Quantum dynamics of hydrogen atoms on graphene

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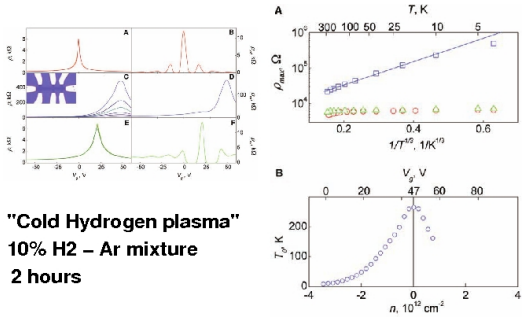
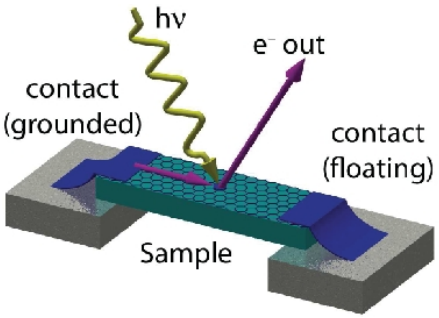
13th International Workshop on Quantum Reactive Scattering
Salamanca, July 6-10, 2015

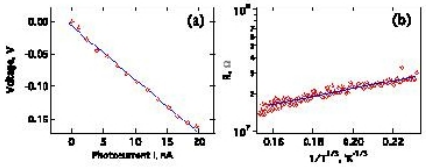
Technology: graphene physics and devices

Graphene is a true 2D-electron gas (2DEG) system with pseudo-relativistic charge-carriers

MIT occurs when hydrogenating graphene







UHV (p ~ 10^{-9} torr)
T(H_2) ~ 2000 C

..σ *vs* T agrees well with VRH in two dimensions

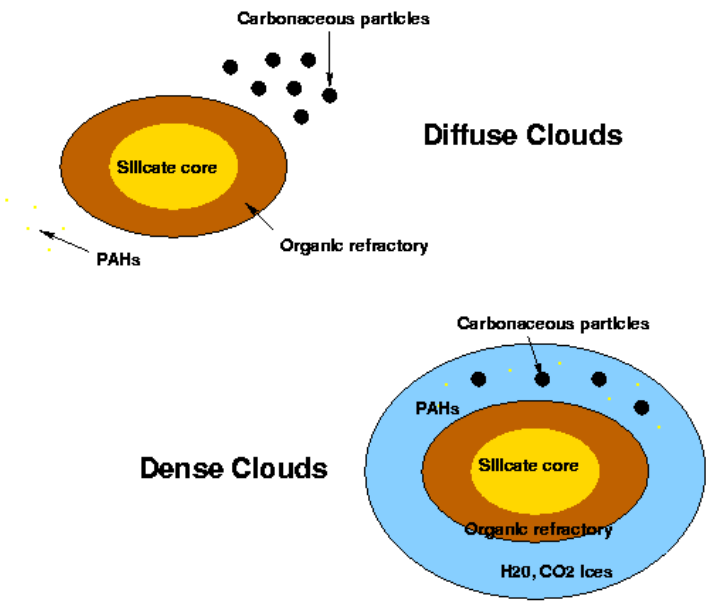
High n_H : D. C. Elias *et al.*, *Science* **323**, 610 (2009)

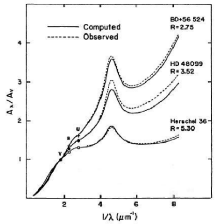
Low n_H : A. Bostwick *et al.*, *Phys. Rev. Lett.* **103**, 056404 (2009)

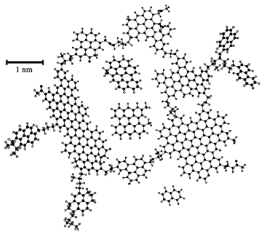
H_2 in the ISM

- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

$f_{grain}=n_{grain}/n_H \sim 10^{-12}$ i.e. ~1% of ISM mass

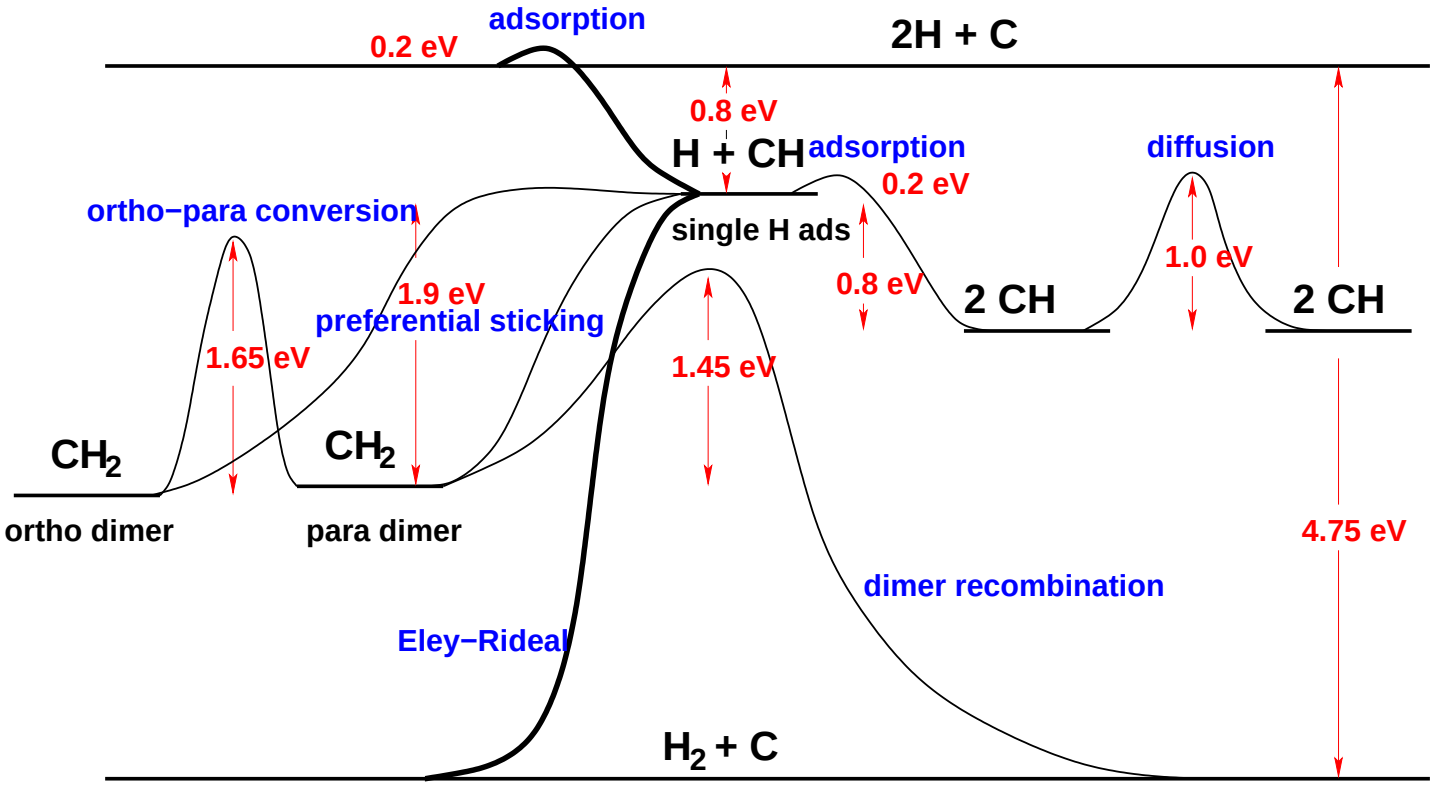






Hydrogen-graphite is an important model for understanding H_2 formation in ISM

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

Outline

Outline

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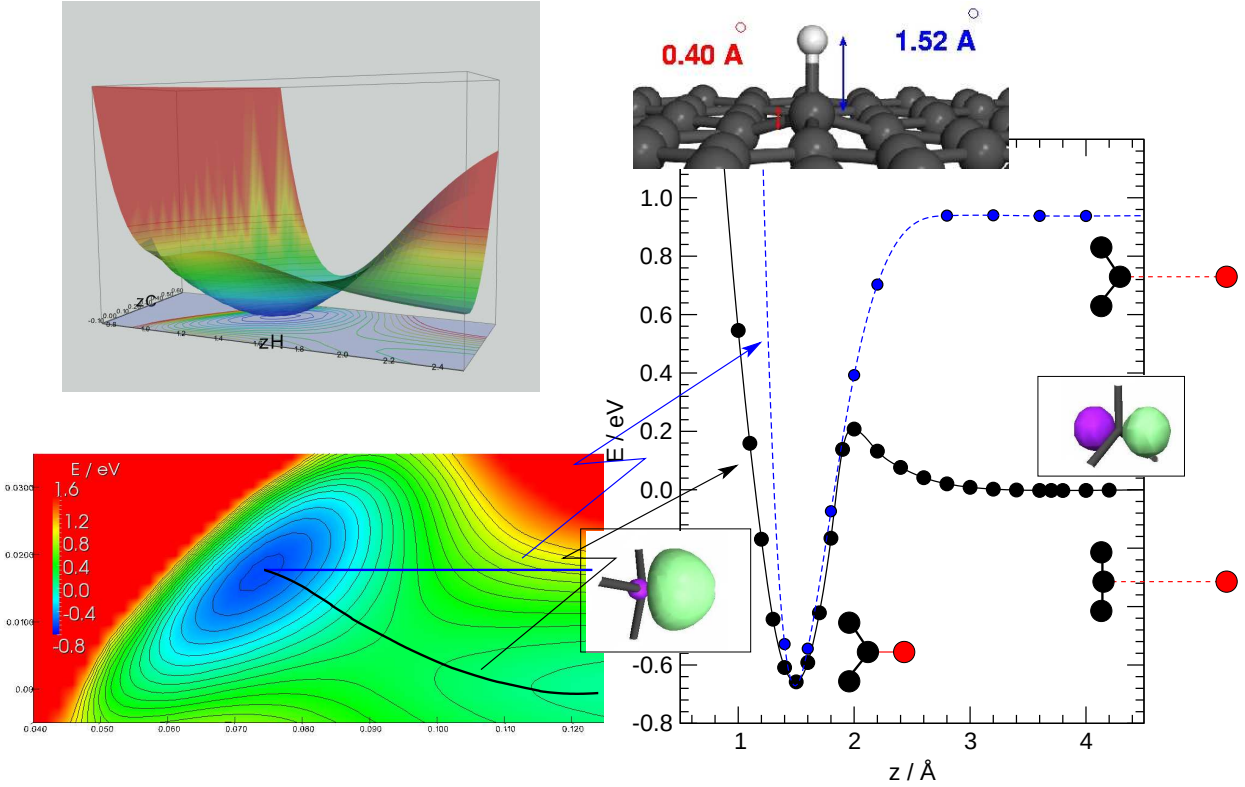
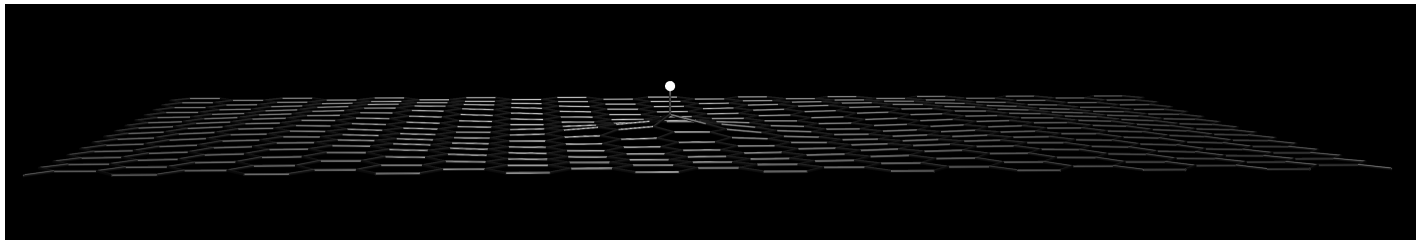
Chemisorption of a H atom



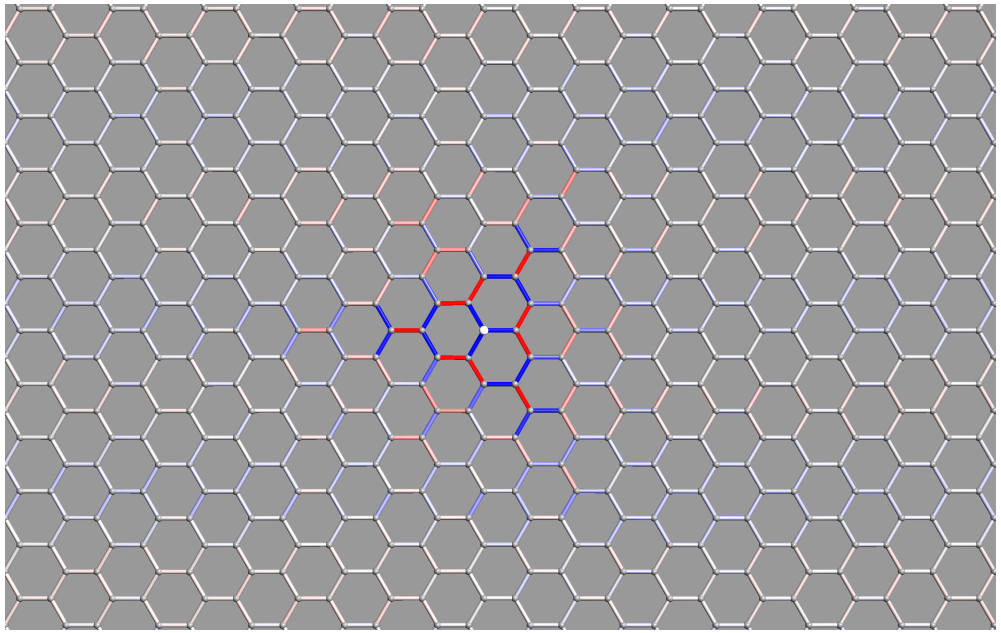
L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

