Adsorption, Clustering and Reaction of Hydrogen Atoms On Graphene

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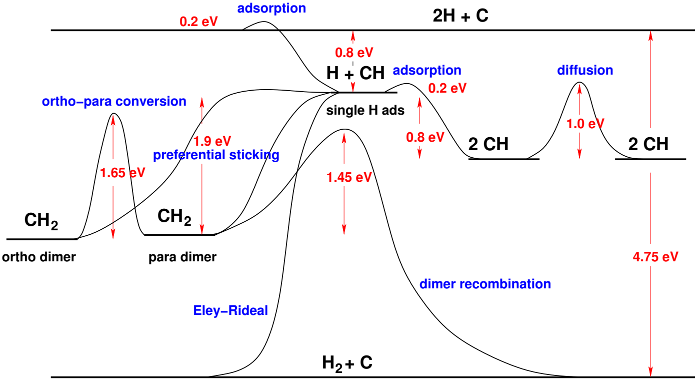
16th Workshop on Dynamical Phenomena at Surfaces
Madrid, October 29-31, 2014

Chemisorption and reaction



R. Martinazzo, S. Casolo and L. Horneaker
in *Dynamics of Gas-Surface Interactions*, Ed.s R. D. Muino and H. F. Busnengo, Springer (2013)

Outline

1. Adsorption energetics
   - Dimer and cluster formation
   - H on Graphene/Ir(111)
2. Eley-Rideal reaction dynamics
   - Reduced-dimensional quantum dynamics
   - *Ab initio* molecular dynamics
3. Sticking dynamics
   - System-bath modeling
   - High-Dimensional Quantum dynamics

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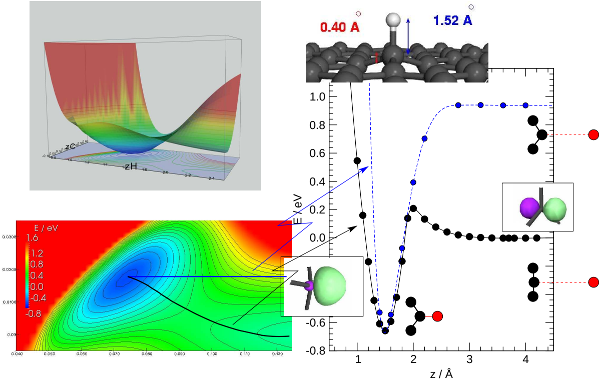
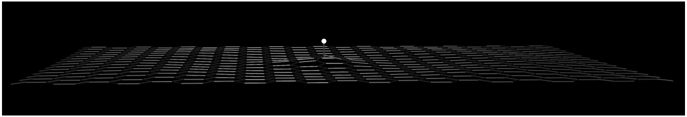
Chemisorption of a H atom



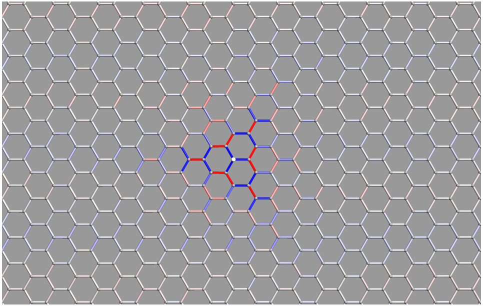
L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

*

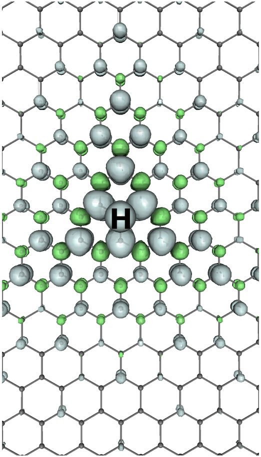
Chemisorption of a H atom

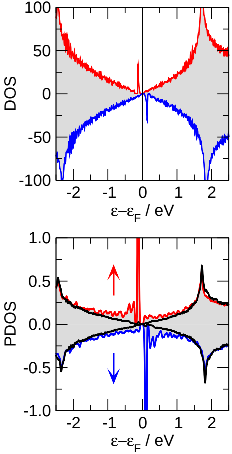


0.5% shorter - d^0_{CC} - 0.5% longer

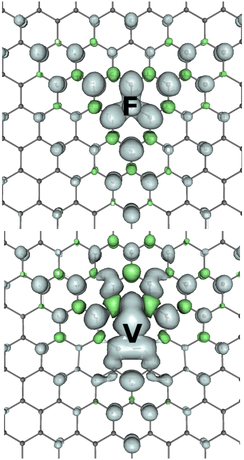


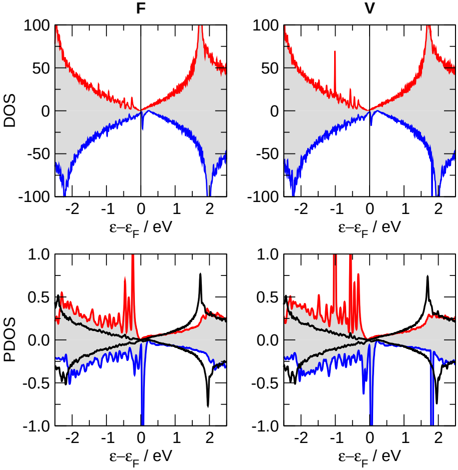
Midgap states





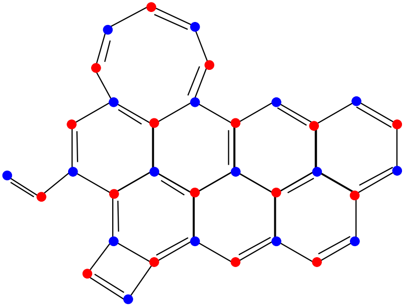
Midgap states

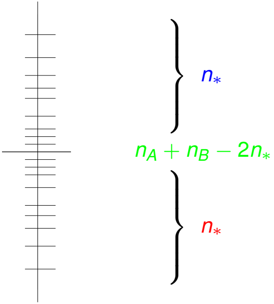




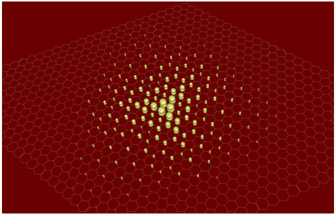
Midgap states: p_z vacancies

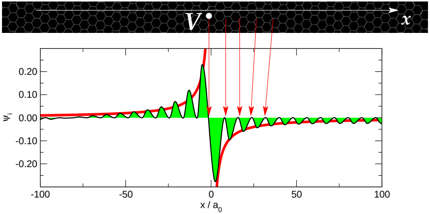
$$H^{\pi} \approx \sum_{\tau,ij}(t_{ij} a^{\dagger}_{i,\tau} b_{j,\tau} + t_{ji} b^{\dagger}_{j,\tau} a_{i,\tau}) + U \sum_i n_{i,\tau} n_{i,-\tau}$$

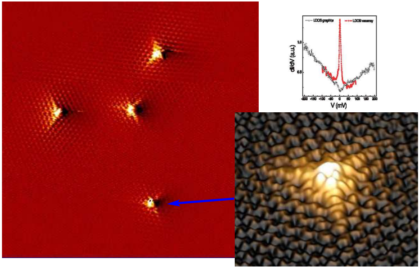




Midgap states: p_z vacancies





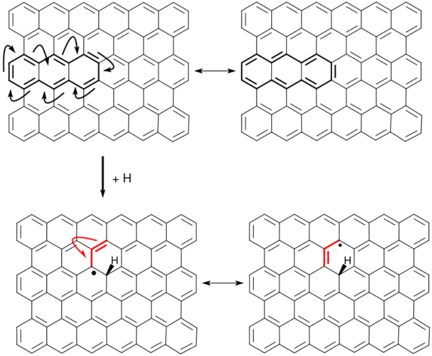


M.M. Ugeda *et al.*, *Phys. Rev. Lett.* **104**, 096804 (2010)

$$\psi(x, y, z) \sim 1/r$$

V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006); *Phys. Rev. B* **77**, 115109 (2008)

