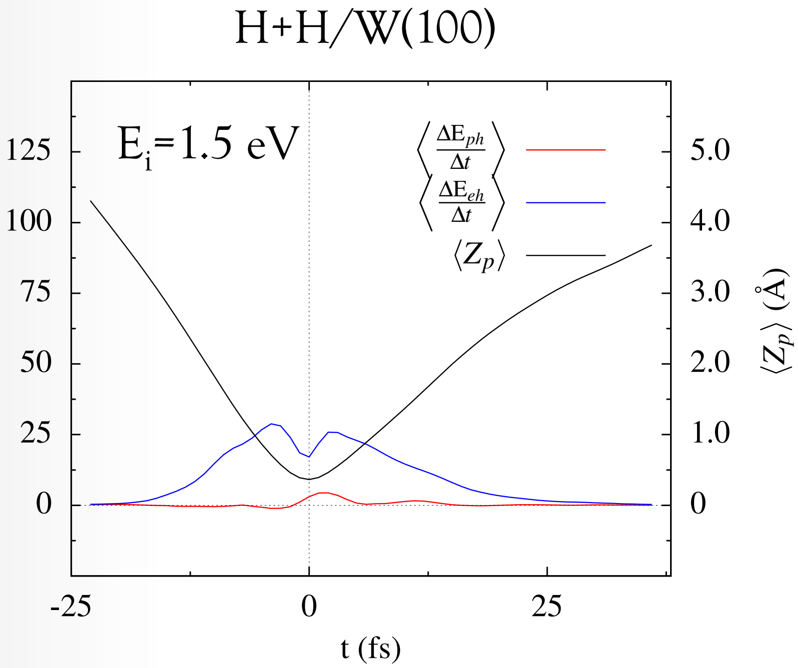
Coupling between dissipation to phonons and electrons for N Abstraction

Results

Eley-Rideal reaction in the single adsorbate limit:

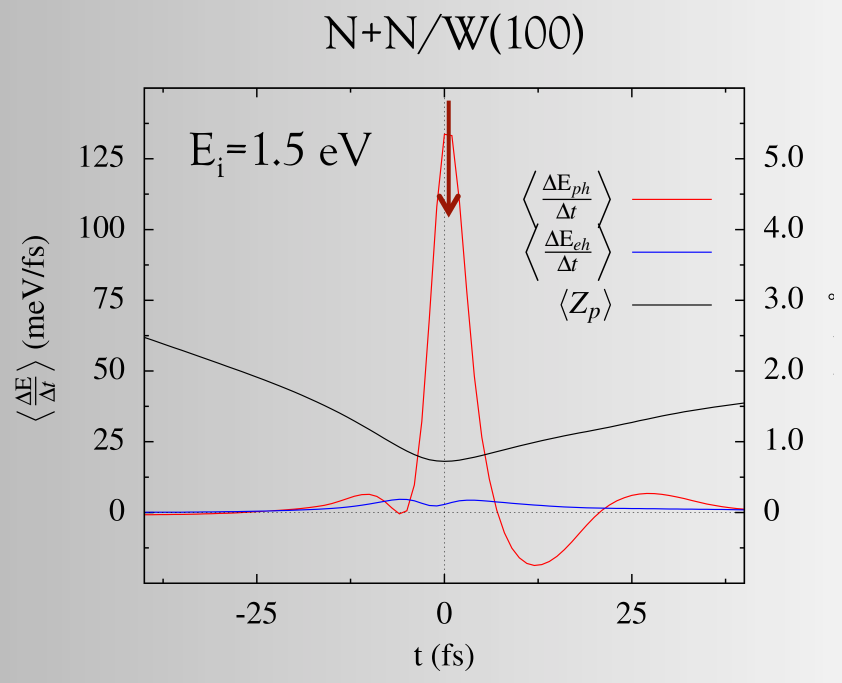
Energy dissipation effects

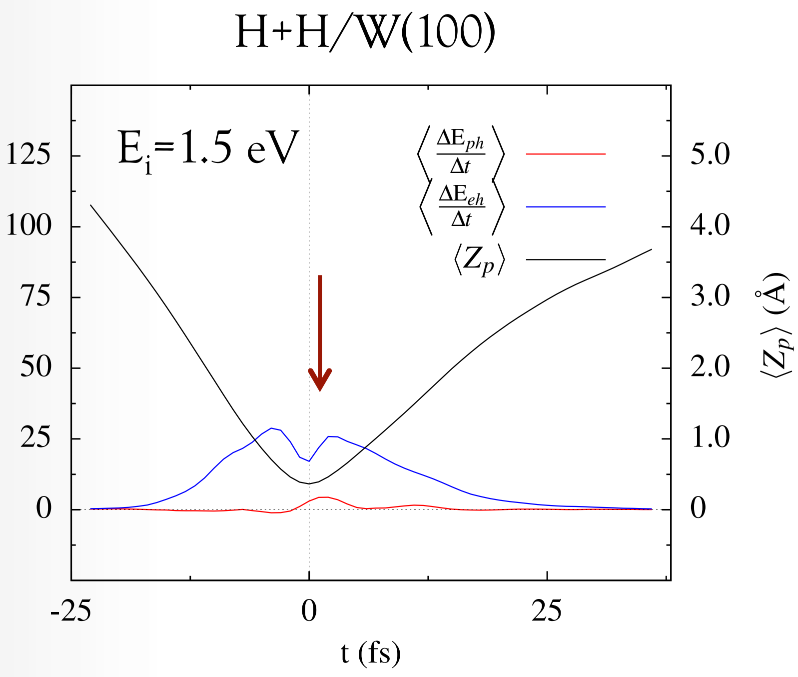

N+N/W(100)


H+H/W(100)

Results

Eley-Rideal reaction in the single adsorbate limit:
Energy dissipation effects

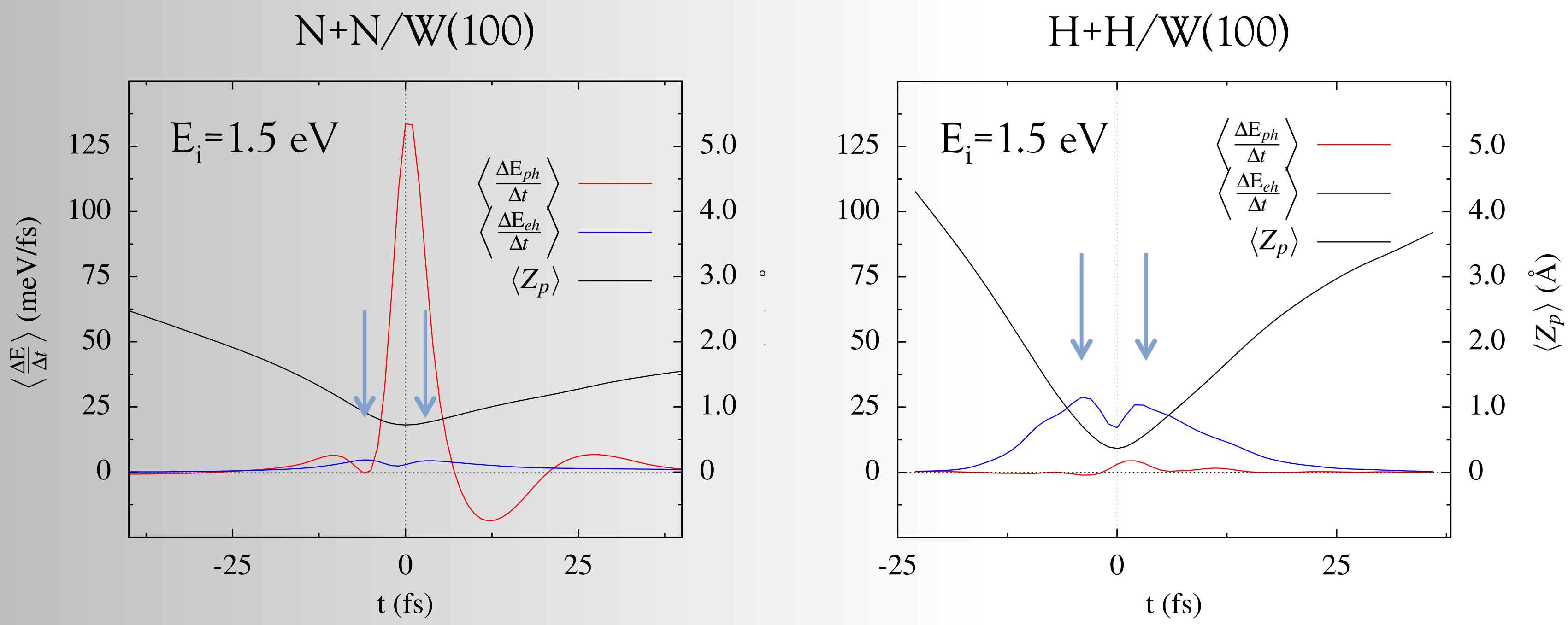

N+N/W(100)