phys

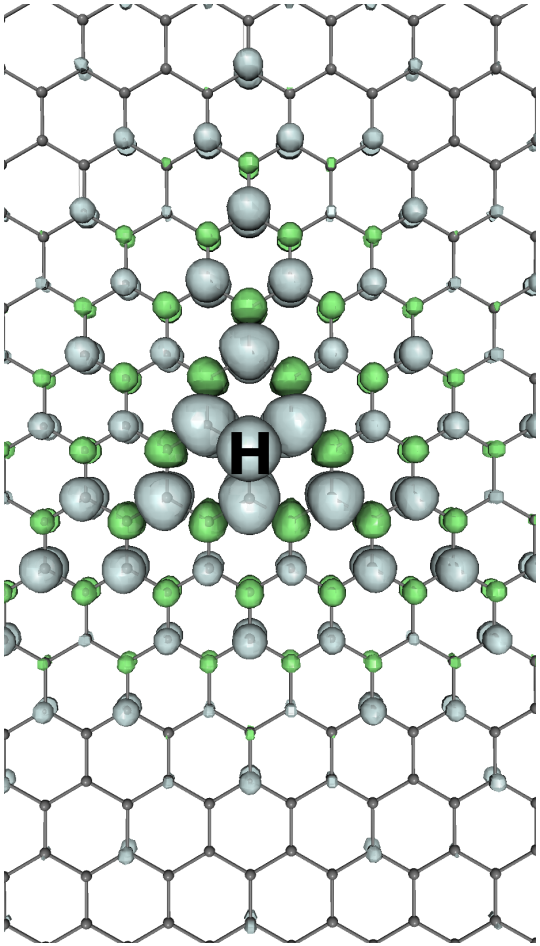
Chemisorption of a H atom

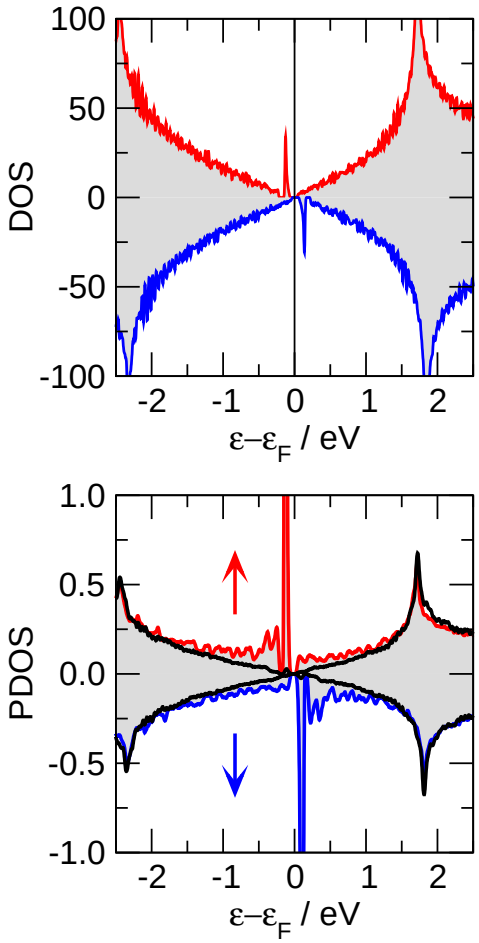


0.5% shorter - d^0_{CC} - 0.5% longer



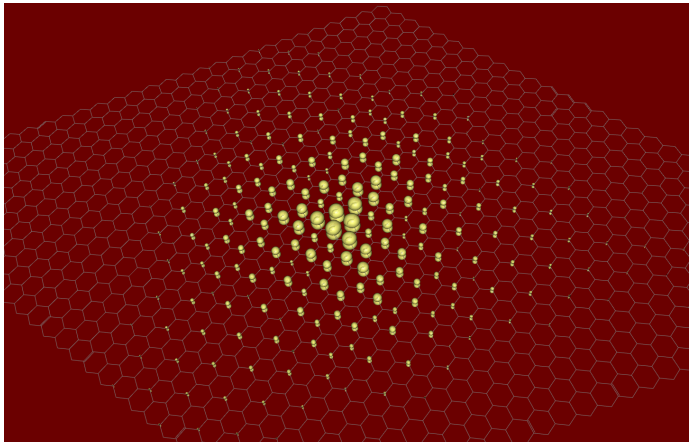
Midgap states

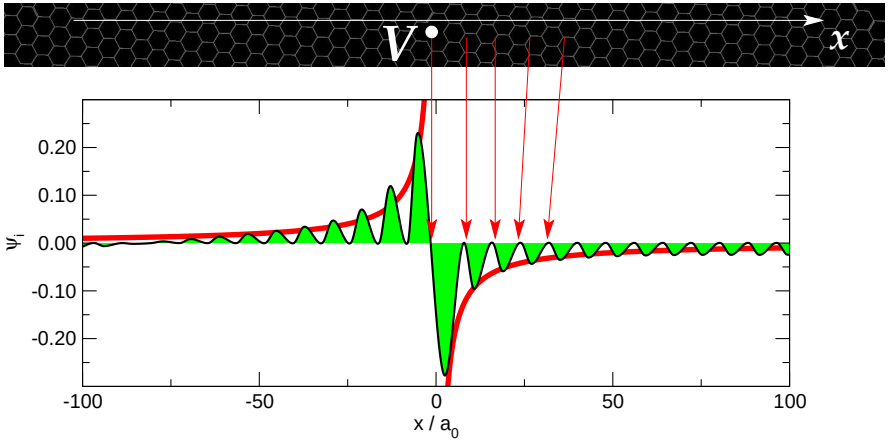


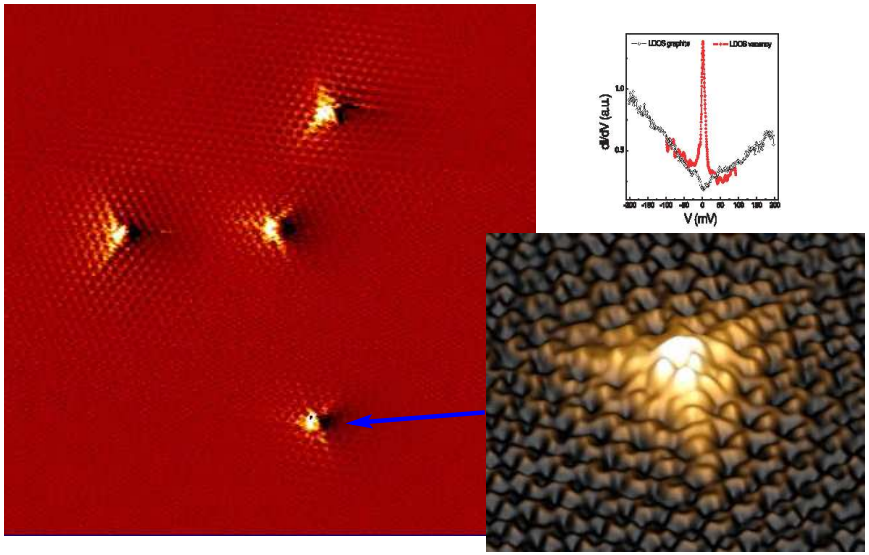


mgap

Midgap states: p_z vacancies







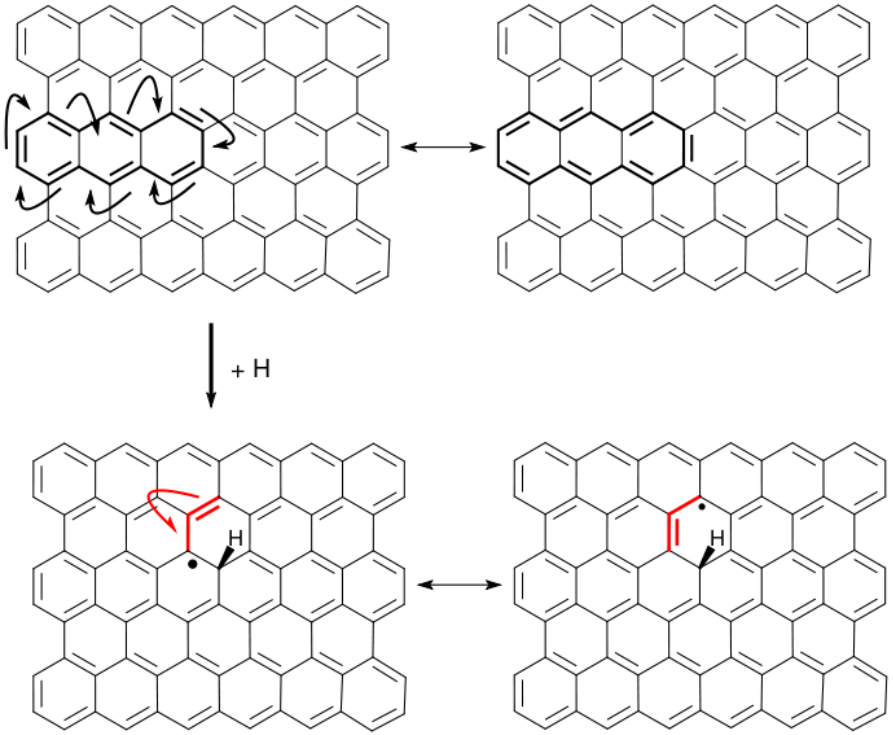
M.M. Ugeda *et al.*, *Phys. Rev. Lett.* **104**, 096804 (2010)