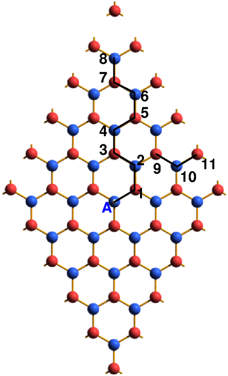
Midgap states: p_z vacancies

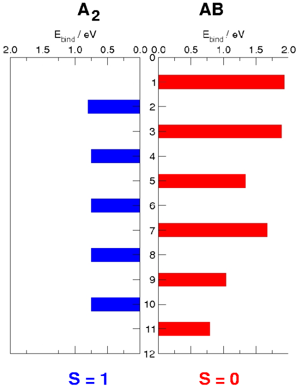


Resonating Valence Bond

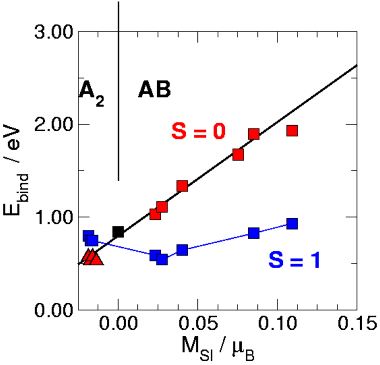
- **Transport**: resonant scatterers explain behavior of σ_{DC} at zero and finite electron densities
- **Magnetism**: local magnetic moments responsible for the observed paramagnetic response
- **Chemistry**: preferential sticking leading to dimer and cluster formation

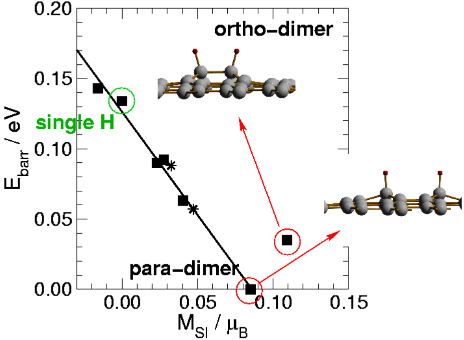
Dimers


8
7
6
5
4
3
2
9
11
10
1
A


A2
AB
E bind / eV
E bind / eV
2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0
0 1 2 3 4 5 6 7 8 9 10 11 12
S = 1
S = 0

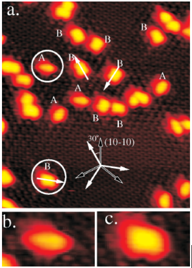
Dimers



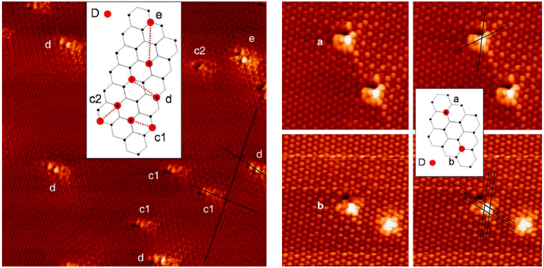


S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)
Preferential sticking: L. Hornekaer *et al.*, *Phys. Rev. Lett.* **96** 156104 (2006)

Dimers



[1]

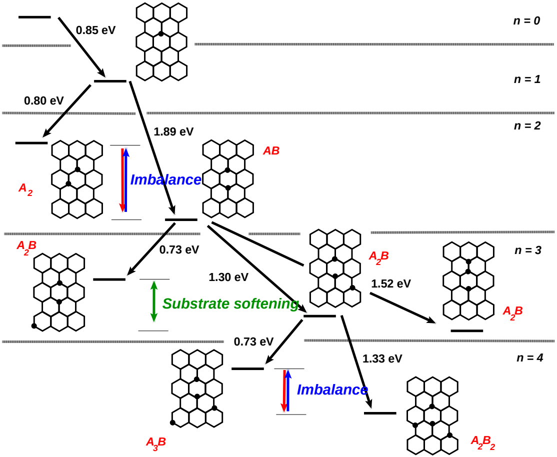


[2]

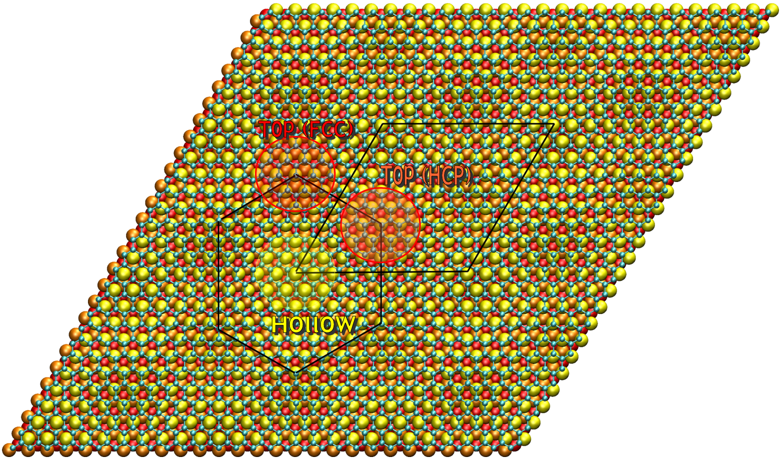
[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. *Phys. Rev. Lett.* **96** 156104 (2006)

[2] A. Andree, M. Le Lay, T. Zecho and J. Kupper, *Chem. Phys. Lett.* **425** 99 (2006)

Clusters

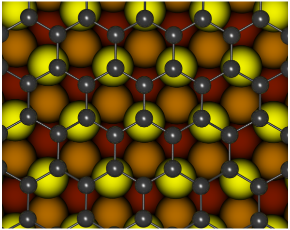

0.85 eV
n = 0
n = 1
0.80 eV
1.89 eV
n = 2
AB
A_2
Imbalance
A_2B
0.73 eV
A_2B
n = 3
1.30 eV
1.52 eV
Substrate softening
A_2B
0.73 eV
n = 4
1.33 eV
Imbalance
A_3B
A_2B_2

Ir(111)/graphene Moiré structure

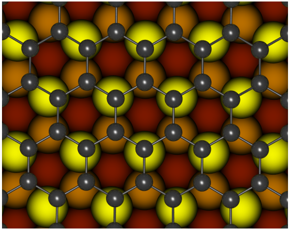


Ir(111)/graphene Moiré structure

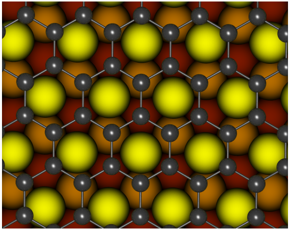
Top-Fcc (or "Hcp")



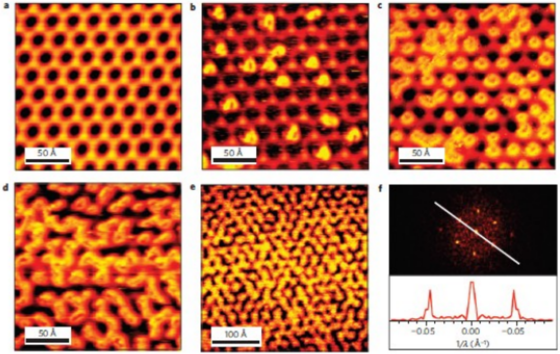
Top-Hcp (or "Fcc")



Hollow (or "Atop")



Patterned H adsorption

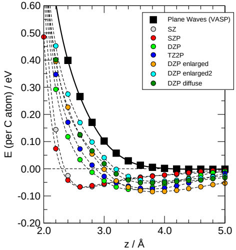


R. Balog *et al.*, *Nat. Mater.*, **9** 315 (2010)

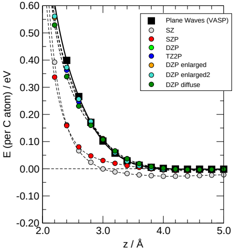
Technicalities

Too large cell for PW calculations.. ⇒ AOs (SIESTA)