H+H/W(100)

The main energy exchange with phonons occurs in the collision,

Results

Eley-Rideal reaction in the single adsorbate limit: Energy dissipation effects



The main energy exchange with phonons occurs in the collision, whereas the energy exchan-ge with e-h pairs is distributed before and after collision

Concluding…

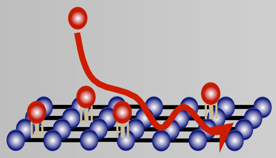
ER reaction dependence on E_i is unchanged when including energy dissipation to the metal. However, a relevant amount of e–h pair excitations are created in, as well as phonon excitations for N recombination

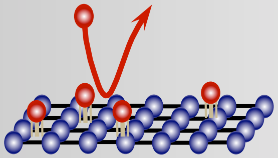
Results

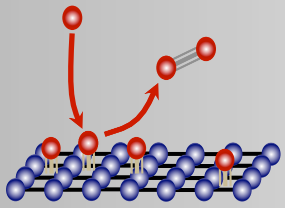
H abstraction from H-covered W(110) and W(100): Non-adiabatic dynamics

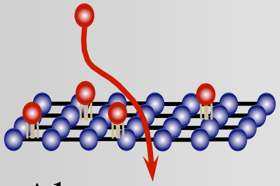
Multi-adsorbate PES

$$V(\{\mathbf{R}_i\}) = \sum_{i=1}^{N} V^{3D}(\mathbf{R}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N} I^{6D}(\mathbf{R}_i, \mathbf{R}_j)$$