Sublattice imbalance + pseduorelativisic massless behavior

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

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

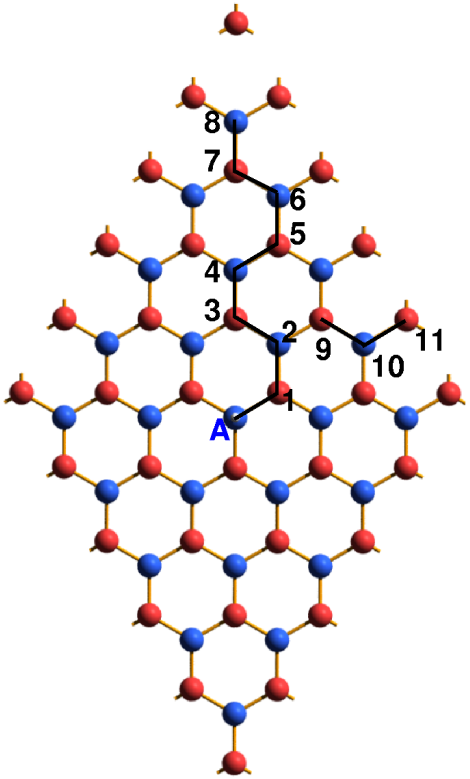
Midgap states: p_z vacancies



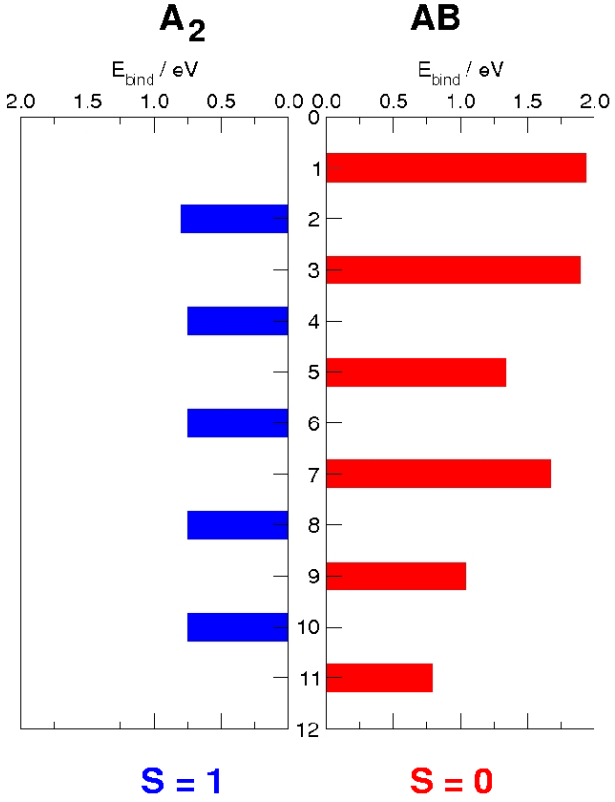
Resonating Valence Bond

- **Charge 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

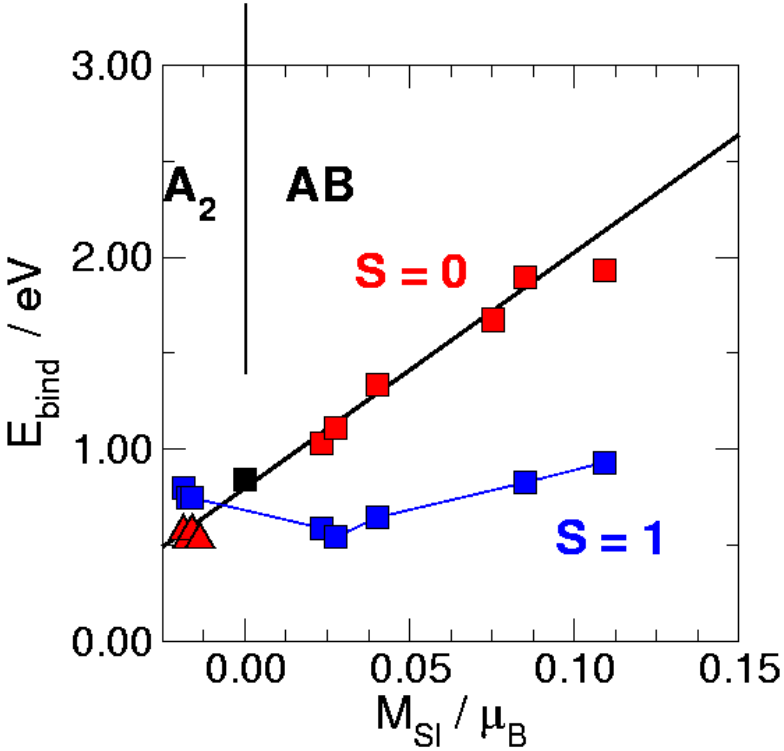
Dimers

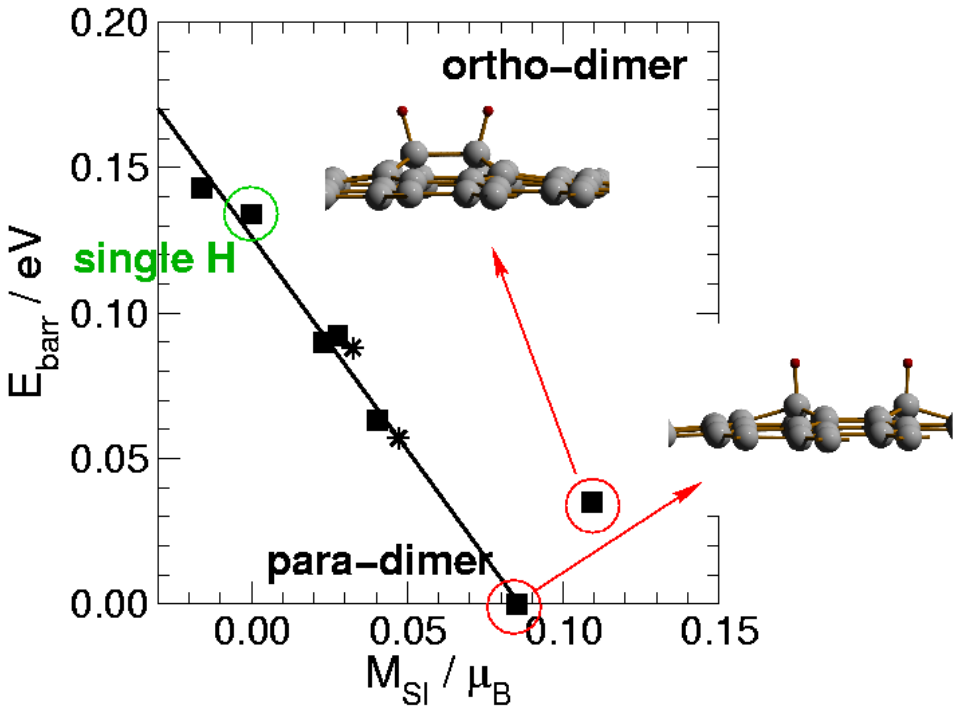


Majority sublattice
Minority sublattice



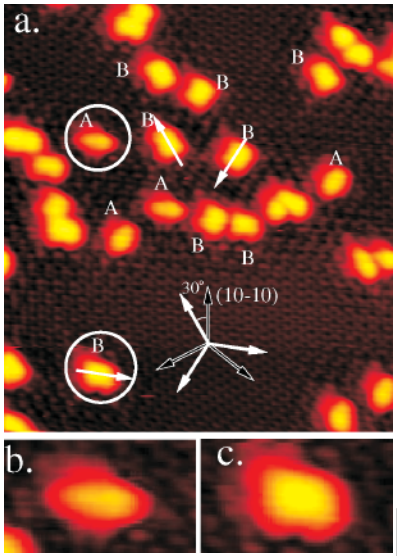
Dimers



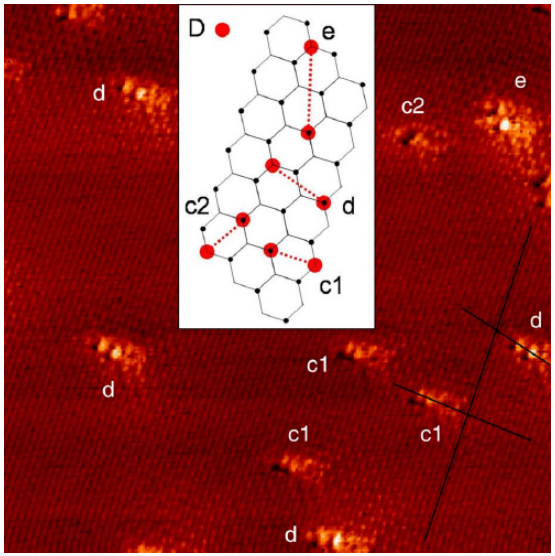


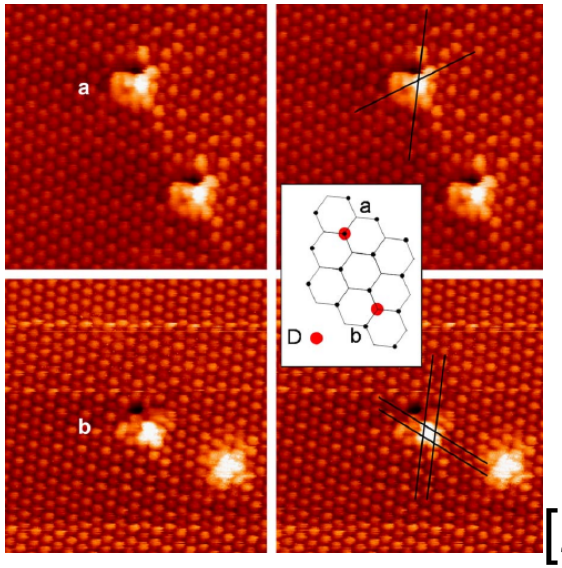
S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)
Preferential sticking: L. Hornekaer *et al.*, *Phys. Rev. Lett.* **96** 156104 (2006)

Dimers



[1]



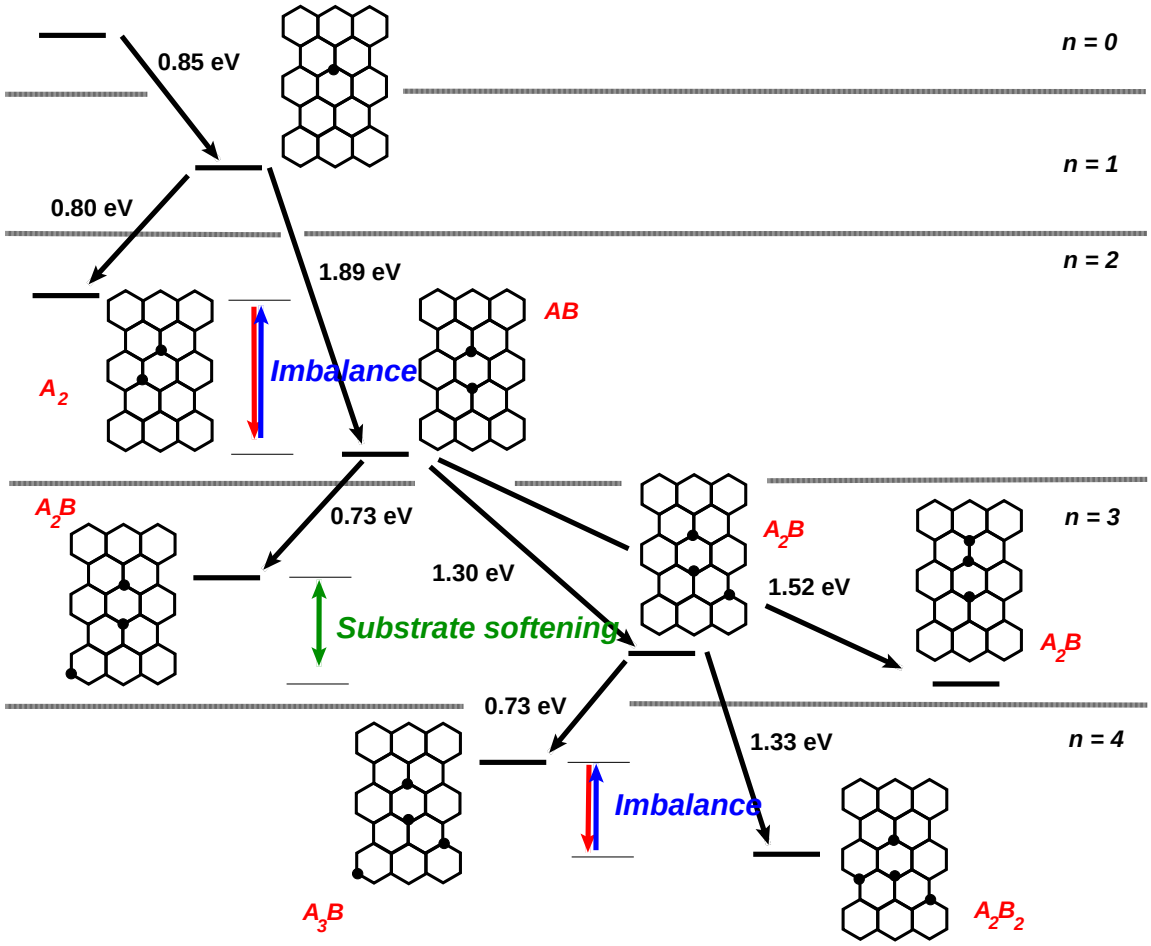


[2]

[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

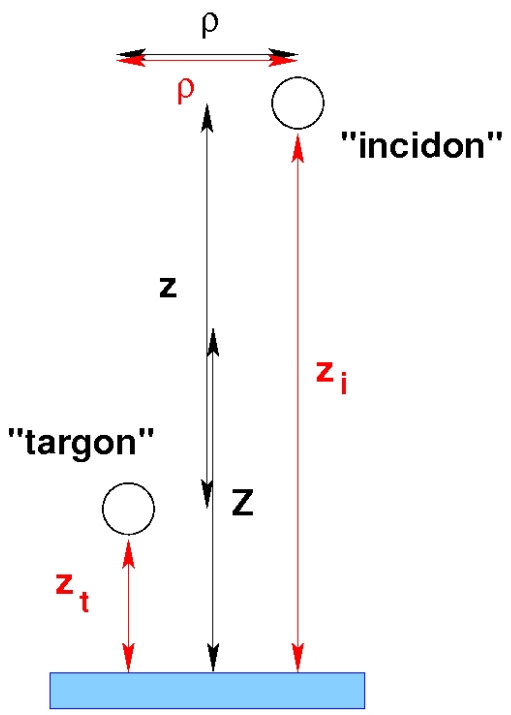

n = 0
n = 1
n = 2
n = 3
n = 4
0.85 eV
0.80 eV
1.89 eV
AB
A2
Imbalance
A2B
0.73 eV
1.30 eV
Substrate softening
A2B
1.52 eV
A2B
0.73 eV
1.33 eV
Imbalance
A3B
A2B2

Outline

ER Reaction: technicalities

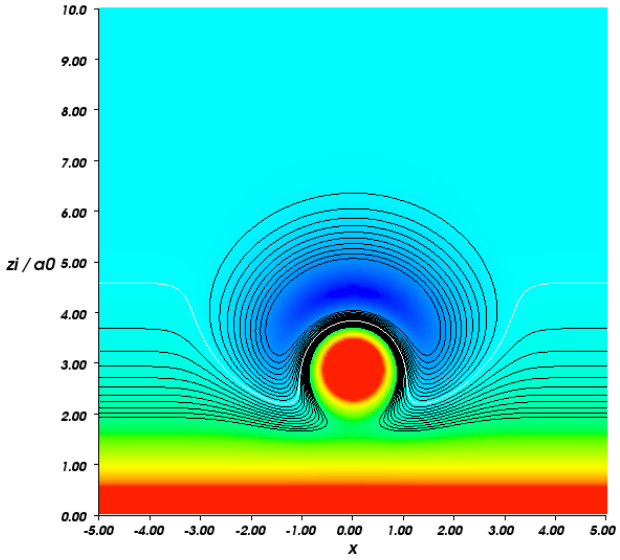
- Rigid, flat surface approximation[1]
- Split-Operator with FFT along cartesian coordinates and DBT along ρ [1]
- propagation in both product and reagent coordinate sets[2]
- DFT PES fitted to modified LEPS[3]

$\Rightarrow$ state-to-state, energy-resolved cross sections for all possible processes

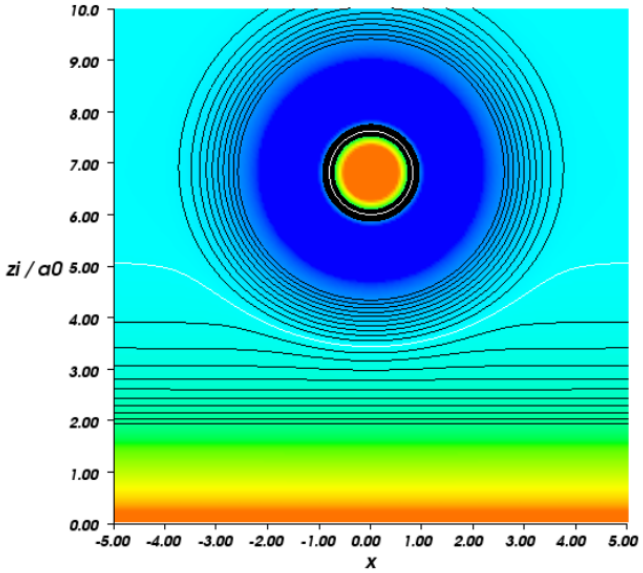


[1] M. Persson and B. Jackson, J. Chem. Phys. 102, 1078 (1995); D. Lemoine and B. Jackson, Comput. Phys. Commun. 137, 415 (2001)
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)
[3] X. Sha, B. Jackson and D.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

ER Reaction: Potential Energy Surfaces



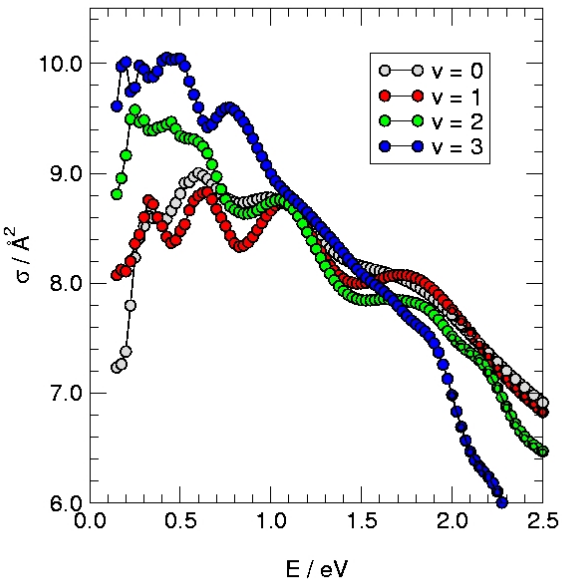
Chemisorbed target H (z_{eq})

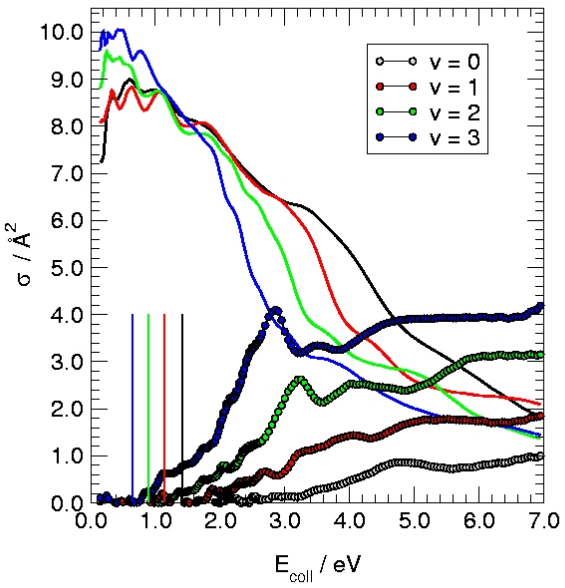


Physisorbed target H (z_{eq})