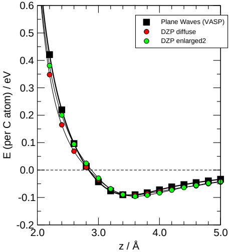
Plain (no vdW)



CP corrected (no vdW)



vdW corrected



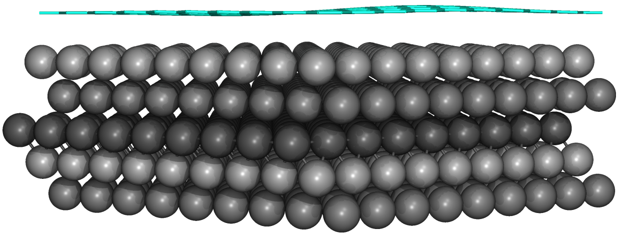
1x1 Top-Fcc (similarly for **Top-Hcp** and **Hollow**)

⇒ Standard Double ζ *plus* Polarization *plus* Diffuse *plus* vdW
⇒ Five 9 × 9 Ir layers + 10 × 10 graphene ⇒ 605 atoms

Ir(111)/Graphene

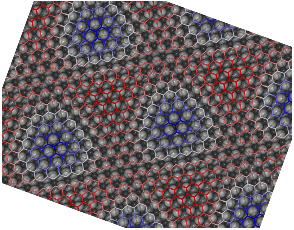
PW91[1] : $h = 3.90$ Å, $\Delta h = 0.27$ Å, $E_b = 200.0$ meV/C
vdW-DFT[2] : $h = 3.41$ Å, $\Delta h = 0.35$ Å, $E_b = 50.0$ meV/C
This work : $h = 3.52$ Å, $\Delta h = 0.57$ Å, $E_b = 124.9$ meV/C

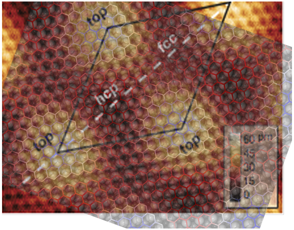
XSW[2] : $h = 3.38 \pm 0.04$ Å, $\Delta h = 0.6 \pm 0.1$ Å
LEED *I(V)* [2] : $h = 3.39 \pm 0.03$ Å, $\Delta h = 0.43 \pm 0.09$ Å
AFM[3] : $h = 3.39 \pm 0.03$ Å, $\Delta h = 0.47 \pm 0.05$ Å



[1] A. T. N'Diaye *et al.*, *Phys. Rev. Lett.* **97** 215501 (2006)
[2] C. Busse *et al.*, *Phys. Rev. Lett.* **107** 036101 (2011)
[3] S. K. Hämäläinen *et al.*, *Phys. Rev. B* **88** 201406(R) (2013)

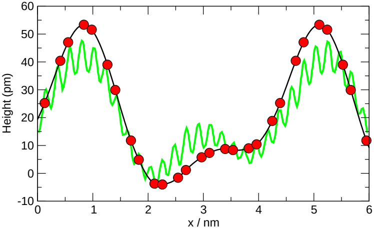
Ir(111)/Graphene





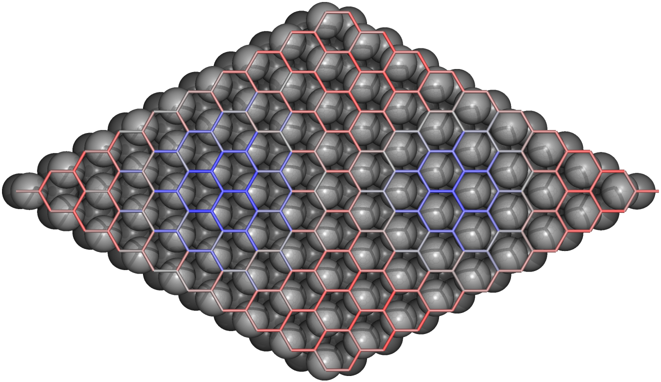
CO-terminated AFM tip

S. K. Hämäläinen *et al.*, *Phys. Rev. B* **88** 201406(R) (2013)

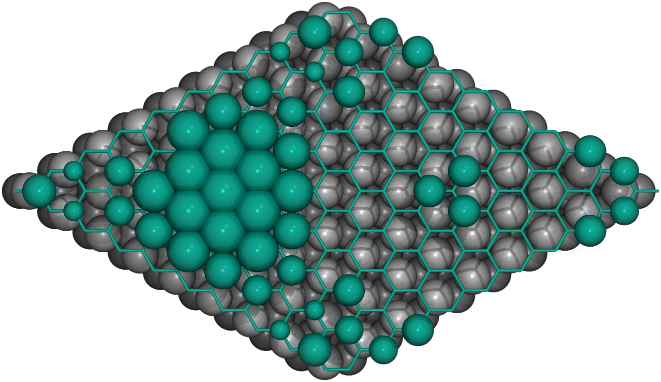


Ir(111)/Graphene

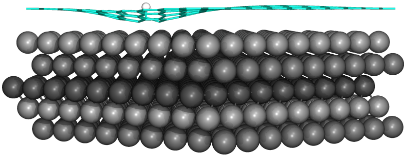
0.1% shorter - d^0_{CC} - 0.1% longer



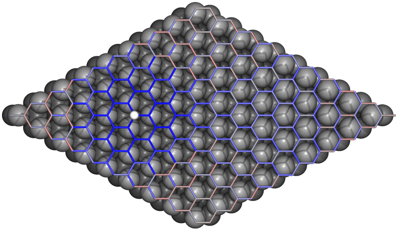
Ir(111)/Graphene+H



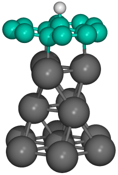
Ir(111)/Graphene+H



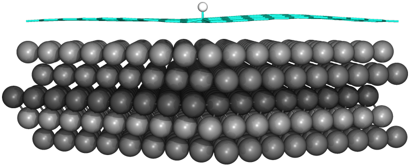
0.5% shorter - d^0_{CC} - 0.5% longer



Top-Fcc region
$E_b = 1.91$ eV



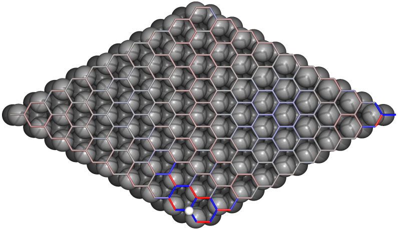
Ir(111)/Graphene+H

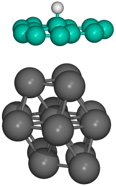


Top-Hcp region

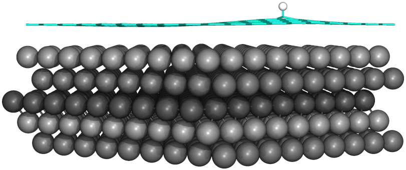
$E_b = 1.30$ eV

0.5% shorter - d^0_{CC} - 0.5% longer

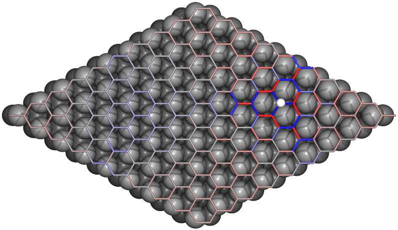




Ir(111)/Graphene+H

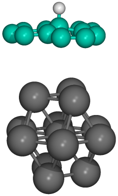


0.5% shorter - d^0_{CC} - 0.5% longer

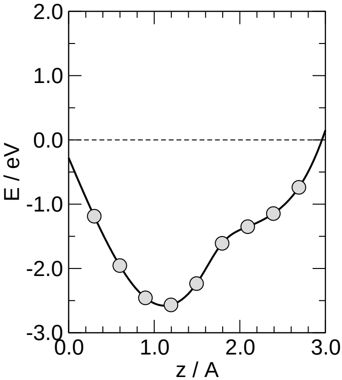


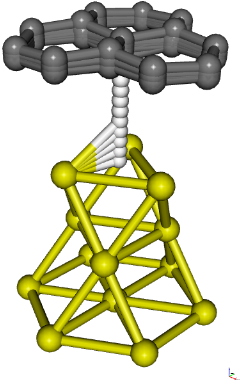
Hollow region

$E_b = 1.25$ eV



Ir(111)/H/Graphene





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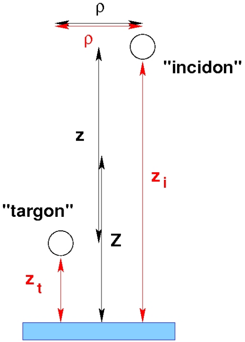
ER Reaction: technicalities