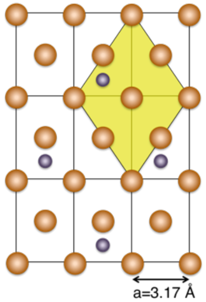

Adsorption


Reflection

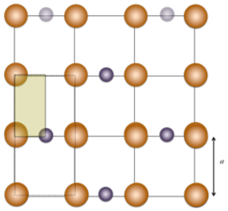

Abstraction

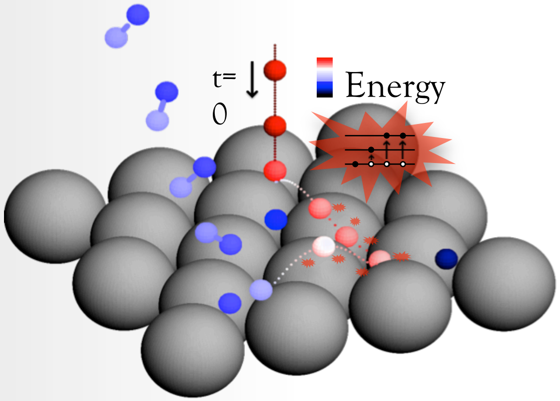

Absorption

W(110)
0.25 ML



W(100)
0.5 ML

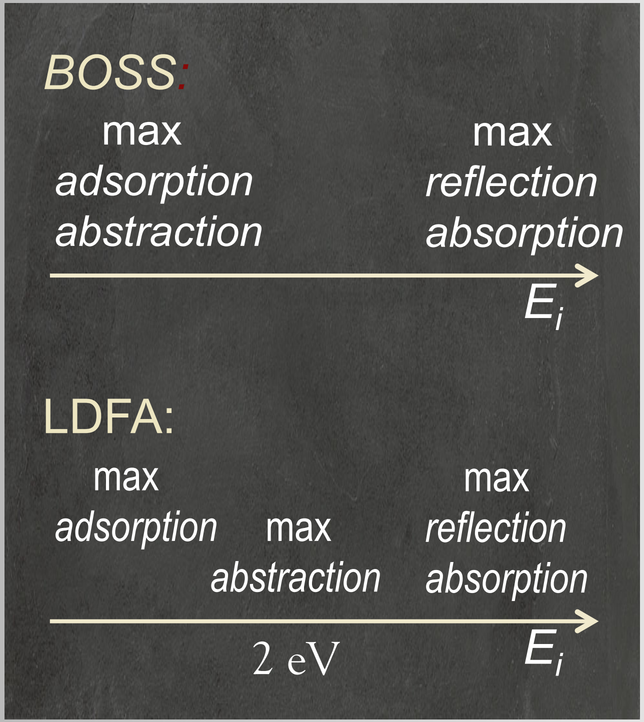




BOSS
LDFA

Results

H abstraction from H-covered W(110) and W(100):
Non-adiabatic dynamics



BOSS:

max *adsorption* *abstraction*

max *reflection* *absorption*

E_i

LDFA:

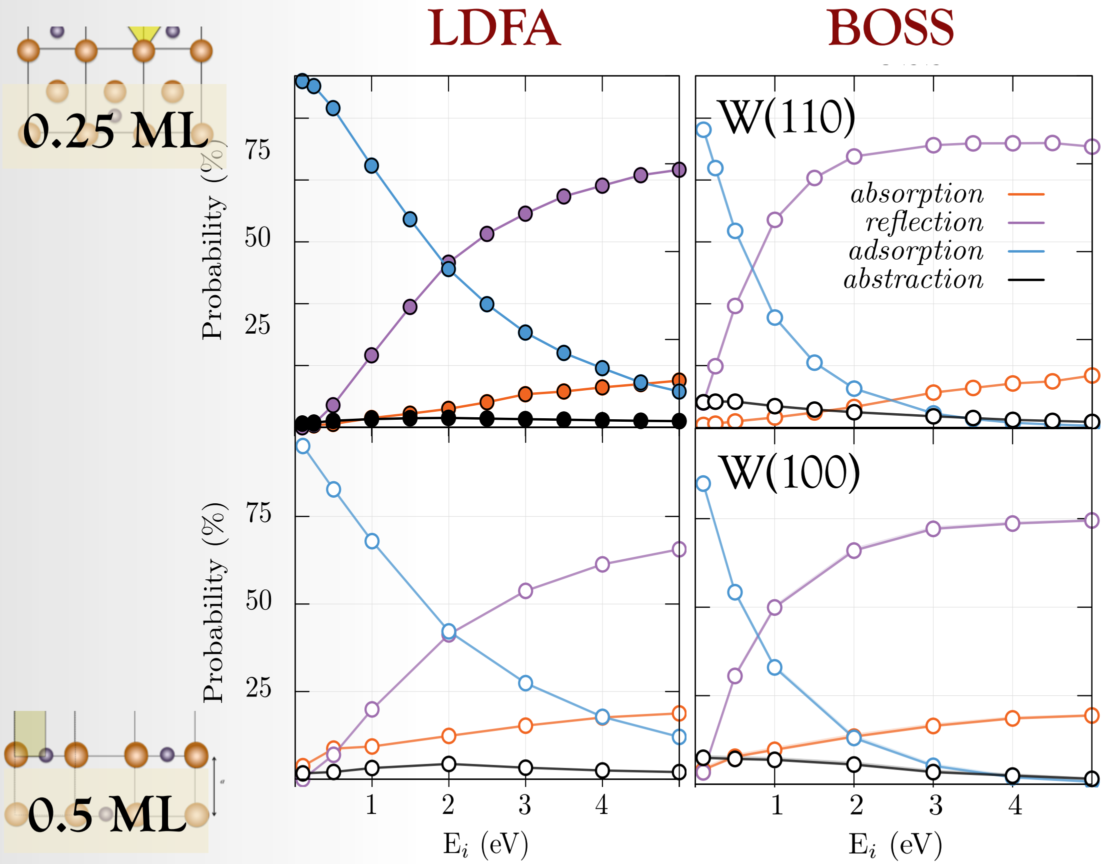
max *adsorption*

max *abstraction*

max *reflection* *absorption*

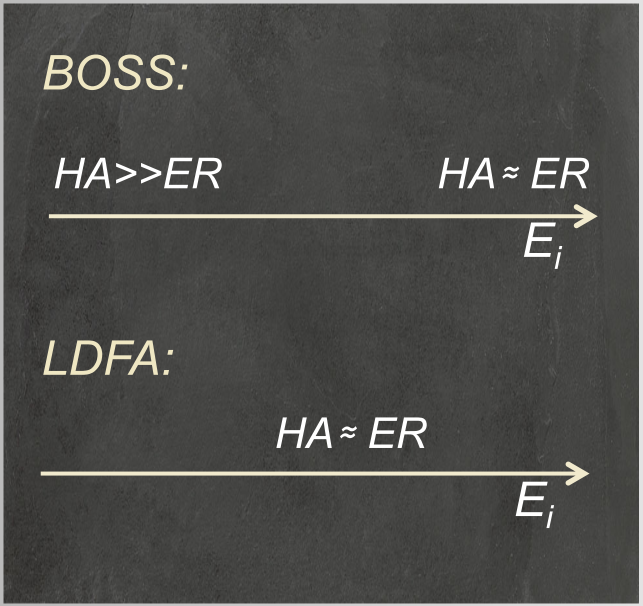
2 eV

E_i



Results

H abstraction from H-covered W(110) and W(100): Non-adiabatic dynamics



BOSS:

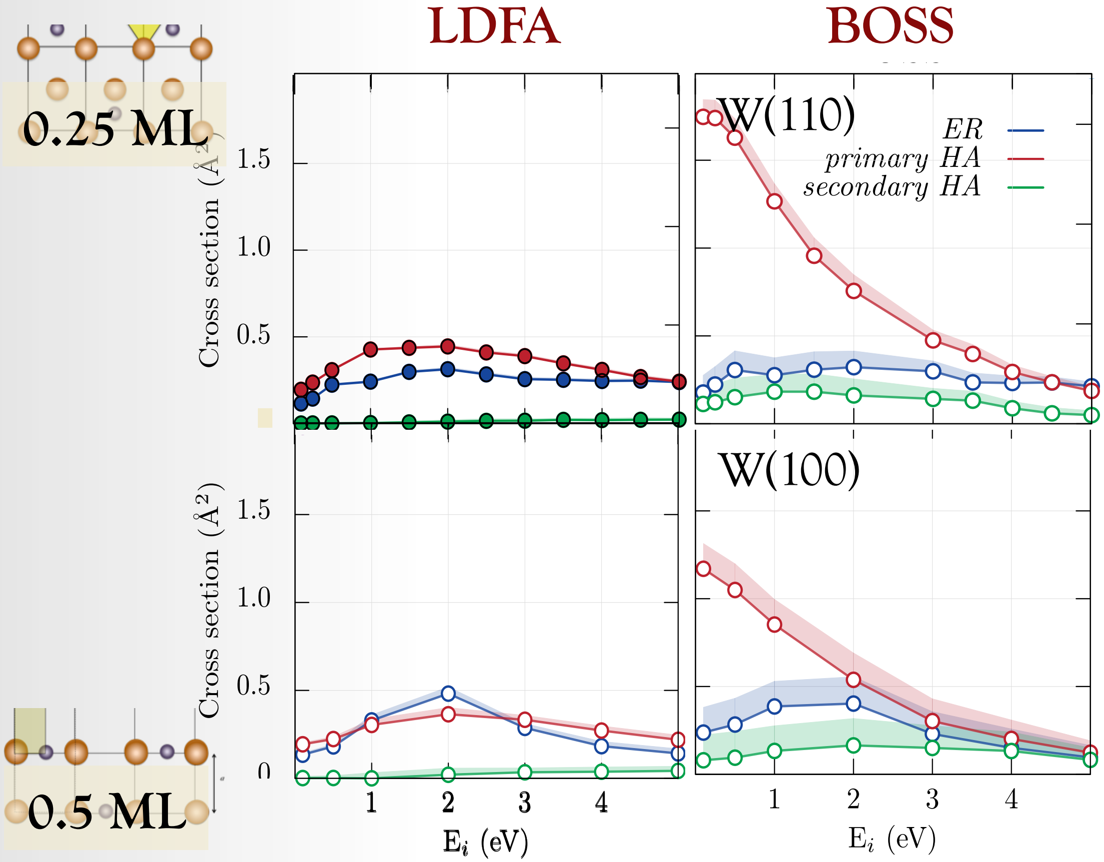
HA>>ER HA ≈ ER

E_i

LDFA:

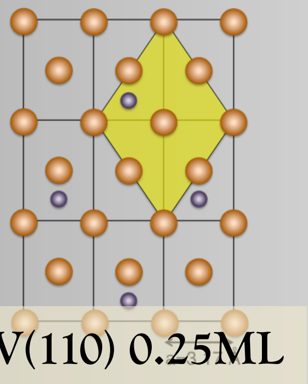
HA ≈ ER

E_i

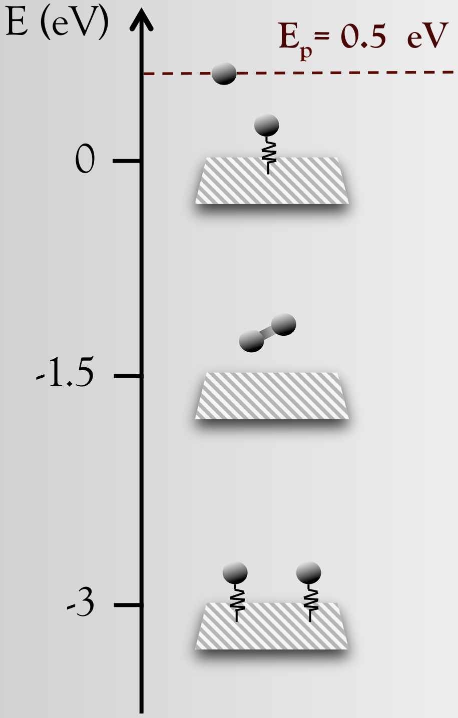


Results

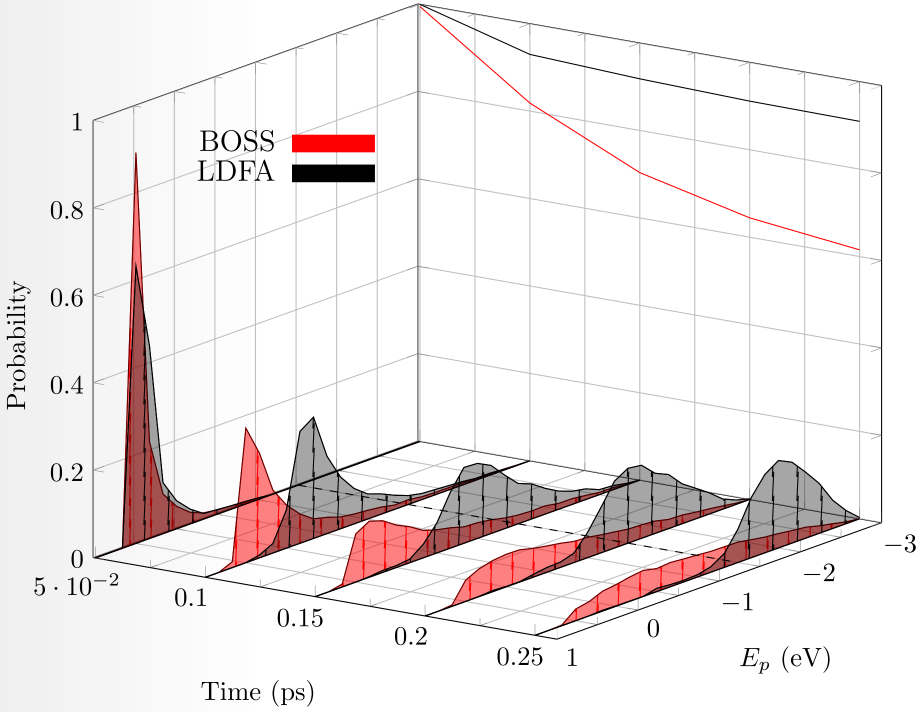
H abstraction from H-covered W(110) and W(100): Non-adiabatic dynamics