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

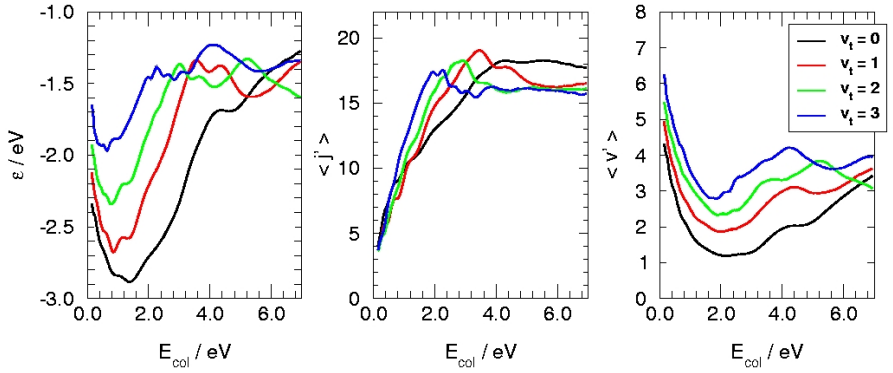
$$H_{chem}(\nu) + H \rightarrow H_2$$
$$\rightarrow H + H$$

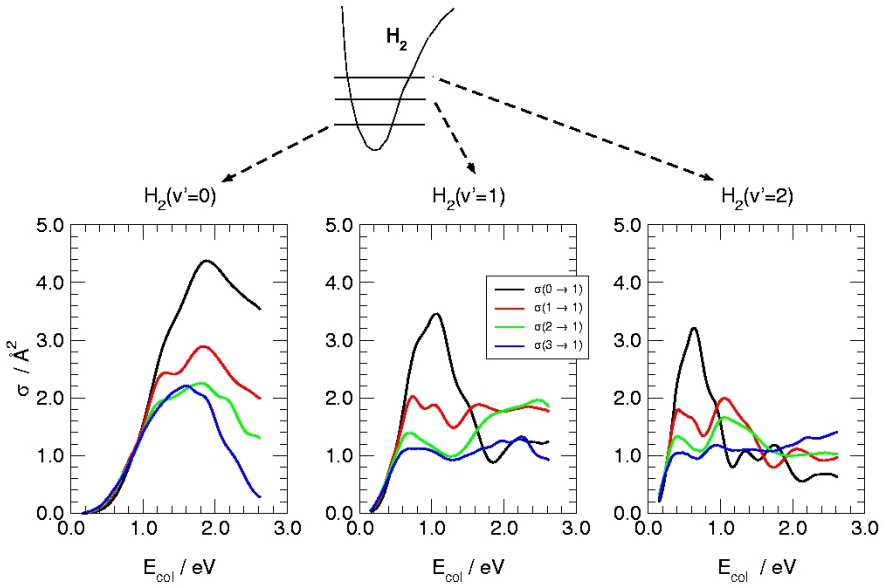




Oscillations in both ER and CID xsections

$H_{chem}(\nu) + H \rightarrow H_2(\nu')$





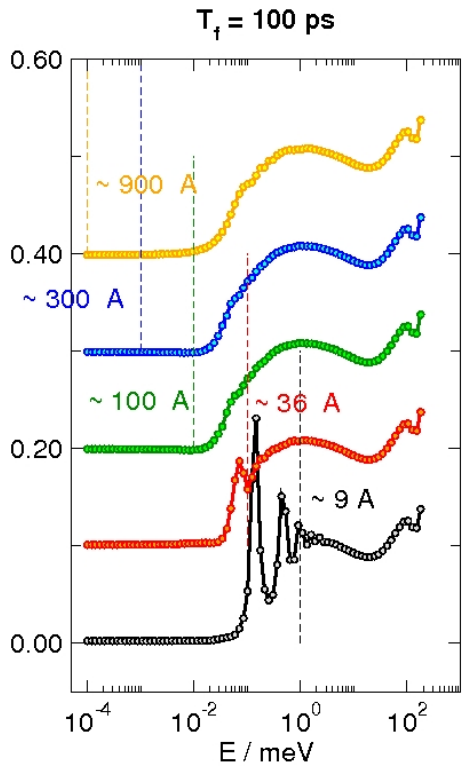
- Product molecules are internally hot
- Internal excitation is a steep decreasing function of E_{coll}

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

ER Reaction: technicalities (low E_{col})

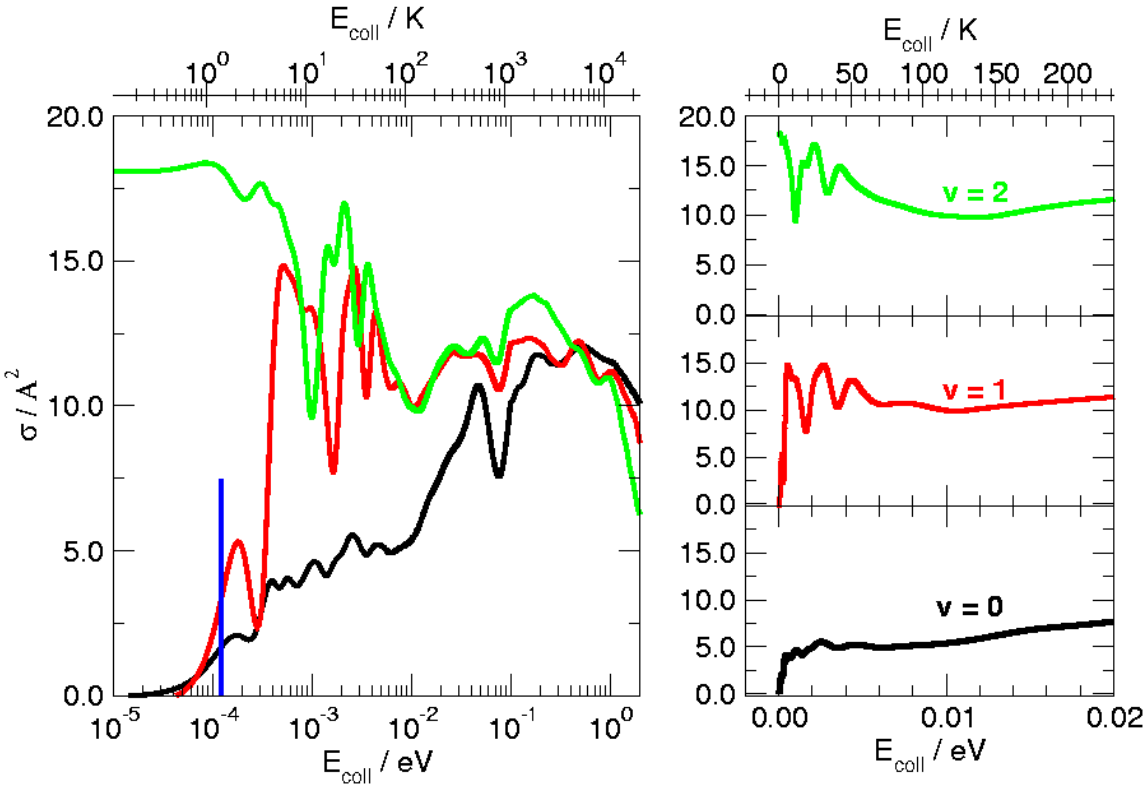
- Two-wavepacket approach[1]
- Transmission-free[2] absorbing potentials and Fourier mapping[3] in reagent coordinates

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



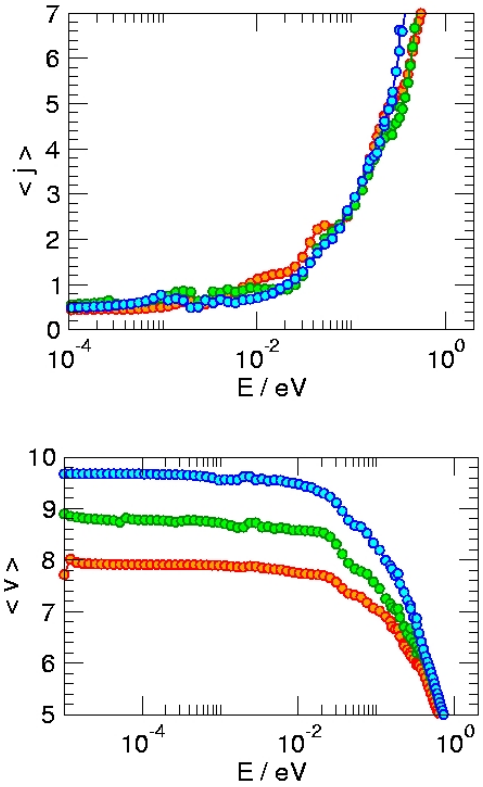
[1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)
[2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)
[3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)

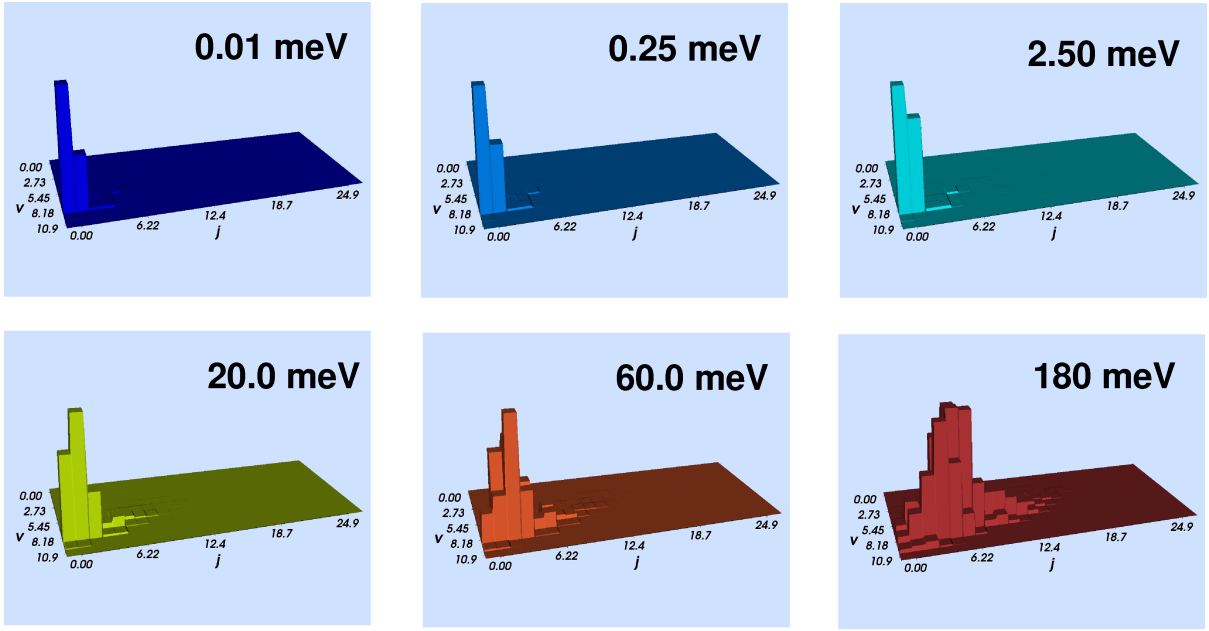
$H_{chem}(\nu) + H \rightarrow H_2$



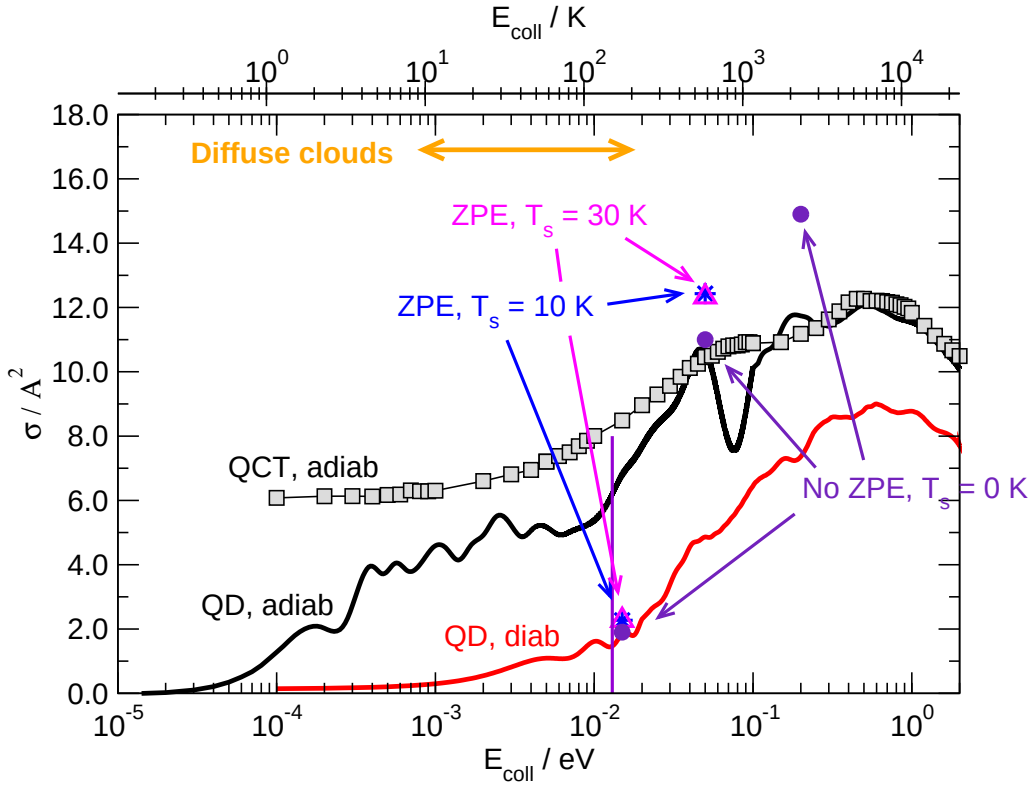
S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