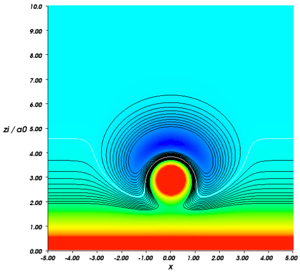
- Rigid, flat surface approximation[1]
- Split-Operator with FFT along cartesian coordinates and DBT along ρ [1]
- propagation in both product and reagent coordinate sets[2]
- DFT PES fitted to modified LEPS[3]



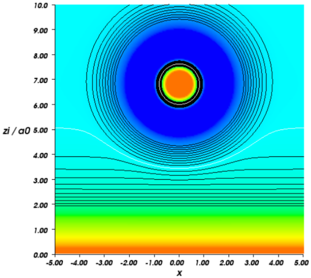
⇒ state-to-state, energy-resolved cross sections for all possible processes

[1] M. Persson and B. Jackson, J. Chem. Phys. 102, 1078 (1995); D. Lemoine and B. Jackson, Comput. Phys. Commun. 137, 415 (2001)
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)
[3] X. Sha, B. Jackson and D. Lemoine, J. Chem. Phys. 116, 7158 (2002)

ER Reaction: Potential Energy Surfaces



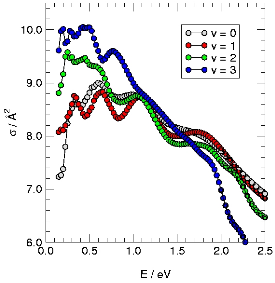
Chemisorbed target H (z_{eq})

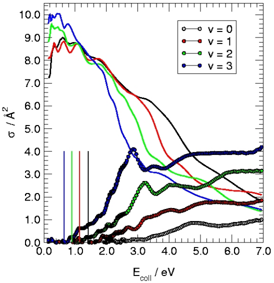


Physisorbed target H (z_{eq})

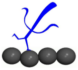
X. Sha, B. Jackson and D. Lemoine, J. Chem. Phys. 116, 7158 (2002)

H-chemisorbed target

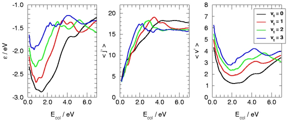




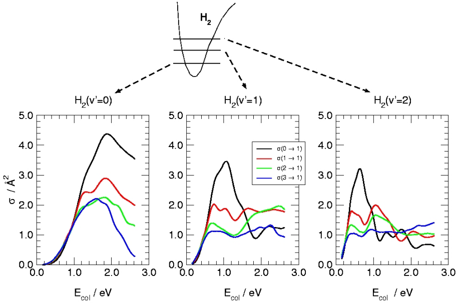
Oscillations in both ER and CID xsections



H-chemisorbed target



- Product molecules are internally hot
- Internal excitation is a steep decreasing function of E_{coll}

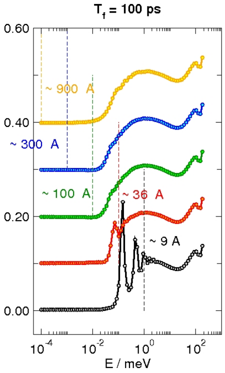


R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A* **109**, 9379; *J. Chem. Phys.* **124** 124272 (2006)

ER Reaction: technicalities (low E_{col})

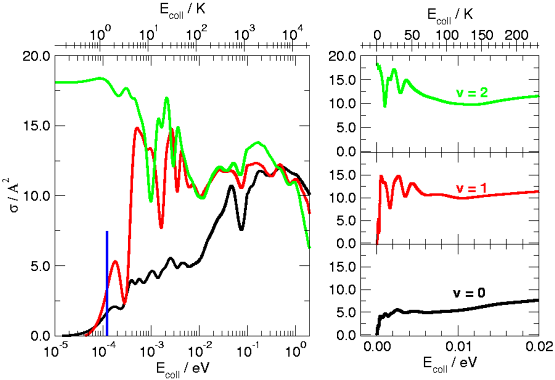
- Two-wavepacket approach[1]
- Transmission-free[2] absorbing potentials and Fourier mapping[3] in reagent coordinates

In 3D T_f=25-30 ps and AP lengths $\sim$ 50Å in order to get converged xsections down to $\sim 10^{-5}$ eV, i.e. $\sim$ 0.1 K



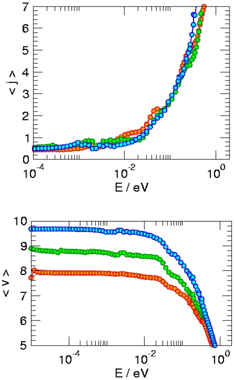
[1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)
[2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)
[3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)

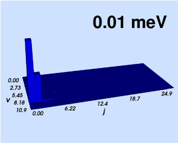
H-chemisorbed target: xsections

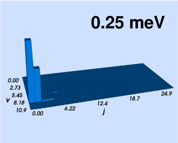


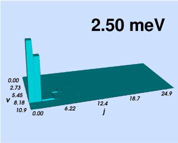
S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

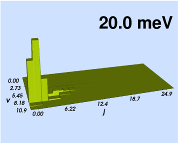
H-chemisorbed target: product v, j

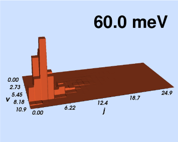


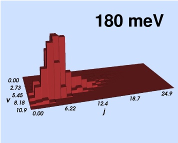






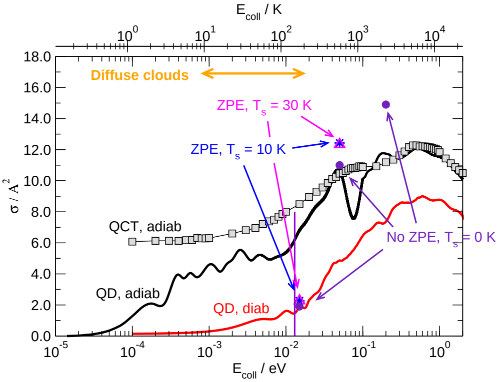






H-chemisorbed target

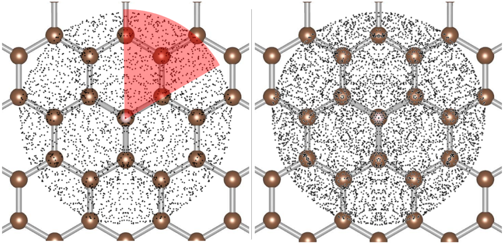
QCT comparison, $v = 0$



M. Sizun, D. Bachellerie, F. Anguillon, V. Sidis *Chem. Phys. Lett.* 32 **498** 2010
D. Bachellerie, M. Sizun, F. Anguillon, D. Teillet-Billy, N. Rougeau, *Phys. Chem. Chem. Phys.* 2715 **11** 2009

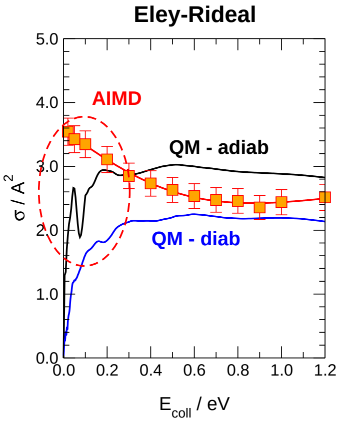
Ab initio molecular dynamics

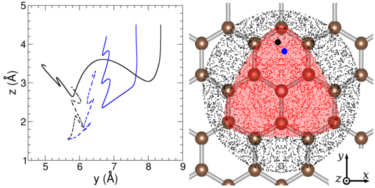
- lattice corrugation
- lattice dynamics
- dimer formation