e-h pair excitations are very efficient drawing energy from the projectile

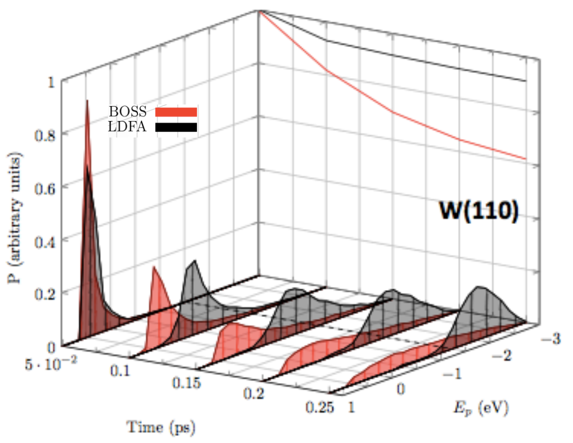


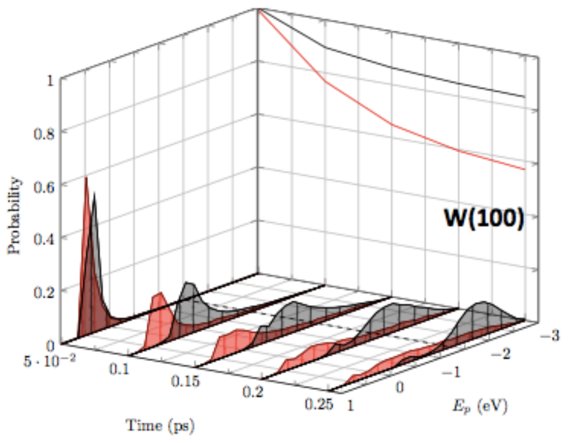
$$E_p = K_p + V^{3D}(\mathbf{R}_p) + \frac{1}{2}\sum_{i\neq p}^{N} I^{6D}(\mathbf{R}_i,\mathbf{R}_p)$$

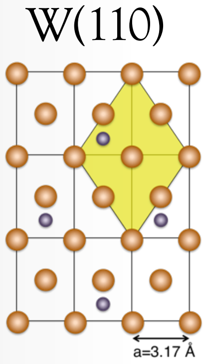


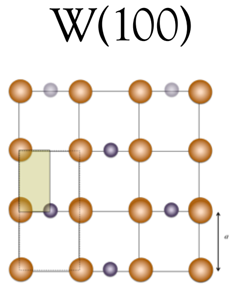
Results

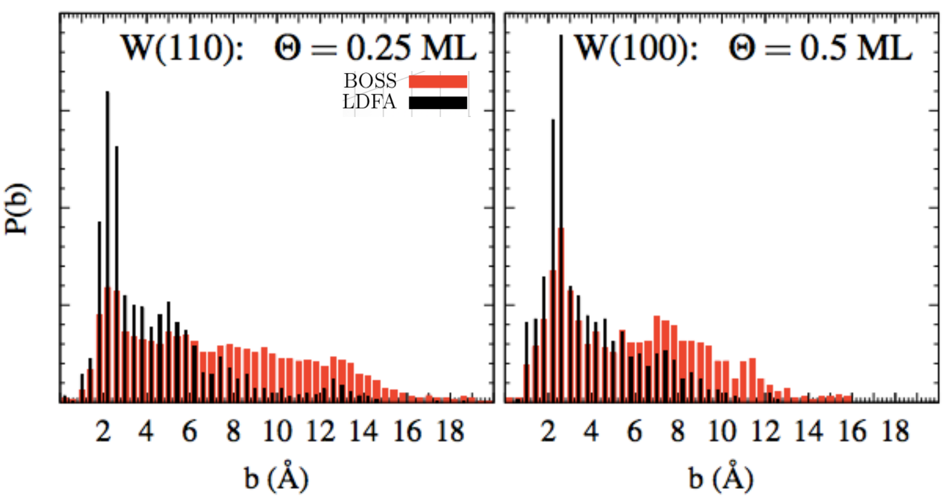
H abstraction from H-covered W(110) and W(100): Non-adiabatic dynamics











Concluding…

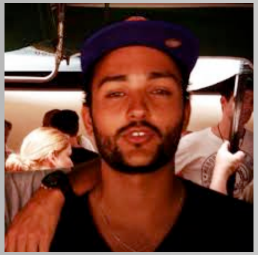
e-h pair excitations importantly affect Hot-Atom abstraction of H adsorbed on W(100) and W(110) by H scattering. As a consequence both ER and HA processes are shown to contribute in a similar way to the total abstraction cross sections.

Thanks for your attention

Acknowldgements

Oihana Galparsoro

Cédric Crespos



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