$H_{chem}(\nu) + H \rightarrow H_2(\nu', j')$





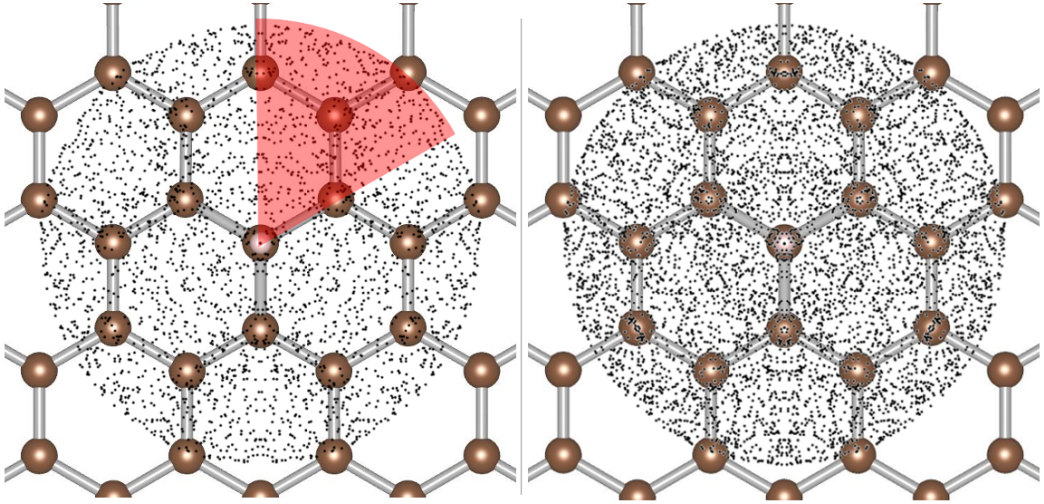
$H_{chem}(\nu = 0) + H \rightarrow H_2$



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

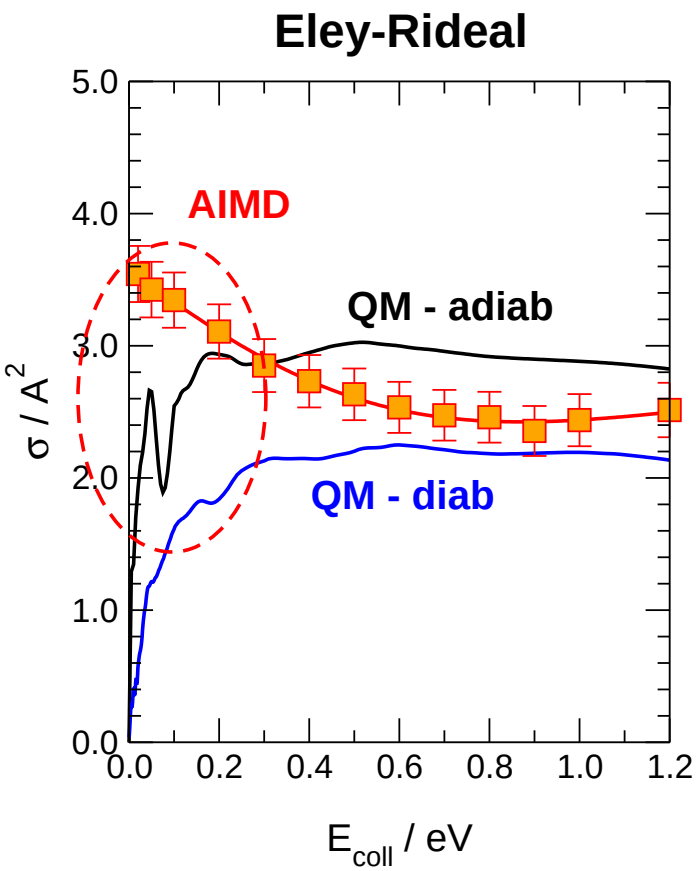
Ab initio molecular dynamics

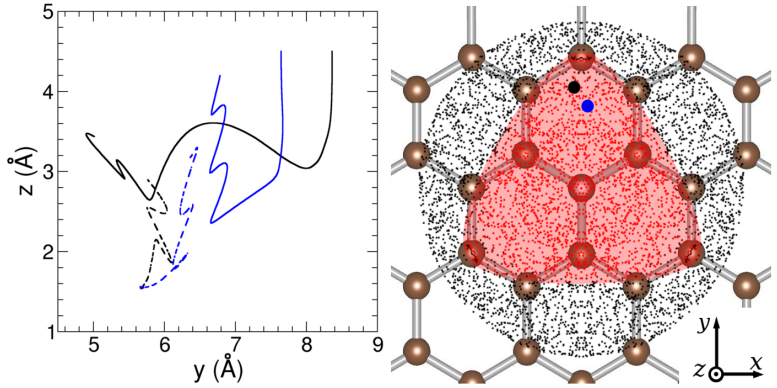
- lattice corrugation
- lattice dynamics
- dimer formation



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

Ab initio molecular dynamics

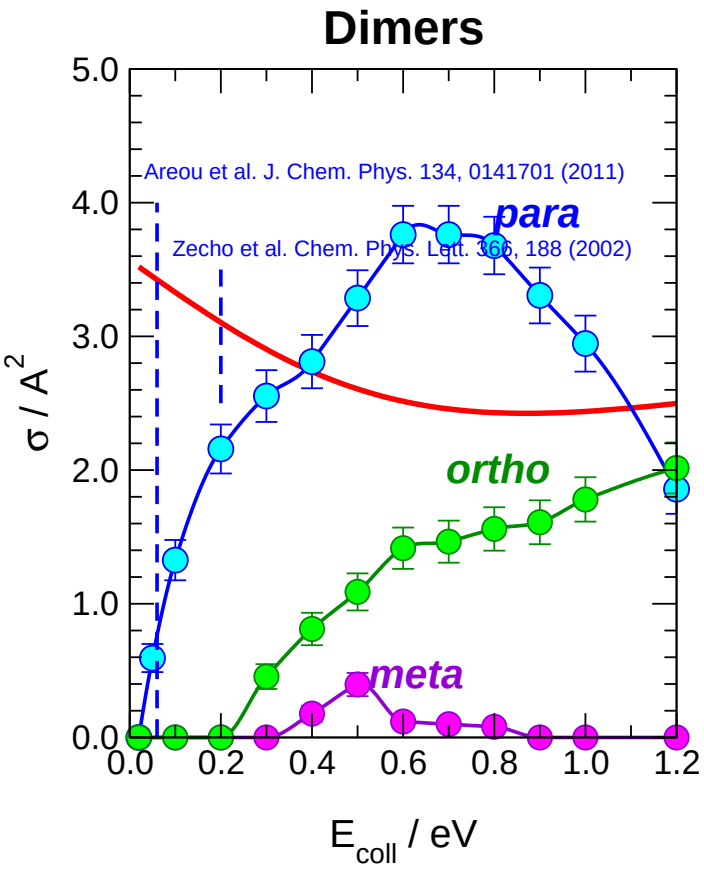




- Scattering off *para* sites increases the reaction xsection at low energies
- diabatiC < AIMD < adiabatiC at higher energies

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

Ab initio molecular dynamics



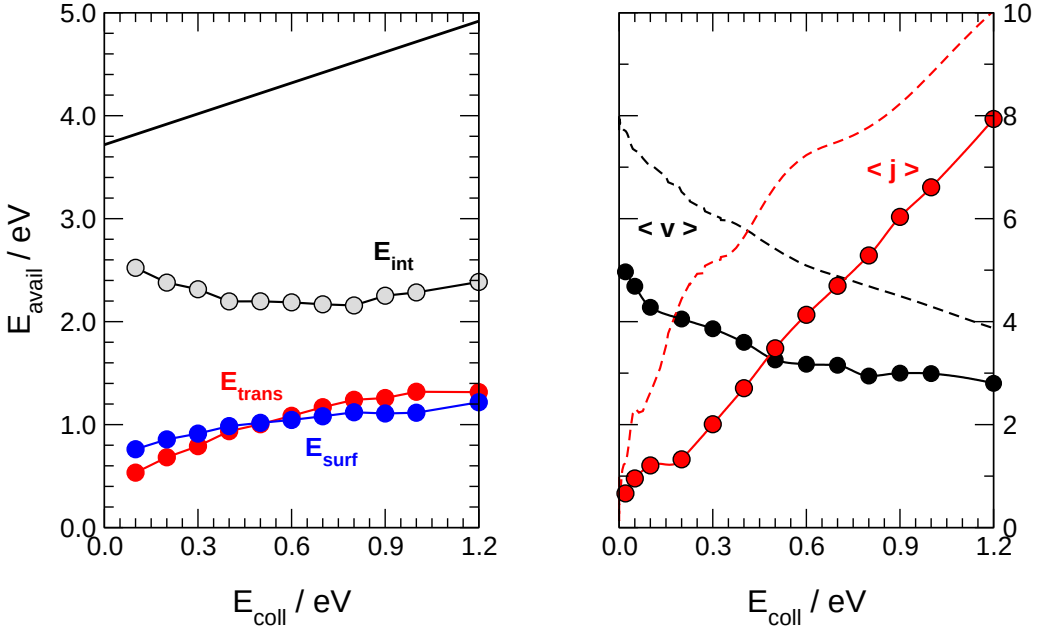
- Competition between reaction and *para*-dimer formation
- Dynamic threshold to *ortho*-dimer formation

..experiments with low energy H atom beams on a pre-covered (low coverage) surface find abstraction only

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

Zexp

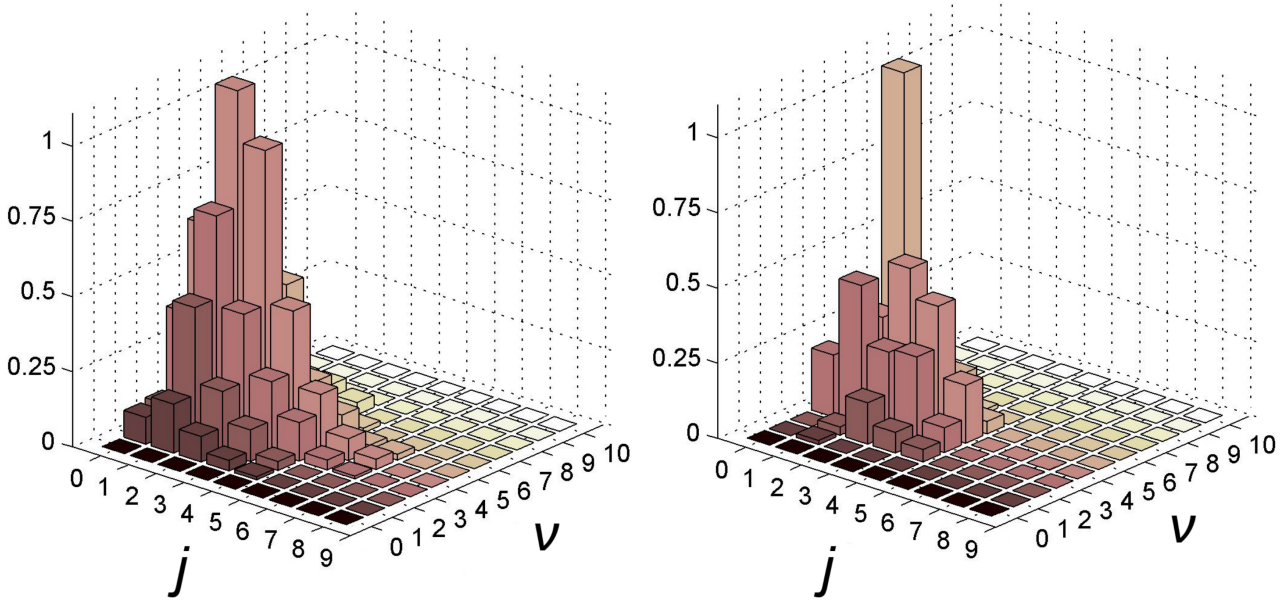
Ab initio molecular dynamics



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

E_{surf} compares well with $\sim$ 0.8 eV of the substrate diabatic picture

Ab initio molecular dynamics



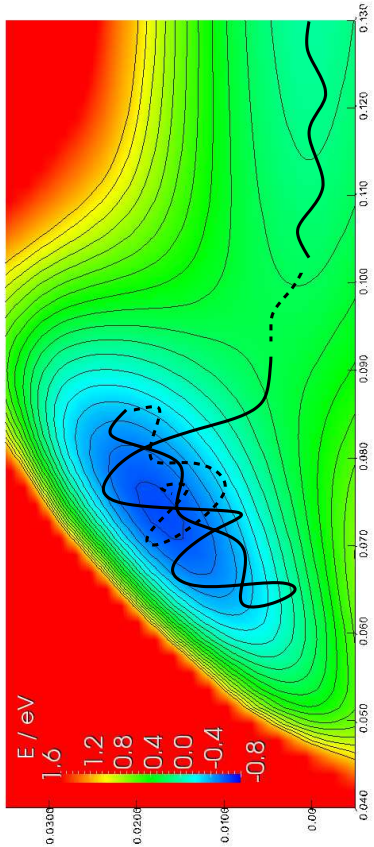
$T_g = 300K$, $T_s = 15K$

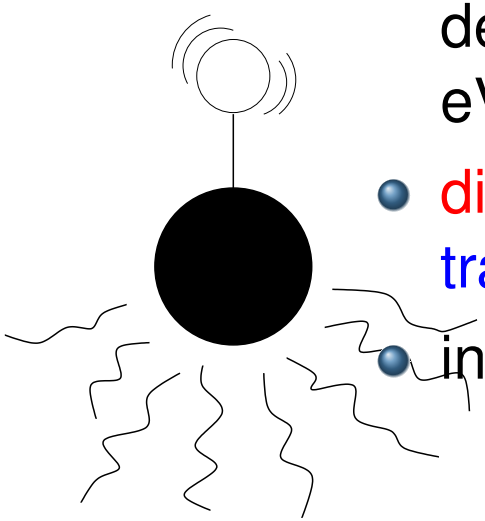
Latimer et al. Chem. Phys. Lett. 455, 174 (2008)

AIMD for H/D @ 0.025 eV

Outline

H sticking dynamics on graphene

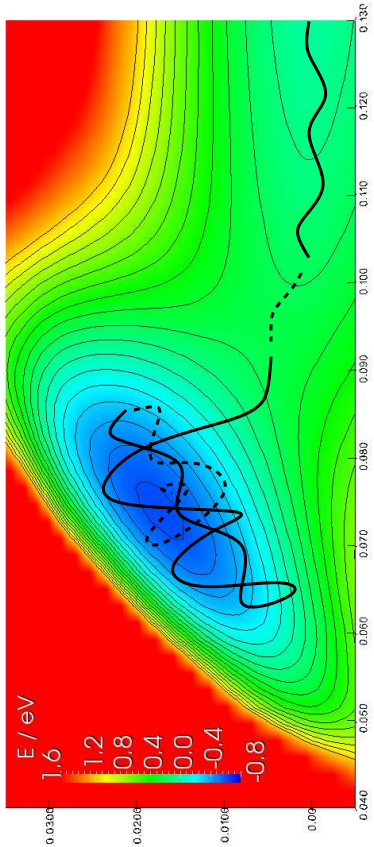


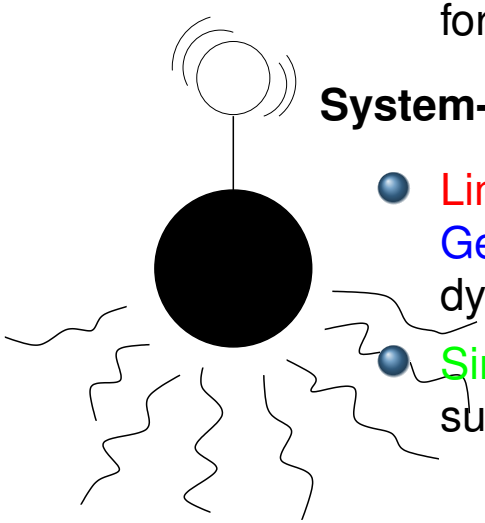


Challenging problem..