..expensive, but solves the problem of computing and fitting a model potential

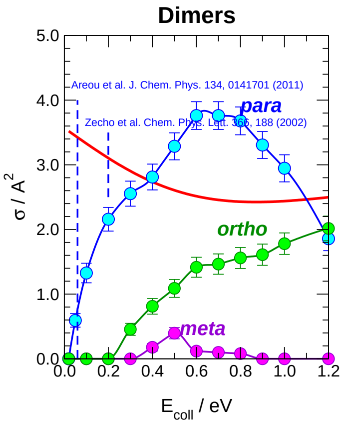
Ab initio molecular dynamics





S. Casolo, G.F. Tantardini and R. Martinazzo, PNAS **110** 6674 (2013)

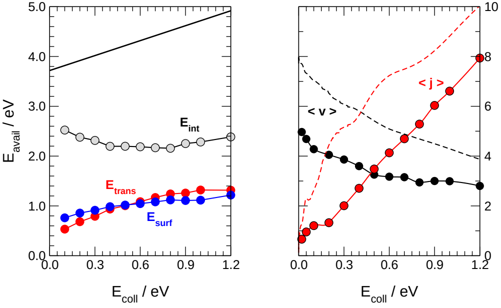
Ab initio molecular dynamics



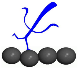
- Competition between reaction and *para*-dimer formation
- Dynamic threshold to *ortho*-dimer formation

S. Casolo, G.F. Tantardini and R. Martinazzo, PNAS **110** 6674 (2013)

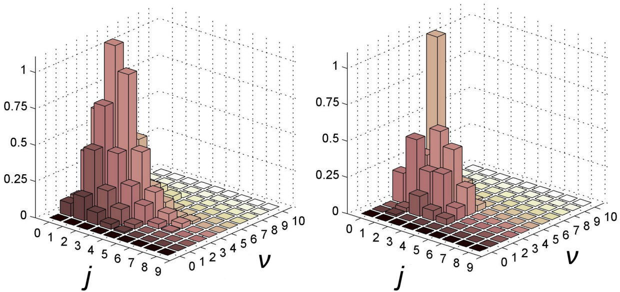
Ab initio molecular dynamics



..most of energy is internal, but energy transfer to the surface is considerable



Ab initio molecular dynamics



$T_g = 300K$, $T_s = 15K$

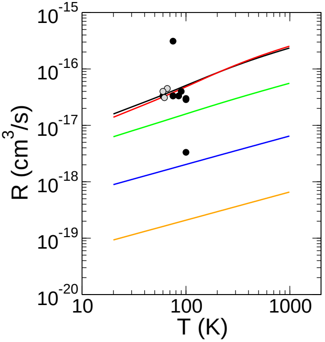
Latimer et al. Chem. Phys. Lett. 455, 174 (2008)

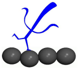
AIMD for H/D @ 0.025 eV

Kinetic modeling

$$\frac{dn_v^{H_2}}{dt} \simeq \frac{k_s k_{ER}}{k_s \Sigma_s + k_{ER}} \Sigma_g n_v^g n_v^H = Rnn_v^H$$

- Facile sticking: $\sigma_s \simeq 20$ Å^2
- $n_* \simeq 10^{-2}$ per C atom
- Porous grains: $\Sigma_g \simeq 30 - 40 \times \Sigma_g^{geom}$





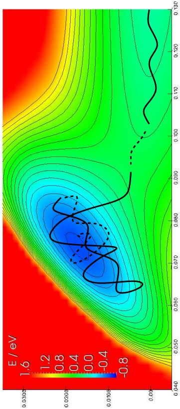
Outline

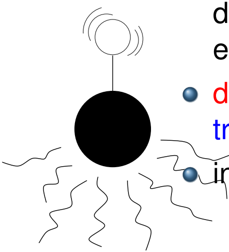
1. Adsorption energetics
   - Dimer and cluster formation
   - H on Graphene/Ir(111)

2. Eley-Rideal reaction dynamics
   - Reduced-dimensional quantum dynamics
   - *Ab initio* molecular dynamics

3. Sticking dynamics
   - System-bath modeling
   - High-Dimensional Quantum dynamics

H sticking dynamics on graphene

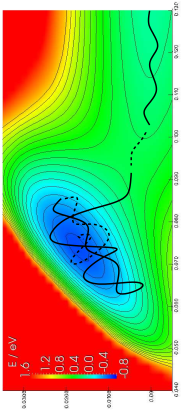


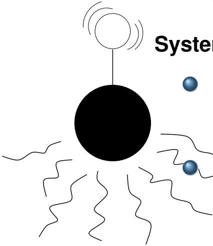


Challenging problem..

- quantum dynamics is needed to describe tunneling for $E_{coll} \leq 0.2$ eV
- dissipation is required to turn trapping into sticking
- involves scattering dynamics

H sticking dynamics on graphene





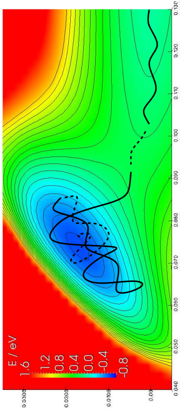
Fully atomistic models

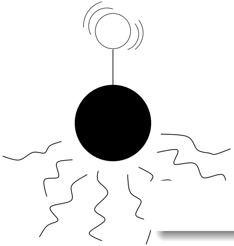
- Accurate representation of adsorbate-lattice interactions and of lattice dynamics
- Complicated form of the potential, inadequate for HD Quantum Dynamics

System-bath models

- Limited applicability, though fine iff a Generalized Langevin description of the dynamics holds
- Simplest possible form for an environment, suited to HD Quantum Dynamics

System-bath modeling





Lattice

$$H_{latt} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}) + \sum_i \frac{p_i^2}{2m_i}$$

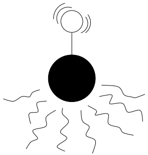
vs.

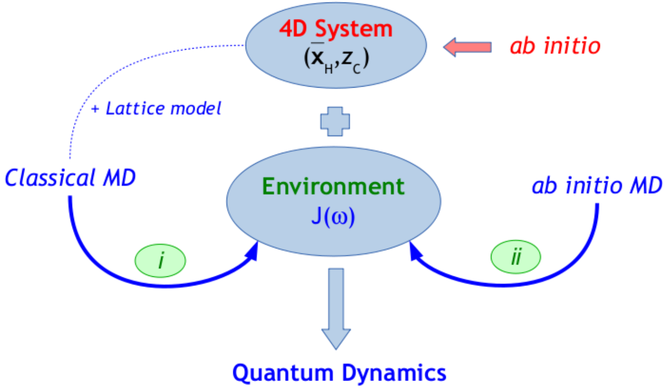
System-bath

$$H_{sb} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq}) + \sum_k \left[\frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(q_k - \frac{c_k}{\omega_k^2} f(z_C) \right)^2 \right]$$

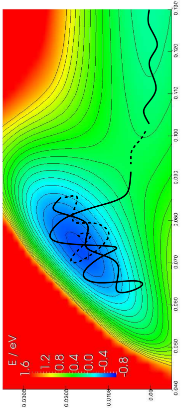
$$\omega_k, c_k \Leftrightarrow J(\omega) \Leftrightarrow \kappa(t)$$

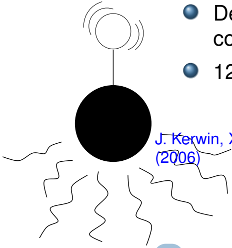
System-bath modeling: our strategy





System-bath modeling: our strategy





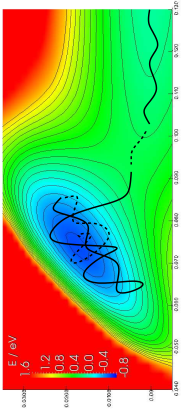
System

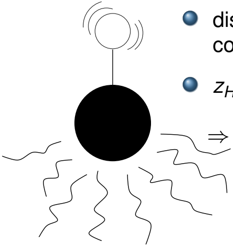
$$H_{sys} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq})$$

- Plane-wave DFT PW91
- Dense grid on x_H, y_H, z_H, z_C, for fixed coordinates of the remaining lattice atoms
- 12-parameter fit to LEPS functional form

J. Kerwin, X. Sha and B. Jackson, *J. Phys. Chem. B*, 18811 **110** (2006)

System-bath modeling: our strategy





Environment

H → C → lattice

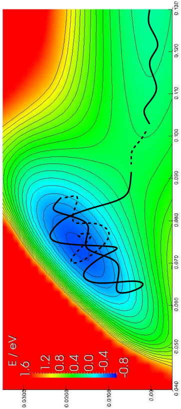
- dissipation mainly occurs at near-equilibrium configurations
- z_H couples only to z_C

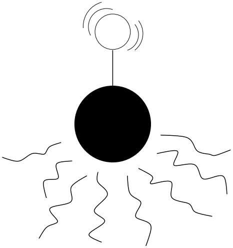
⇒ Canonical, classical dynamics: $\delta z^i_H(t)$

$$C_{zz}(t) = < \delta z(t)\delta z(0) >$$

$$(\ C_{vv}(t) = < \dot{z}(t)\dot{z}(0) >\ )$$

System-bath modeling: our strategy





Environment

$$\delta\tilde{z}^i_H(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t}\delta z^i_H(t)dt$$

$$\tilde{C}(\omega) = \frac{1}{N}\sum_{i=1}^{N} |\delta\tilde{z}^i_H(\omega)|^2$$

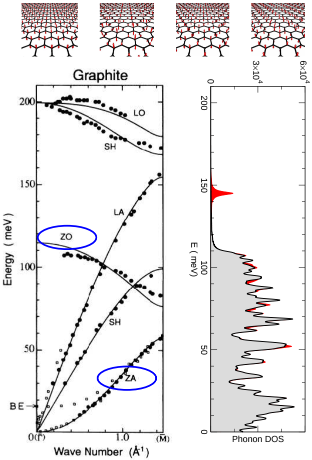
$$\sigma(\omega) = \tilde{C}(\omega)\omega/2$$

$$J_H(\omega) = k_B T \frac{\sigma(\omega)}{|S^+(\omega)|^2}$$

$$D_0^2 = \frac{2}{\pi}\int_0^{+\infty} J_H(\omega)\omega d\omega$$

$$J_C(\omega) = m_C \frac{D_0^2 J_H(\omega)}{|W^+(\omega)|^2}$$

Atomistic model for MD (i)



System

Same as above

Lattice

$$H_{latt} = \sum_i^N \frac{p_i^2}{2m_i} + V_{latt}(z_1, z_2, ...z_N)$$

- Lattice model of graphene containing stretching, bending, twisting modes
- ZA, ZO branches only

T. Aizawa *et al.*, *Phys. Rev. B*, 11469 **42** (1990)

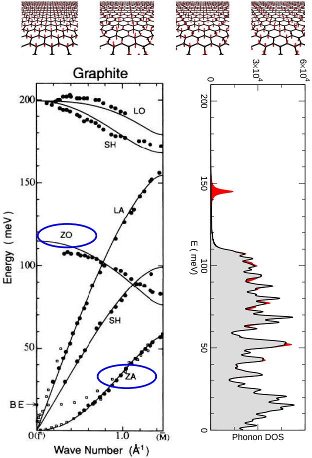
Coupling

$$V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq}) \Rightarrow$$

$$V(x_H, y_H, z_H - Q, z_C - Q, \boldsymbol{q}^{eq}) - \frac{k_C}{2}(z_C - Q)^2$$

$$Q = (z_1 + z_2 + z_3)/3$$

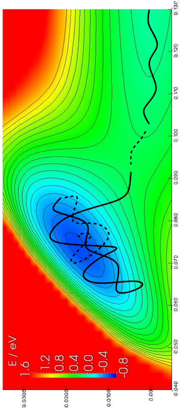
Atomistic model for MD (i)

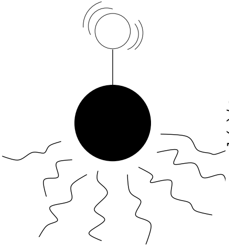


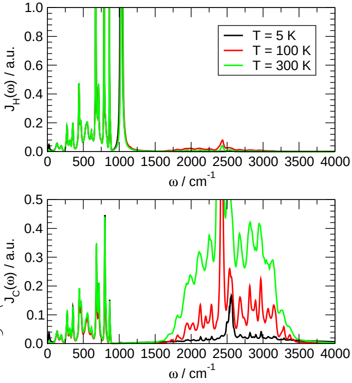
Canonical MD

- Finite slab with 120 carbon atoms
- Equilibration at different T
- 1000 trajectories with Langevin atoms at the slab edges
- $t_{fin} = 10$ ps

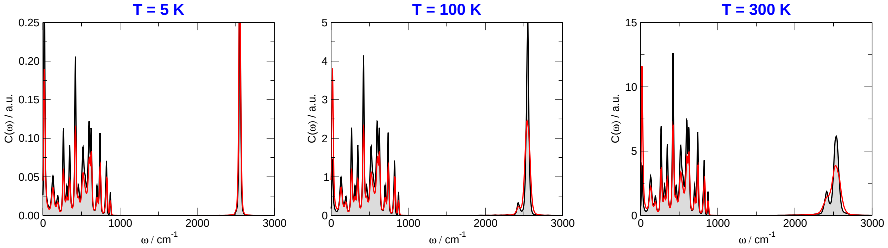
Environment from MD (i)





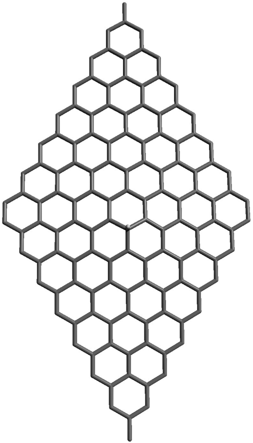


Environment from MD (i)



Lattice - IO Bath ($J_{5K}(\omega)$)

Environment from AIMD (ii)



Canonical *ab initio* MD

- 8×8 supercell (129 atoms)
- Atomic Orbital DFT PBE, Double-ζ *plus* Polarization
- Equilibration at several T (velocity rescaling)
- 128 trajectories in *NEV*
- $t_{fin} = 2.5$ ps

...in progress

Quantum dynamics with MCTDH ($T = 0$ K)

$$\Psi(x_1, x_2, .., x_N) = \sum_{i_1,i_2,\ldots i_N} c_{i_1,i_2,\ldots i_N}\, \phi^{(1)}_{i_1}(x_1)\phi^{(2)}_{i_2}(x_2)\ldots\phi^{(N)}_{i_N}(x_N)$$

- $c_{i_1,i_2,\ldots i_N} = c_{i_1,i_2,\ldots i_N}(t)$ are time-evolving amplitudes for the configurations
- $\phi^{(k)}_i(x) = \phi^{(k)}_i(x,t)$ are time-evolving single-particle functions
- $\langle\phi^{(k)}_i|\phi^{(k)}_j\rangle = \delta_{ij}$ for any $k = 1, ..N$

Equations of motion from DF variational principle

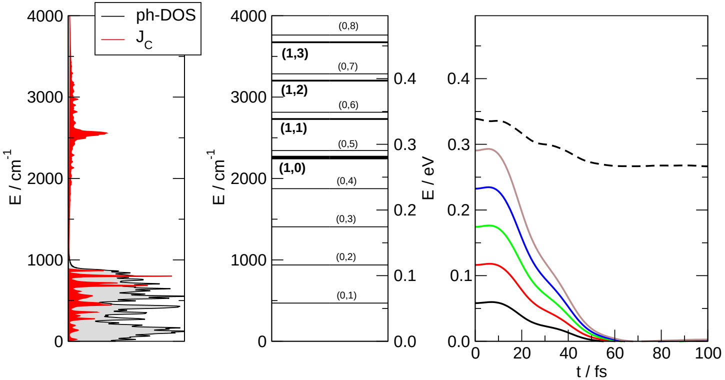
M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