- 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





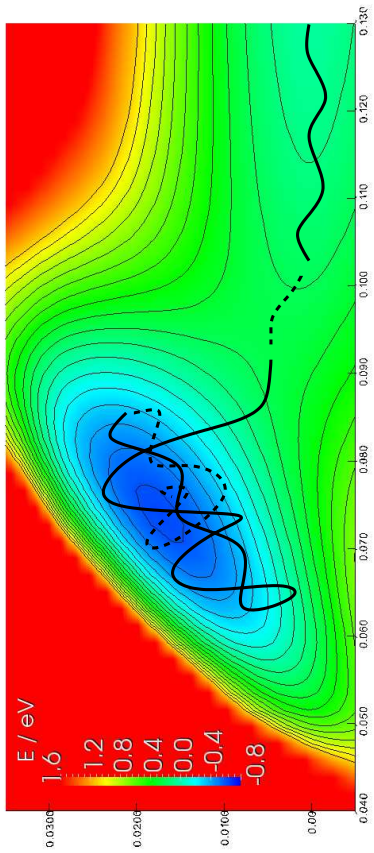
Fully atomistic models

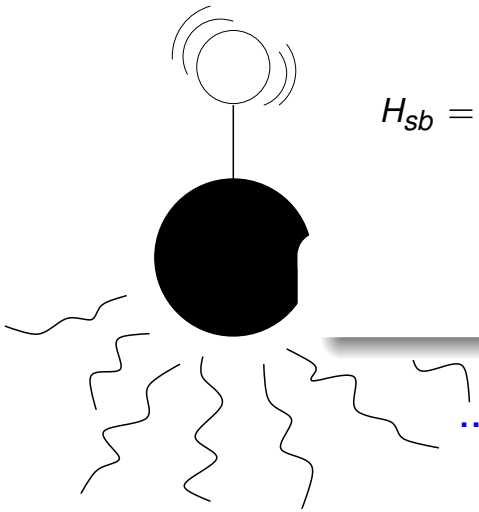
- Accurate representation of adsorbate-lattice interactions and of lattice dynamics
- Complicated form of the potential, inadequate for Quantum Dynamics

System-bath models

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

System-bath modeling





Lattice

$$H_{latt} = \frac{p_s^2}{2m_s} + V(s, \boldsymbol{q}) + \sum_i \frac{p_i^2}{2m_i}$$

vs.

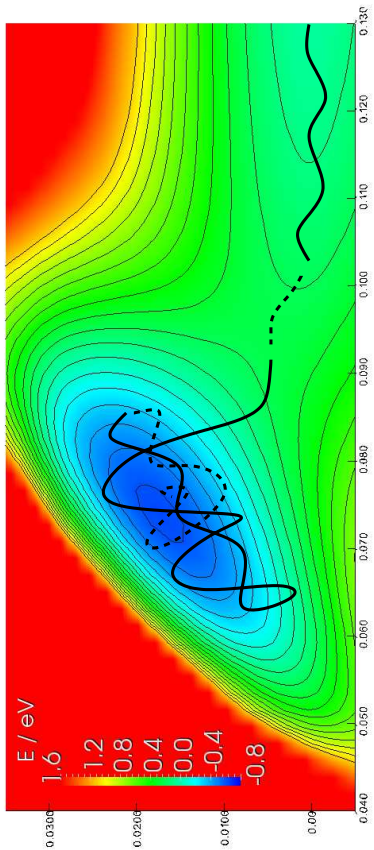
System-bath

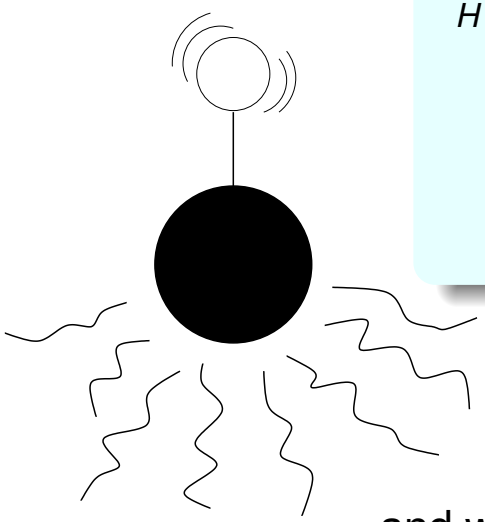
$$H_{sb} = \frac{p_s^2}{2m_s} + \tilde{V}(s) + \sum_k \left[\frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(q_k - \frac{c_k}{\omega_k^2} f(s) \right)^2 \right]$$

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

..our Brownian particle should be 'CH'
$\Rightarrow$ multidimensional GLE
$\Rightarrow$ spectral density matrix

System-bath modeling: our strategy





Simplifying assumption

H → C → lattice

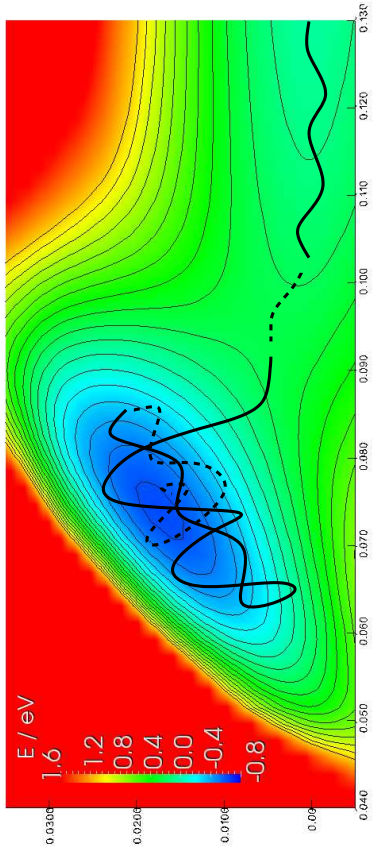
$$H = \frac{\mathbf{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V_s(\mathbf{x}_H, z_C) + \sum_{k=1}^{F}\left[\frac{p_k^2}{2} + \frac{\omega_k^2}{2}\left(q_k - \frac{c_k}{\omega_k^2}(z_C - z_C^{eq})\right)^2\right]$$

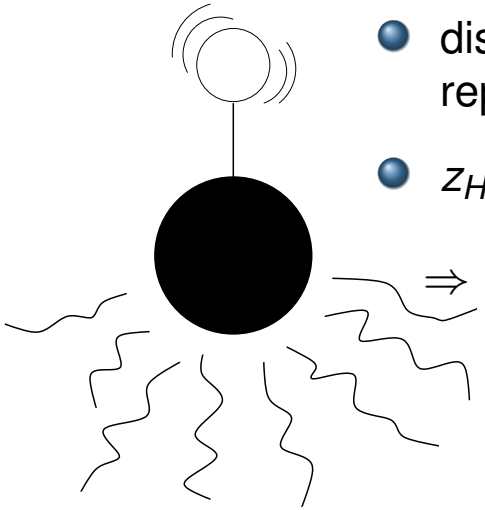
..only z_C couples to the lattice,

$$V_s(\mathbf{x}_H, z_C) = \underset{\{\mathbf{Q}\}}{\mathrm{Min}}\, V_{tot}(\mathbf{x}_H, z_C, \mathbf{Q})$$

..and we need the environmental coupling $J_C(\omega)$

System-bath modeling: our strategy





Environmental coupling from MD

H → C → lattice

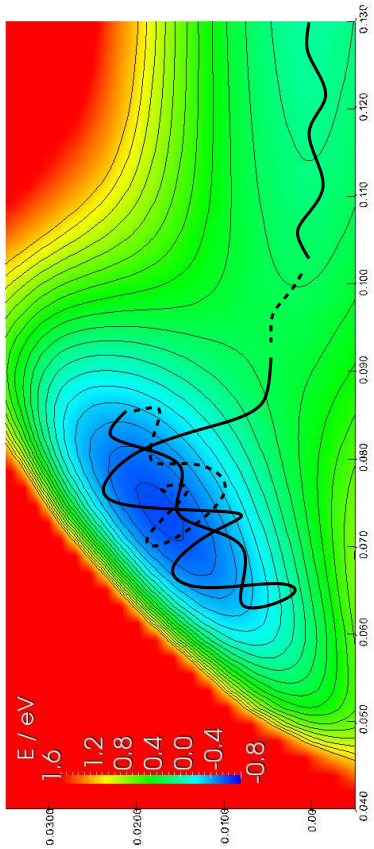
- dissipation near-equilibrium configurations is representative of the coupling
- z_H couples only to z_C

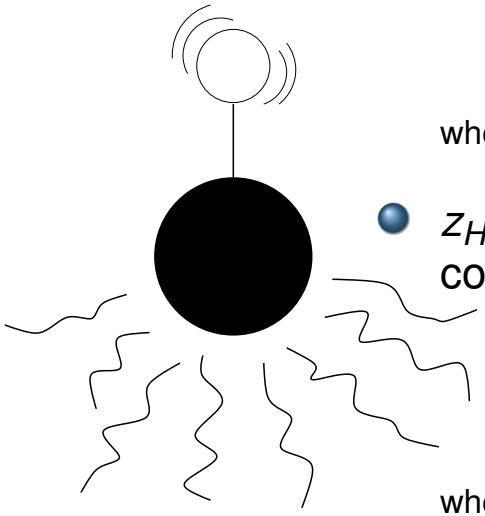
$\Rightarrow$ Equilibrium classical dynamics: $\delta z_H^i(t)$

$$C_H(t) =< \delta z_H(t) \delta z_H(0) >$$

$$(\; C_H^v(t) =< \dot{z}_H(t) \dot{z}_H(0) > \;)$$

System-bath modeling: our strategy





Environmental coupling from MD

$$C_H(t) \rightarrow J_H(\omega) \rightarrow J_C(\omega)$$

- z_H undergoes Harmonic Brownian motion[1]

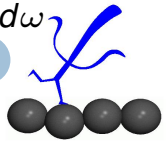
$$J_H(\omega) = k_B T \frac{\omega \tilde{C}_H(\omega)}{|\Gamma^+(\omega)|^2}$$

where $\Gamma(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\omega \tilde{C}_H(\omega)/2}{\omega - z} d\omega$

- z_H couples bilinearly to z_C only which in turn couples to the bath[2]

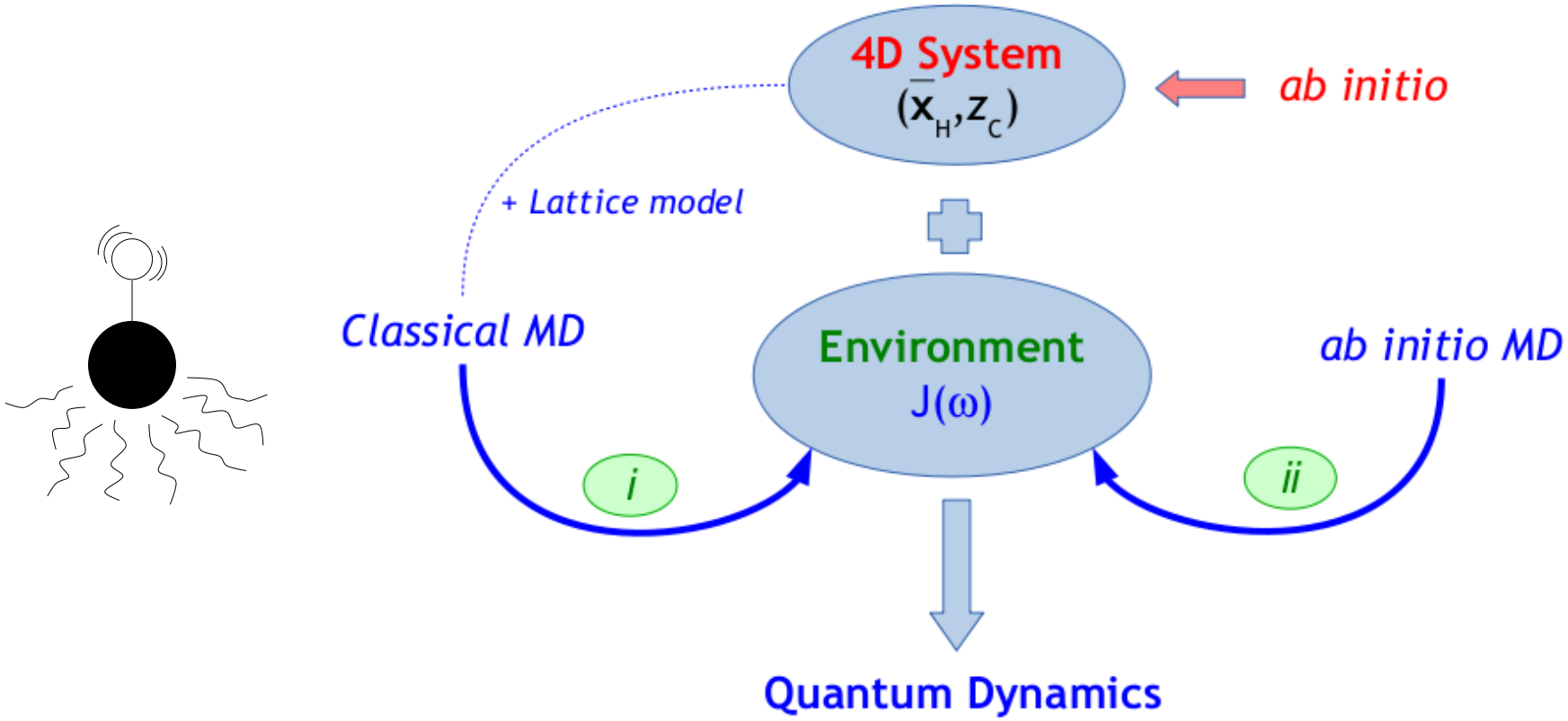
$$J_C(\omega) = m_C \frac{D_0^2 J_H(\omega)}{|W_H^+(\omega)|^2}$$

where
$W_H(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J_H(\omega)}{\omega - z} d\omega$, $D_0^2 = \frac{2}{\pi} \int_0^{+\infty} J_H(\omega) \omega d\omega$

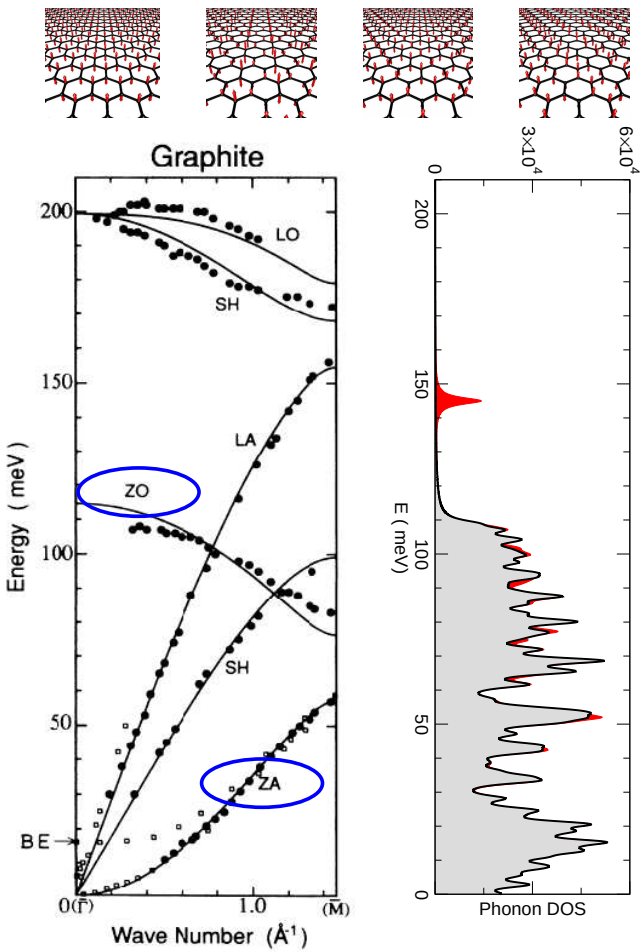


[1] See *e.g.* M. Bonfanti *et al.*, *Ann. Phys.*, in press
[2] R. Martinazzo *et al.*, *J. Chem. Phys.* **134** 011101 (2011)

System-bath modeling: our strategy



Atomistic model for MD[1] (i)



CH system

Plane-wave DFT PW91 on a dense $\boldsymbol{x}_H, z_C$ grid[2]

Lattice

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

Lattice model of graphene[3] containing stretching, bending, twisting modes, restricted to ZA, ZO branches only

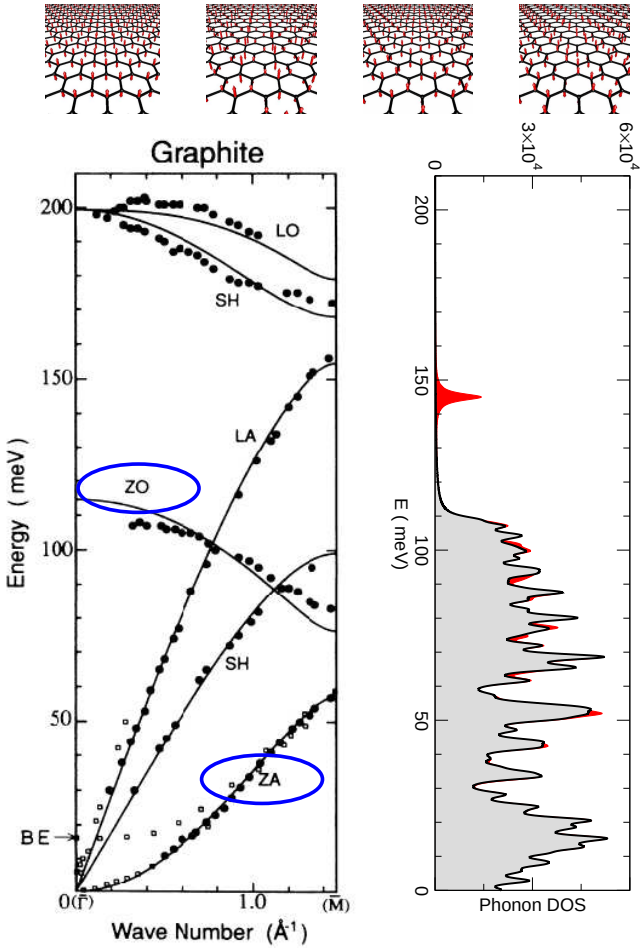
SO-like Coupling

$$V_{CH}(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq}) \Rightarrow$$
$$V_{CH}(x_H, y_H, z_H - Q, z_C - Q, \boldsymbol{q}^{eq}) - \frac{k_C}{2}(z_C - Q)^2$$

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

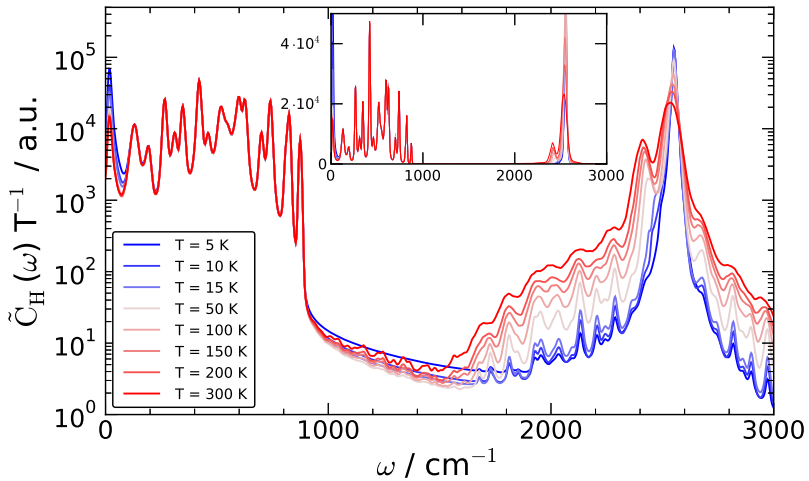
[1]J. Kerwin and B. Jackson, J. Chem. Phys. 128, 084702 (2008)
[2]J. Kerwin, X. Sha and B. Jackson, *J. Phys. Chem. B*, 18811 **110** (2006)
[3]T. Aizawa *et al.*, *Phys. Rev. B*, 11469 **42** (1990)

Atomistic model for MD (i)

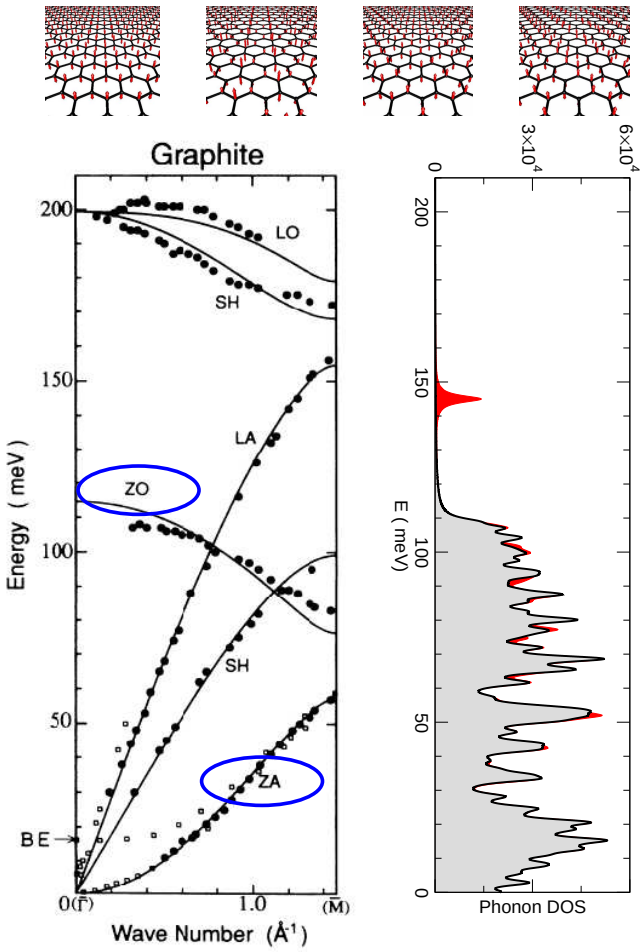


Canonical MD

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



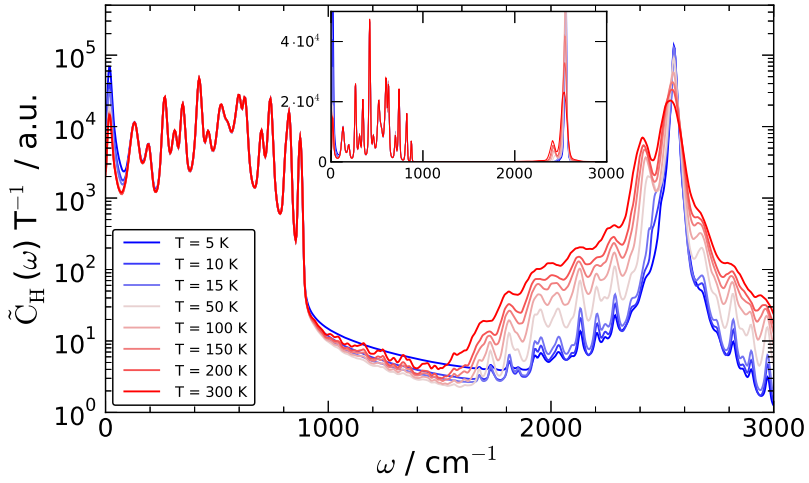
Atomistic model for MD (i)



Canonical MD

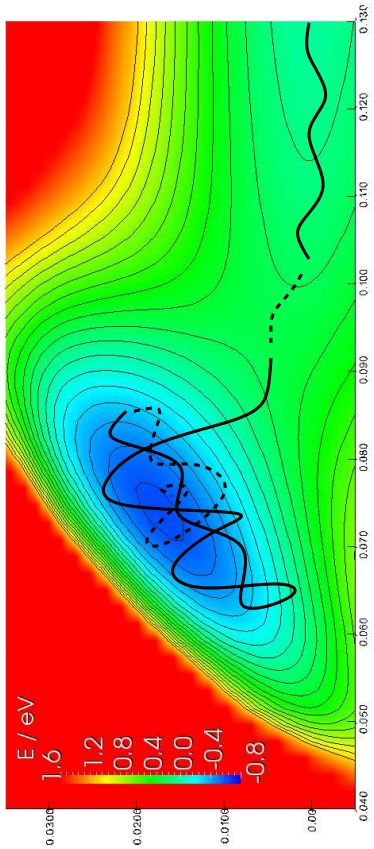
..the high frequency region $\omega > \omega_D$ is markedly T-dependent

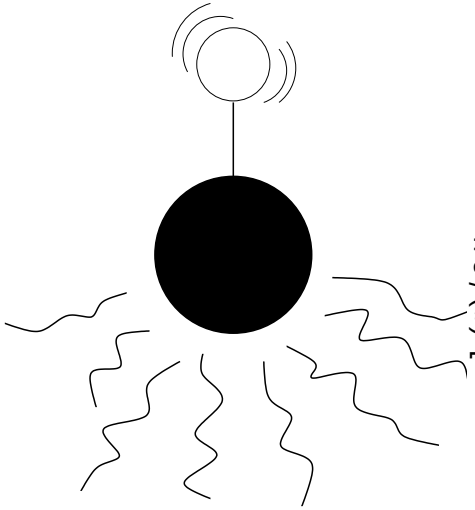
- Anharmonicity in the system potential
- Failure of the bilinear coupling model
- bending-mediated relaxation
- dissipative-like propagation conditions in MD

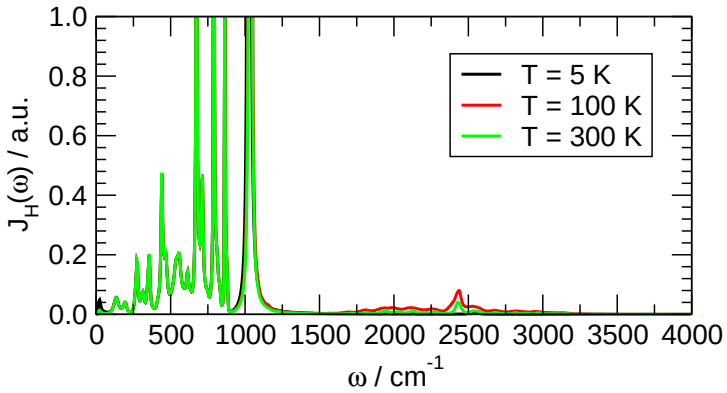


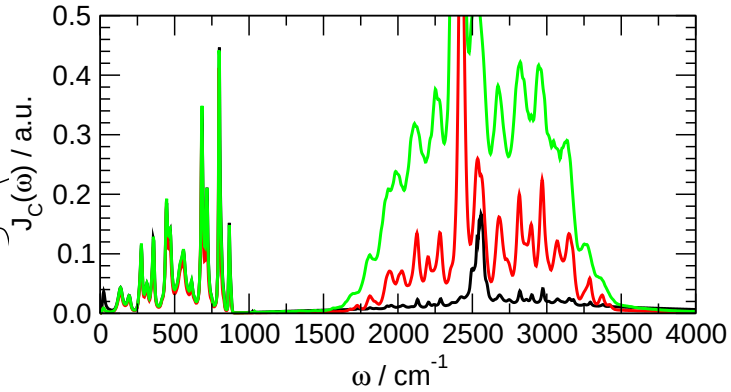
Environment from MD (i)