Vibrational relaxation ($T_s = 0$ K)

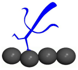
$$\Psi(\mathbf{x}_H, z_C, \mathbf{Q}_1, .., \mathbf{Q}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}}\, \psi_{i_s}(\mathbf{x}_H, z_C)\phi^{(1)}_{i_1}(\mathbf{Q}_1)\ldots\phi^{(N)}_{i_N}(\mathbf{Q}_N)$$

- Hermite-DVR for system's spfs $\psi_{i_1}(\mathbf{x}_H, z_C)$
- Mode combination & Hermite-DVR for bath spfs $\phi^{(k)}_{i}(\mathbf{Q}_k)$
- Product initial state, $\psi_\nu(\mathbf{x}_H, z_C)\ldots\phi_{\nu=0}(q_k)\ldots$
- Lanczos diagonalization to obtain the 4D eigenvalues and eigenfunctions

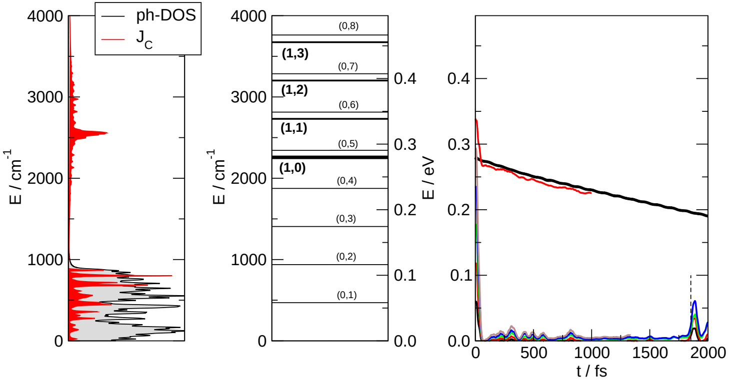
Vibrational relaxation



(ν_1, ν_2) for CH and surface-CH stretching



Vibrational relaxation



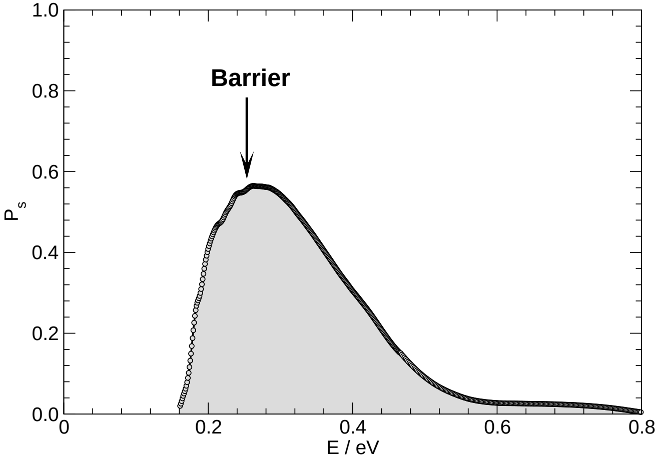
(ν_1, ν_2) for CH and surface-CH stretching

Sticking ($T_s = 0$ K)

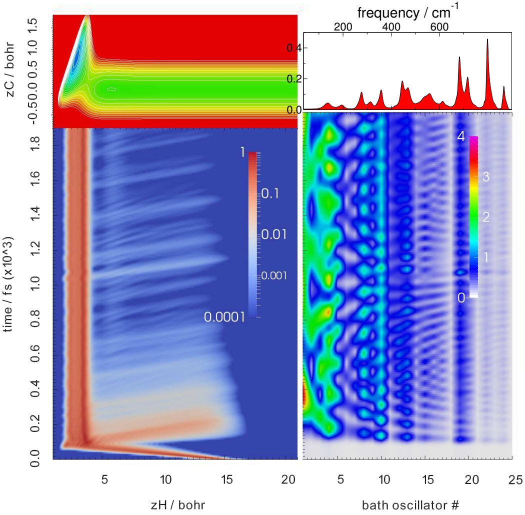
$$\Psi(\mathbf{x}_H, z_C, \mathbf{Q}_1, .., \mathbf{Q}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}} \, \psi_{i_s}(\mathbf{x}_H, z_C)\phi^{(1)}_{i_1}(\mathbf{Q}_1) \dots \phi^{(N)}_{i_N}(\mathbf{Q}_N)$$

- Fourier grid representation of system's spfs $\psi_{i_1}(\mathbf{x}_H, z_C)$
- Mode combination & Hermite-DVR for bath spfs $\phi^{(k)}_i(\mathbf{Q}_k)$
- Product initial state, $\psi_{scatt}(\mathbf{x}_H, z_C) \dots \phi_{\nu=0}(q_k) \dots$
- Time-energy mapping

Sticking (2D + bath)



Sticking (2D + bath)



Summary

- Midgap states modulate reactivity: dimers (cluster) which minimize sublattice imbalance form easily
- Substrates (even if not strongly binding) may affect chemical activity
- Eley-Rideal reaction out of chemisorbed species is reasonably efficient and dominates over dimer formation
- Sticking dynamics can be investigated at a full quantum level

Acknowledgements

Gian Franco Tantardini

Simone Casolo

Matteo Bonfanti

http://users.unimi.it/cdtg

Eckart Hasselbrink

Geert-Jan Kroes

Bret Jackson

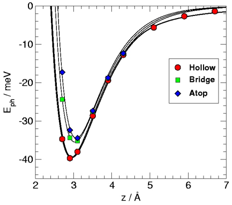
Keith Hughes

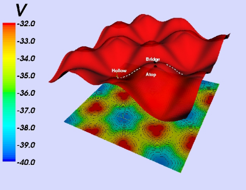
Irene Burghardt

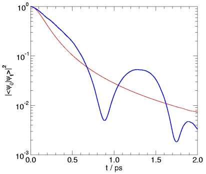
Acknowledgements

Thank you for your attention!

Physisorption







- HF-MP2 / aug-cc-pVDZ + BFs / CP-BSSE
- D_e = 39.5 meV *vs* D_e(exp)=39.2±0.5 meV
- E_{barr} = 4.0 meV, $D_{T=0K}$ = 1.7 10^{-4} cm^2s^{-1}

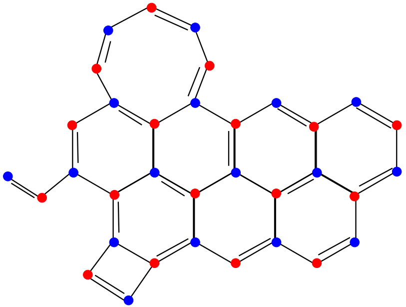
M. Bonfanti, R. Martinazzo, G.F. Tantardini and A. Ponti, *J. Phys. Chem. C*,**111**, 5825 (2007)

Exp: E. Ghio *et al.*, *J. Chem. Phys.*, **73**, 596 (1980)

*

Midgap states

$$H^{\pi} \approx \sum_{\sigma,ij}(t_{ij} a^{\dagger}_{i,\sigma} b_{j,\sigma} + t_{ji} b^{\dagger}_{j,\sigma} a_{i,\sigma})$$



Electron-hole symmetry

$$b_i \to -b_i \Longrightarrow H^{\pi}_e \to -H^{\pi}_e$$

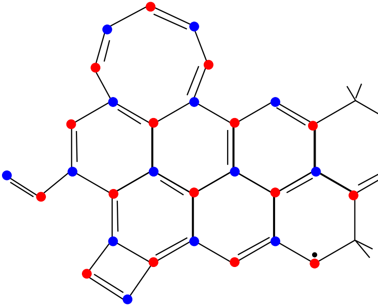
$$\epsilon_i, |\psi_i^{(+)}\rangle = \sum_k \alpha_k |a_k\rangle + \sum_j \beta_i |b_j\rangle$$

$$\Downarrow$$

$$-\epsilon_i, |\psi_i^{(-)}\rangle = \sum_k \alpha_k |a_k\rangle - \sum_j \beta_i |b_j\rangle$$

Midgap states

$$H^{\pi} \approx \sum_{\sigma,ij}(t_{ij} a^{\dagger}_{i,\sigma} b_{j,\sigma} + t_{ji} b^{\dagger}_{j,\sigma} a_{i,\sigma})$$



Imbalance rule

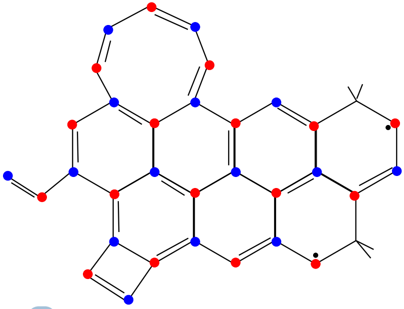
Let $n_A > n_B$, $\mathbf{T}(n_B x n_A)$

$$\begin{bmatrix} \mathbf{0} & \mathbf{T}^{\dagger} \\ \mathbf{T} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{\alpha} \\ \boldsymbol{\beta} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix}$$

$\Longrightarrow \mathbf{T}\boldsymbol{\alpha} = \mathbf{0}$ has $n_A - n_B$ solutions

Midgap states

$$H^{\pi} \approx \sum_{\sigma,ij}(t_{ij}a^{\dagger}_{i,\sigma}b_{j,\sigma} + t_{ji}b^{\dagger}_{j,\sigma}a_{i,\sigma}) + U\sum_i n_{i,\tau}n_{i,-\tau}$$



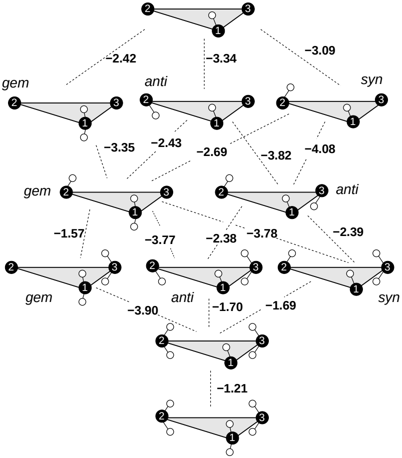
Spin alignment

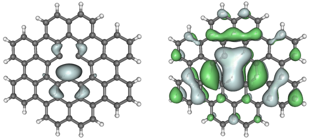
If $U > 0$, the ground-state at *half-filling* has

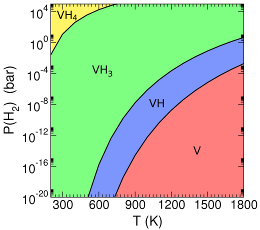
$$S = |n_A - n_B|/2 = n_I/2$$

E.H. Lieb, *Phys. Rev. Lett.* **62**, 1201 (1989)

Vacancy

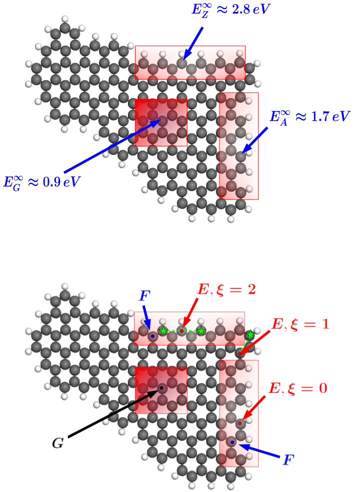




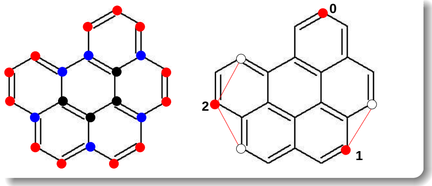


M. Casartelli *et al.*, *Phys. Rev. B*, **88** 195424 (2013)
M. Casartelli *et al.*, *Carbon*, **77** 165 (2014)

Edges



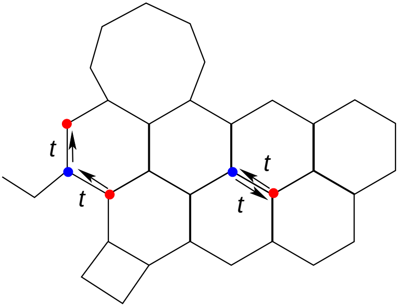
$Z = 2 \Rightarrow$ **E** $\quad Z = 3 \Rightarrow$ **F**,**G**



M. Bonfanti *et al.*, *J. Chem. Phys.*, **135** 164701 (2011)

Hints from the tight-binding Hamiltonian H^π

$$H^\pi \approx \sum_{\sigma,ij}(t_{ij} a^\dagger_{i,\sigma} b_{j,\sigma} + t_{ji} b^\dagger_{j,\sigma} a_{i,\sigma})$$



'Lattice renormalization'

$$\tilde{H}_{AA} = H_{AB} H_{BA}$$

$$\tilde{\epsilon}_i,\ |\psi_{A,i}\rangle$$

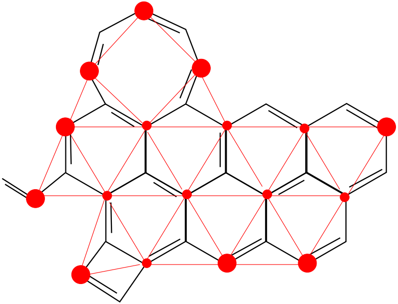
$$\Downarrow$$

$$\epsilon_i^{\pm} = \pm\sqrt{\tilde{\epsilon}_i},\ |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle$$

$$|\psi_{B,i}\rangle = \tilde{\epsilon}_i^{-1/2} H_{BA} |\psi_{A,i}\rangle$$

Hints from the tight-binding Hamiltonian H^π

$$\tilde{H}^\pi \approx \sum_i Z_i t^2 a_i^\dagger a_i + \sum_{ij} t^2 a_i^\dagger a_j$$



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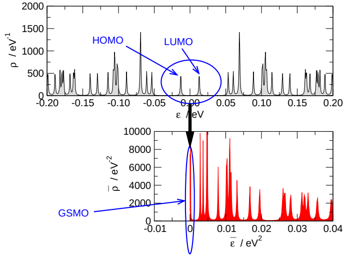

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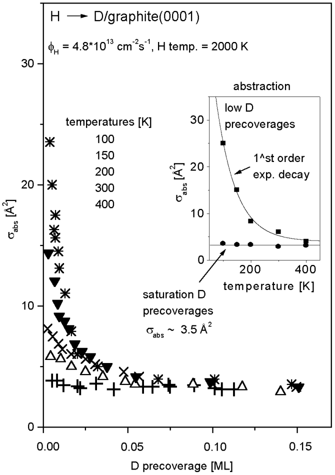
Zecho's kinetic experiments



System-bath

..choosing the system potential

$$V_s(s_1, s_2, ..s_N) = \text{Min}_{\xi_1,\xi_2,..\xi_F} V(s_1, s_2, ..s_N, \xi_1, \xi_2, ..\xi_F)$$

In our case,

$$\xi_i \equiv z_i,\ \ s_1 = x_H,\ s_2 = y_H,\ s_3 = z_H - Q,\ s_4 = z_C - Q$$

where $Q = \sum_i z_i$ and

$$V = V_{4D}(s_1, s_2, s_3, s_4) + V_{latt}(s_4 + Q, z_1, z_2, ..z_F) - V_{puck}(s_4)$$

$$\Downarrow$$

$$V_s(\boldsymbol{s}) \equiv V_{4D}(\boldsymbol{s}) - V_{puck}(s_4) + \text{Min}_{z_1,z_2,..z_F} V_{latt}(s_4 + Q, z_1, z_2, ..z_F)$$

if $V_{puck}(s) := \text{Min}_{z_1,z_2,..z_F} V_{latt}(s + Q, z_1, z_2, ..z_F) \approx \frac{k_C}{2} s^2$

$$V_s(\boldsymbol{s}) \equiv V_{4D}(\boldsymbol{s})$$

*