$$C_H(t) \rightarrow J_H(\omega) \rightarrow J_C(\omega)$$



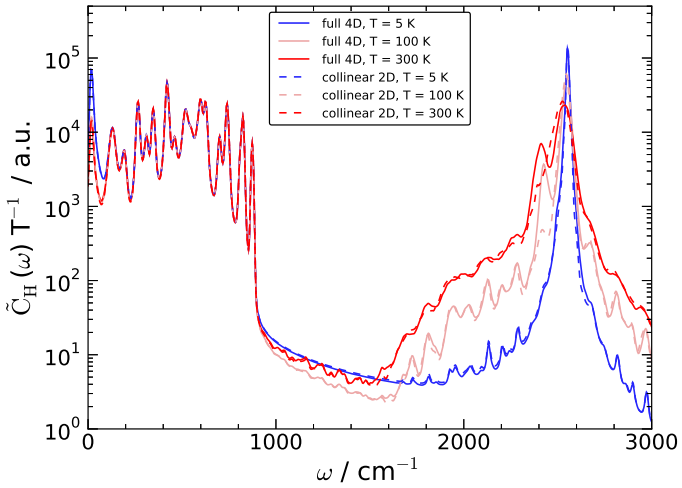






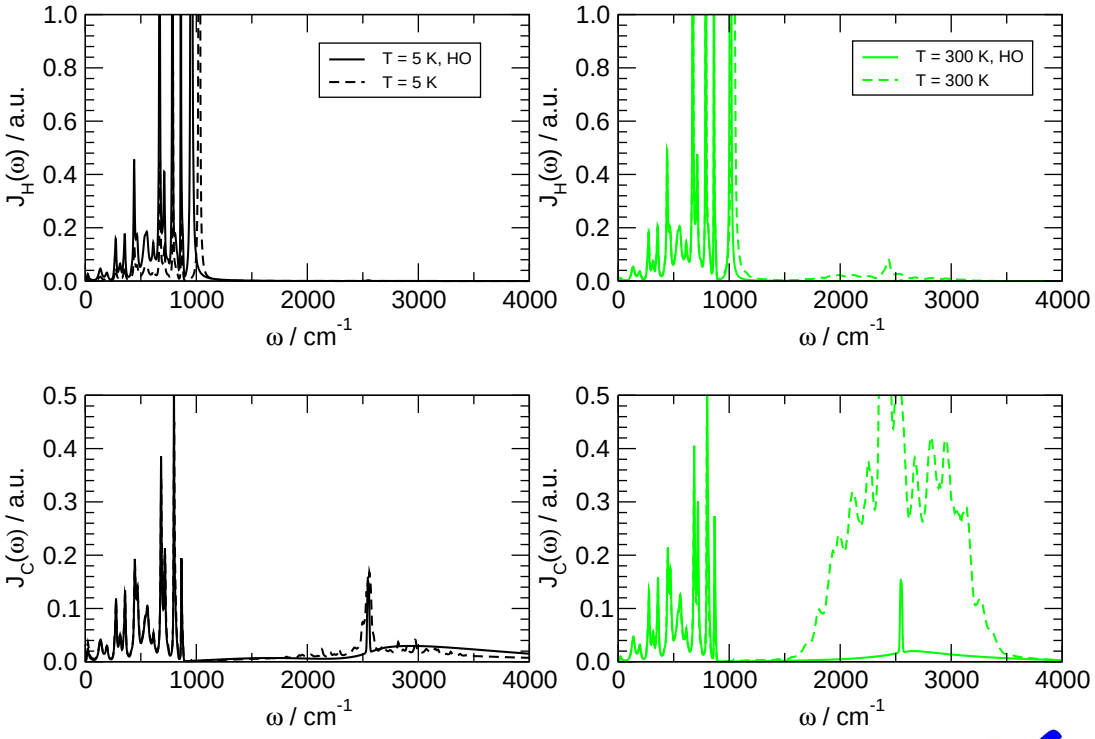
Environment from MD (i)

4D *vs.* 2D

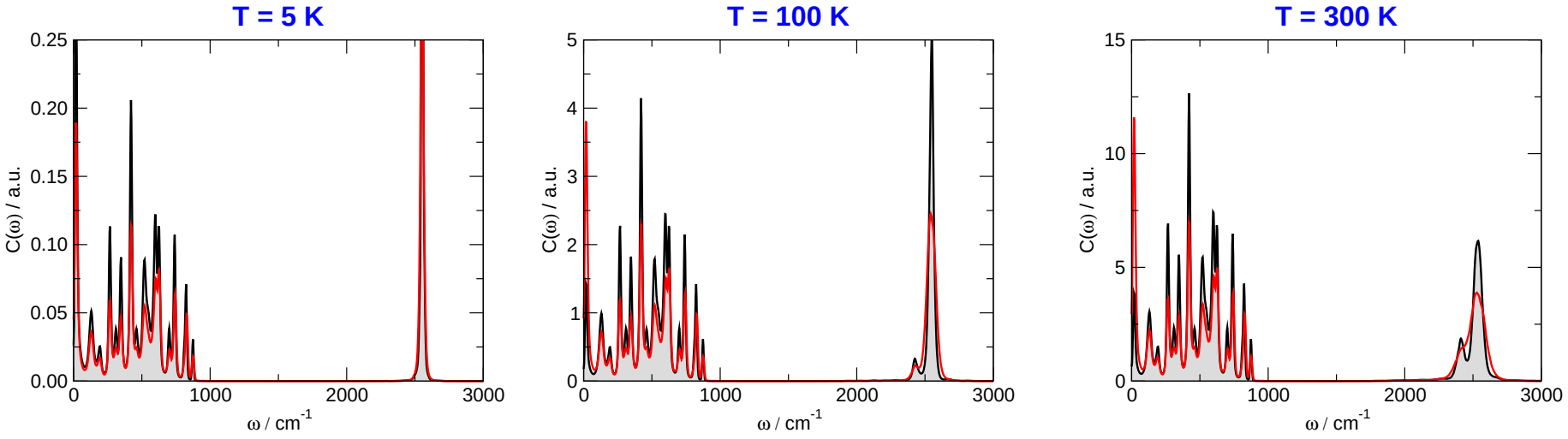


high-ω features are mainly due to the anharmonicity in the CH potential

CH harmonic



Environment from MD (i)



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

..using the low frequency region only, $\omega < 1000$ cm^{-1}

Vibrational relaxation ($T_s = 0$ K) with MCTDH

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

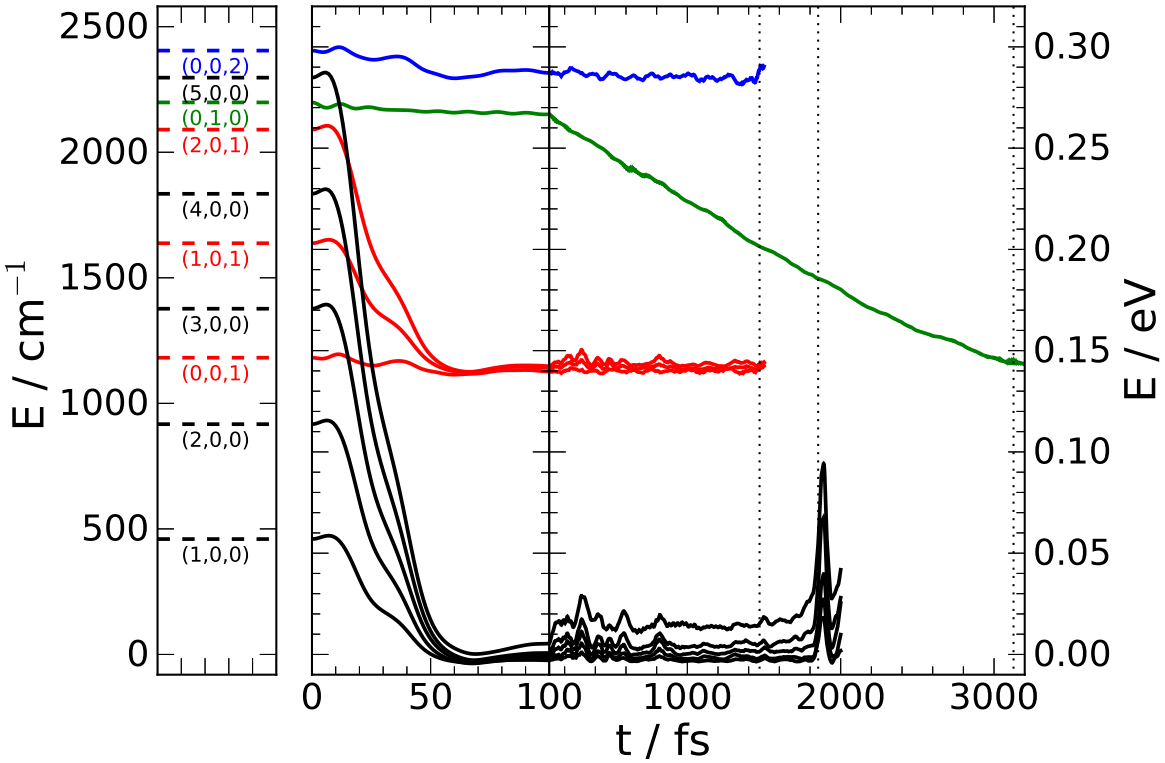
- Hermite-DVR for system's spfs $\psi_{i_1}(\mathbf{x}_H, z_C)$
- Mode combination & Hermite-DVR for bath spfs $\phi^{(k)}_i(\mathbf{Q}_k)$
- Product initial state, $\psi_\nu(\mathbf{x}_H, z_C)\ldots\phi_{\nu=0}(q_k)\ldots$
- Lanczos diagonalization to obtain the 4D eigenvalues and eigenfunctions

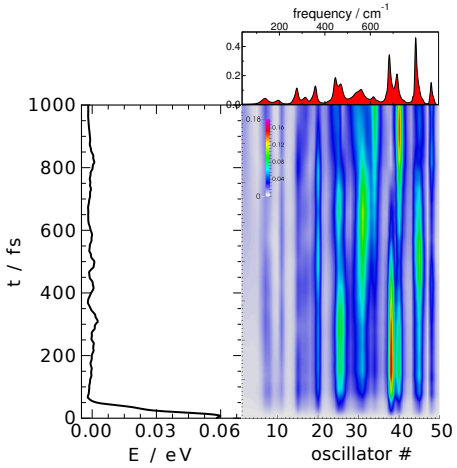
M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

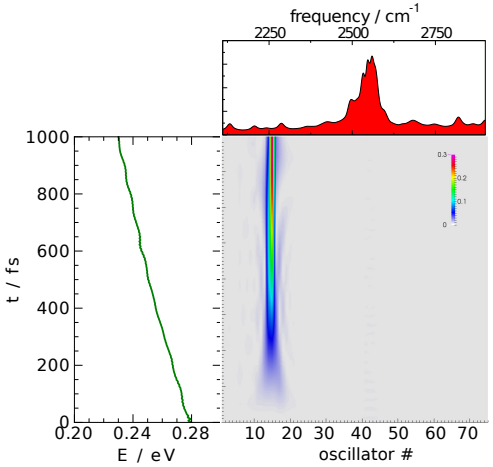
Vibrational relaxation

Bath size	F = 50	F = 75	F = 75
Frequency range / cm^{-1}	[0, 900]	[2100, 2900]	[0,900] + [2100,2900]
System	8	8	7
$q_1 \dots q_5$	3	2	2
$q_6 \dots q_{10}$	3	2	3
$q_{11} \dots q_{15}$	3	3	3
$q_{16} \dots q_{20}$	4	3	3
$q_{21} \dots q_{25}$	4	3	3
$q_{26} \dots q_{30}$	4	3	3
$q_{31} \dots q_{35}$	4	3	3
$q_{36} \dots q_{40}$	4	3	3
$q_{41} \dots q_{45}$	4	3	2
$q_{46} \dots q_{50}$	3	2	2
$q_{51} \dots q_{55}$		2	2
$q_{56} \dots q_{60}$		2	4
$q_{61} \dots q_{65}$		2	2
$q_{66} \dots q_{70}$		2	2
$q_{71} \dots q_{75}$		2	2

Vibrational relaxation from $(\nu_{s,surf}, \nu_{s,CH}, \nu_b)$







Sticking ($T_s = 0$ K) with MCTDH

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

- 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, $\psi_{scatt}(\mathbf{x}_H, z_C)\ldots\phi_{\nu=0}(q_k)\ldots$
- Time-energy mapping

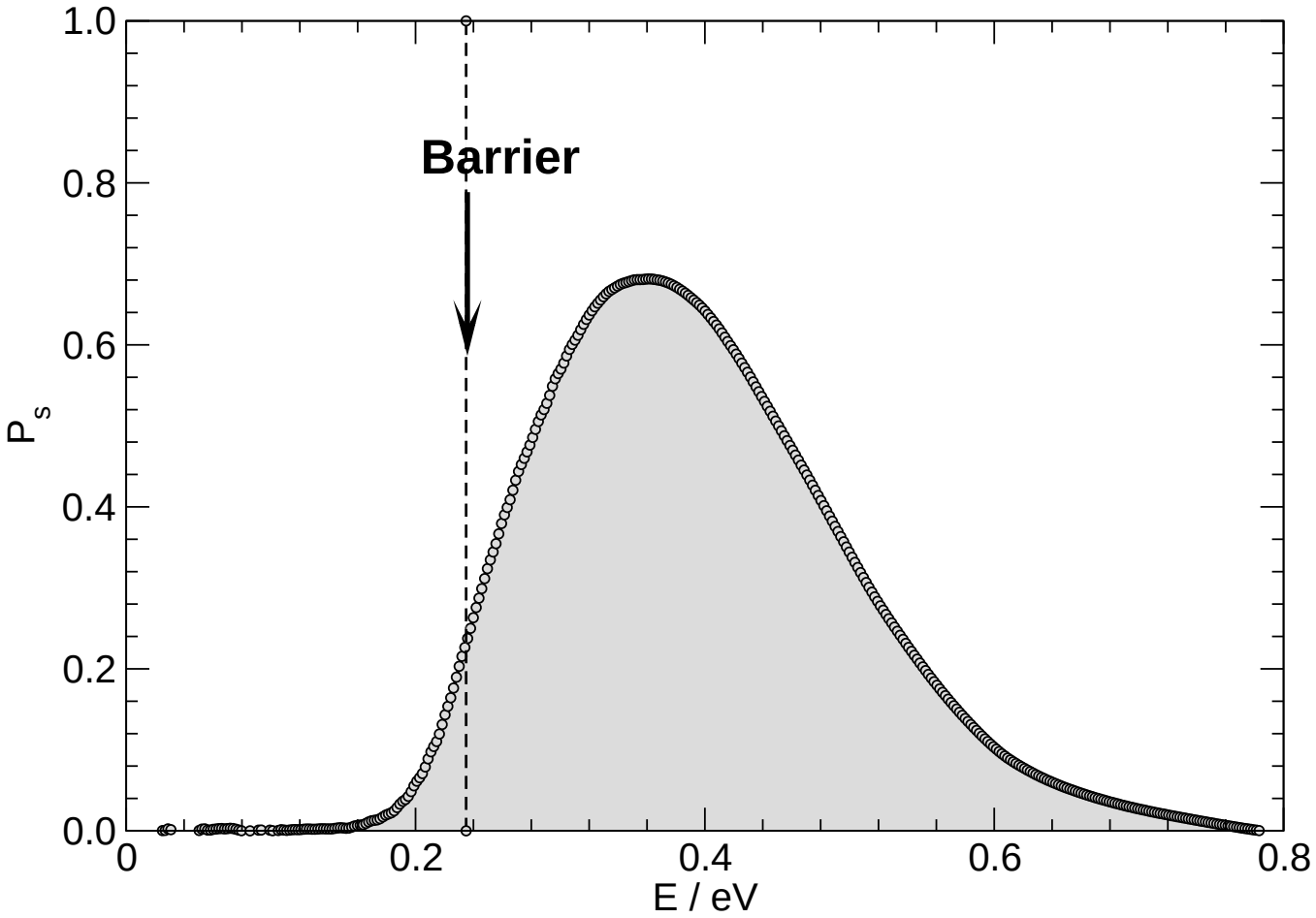
M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

2D Sticking ($T_s = 0$ K) with MCTDH

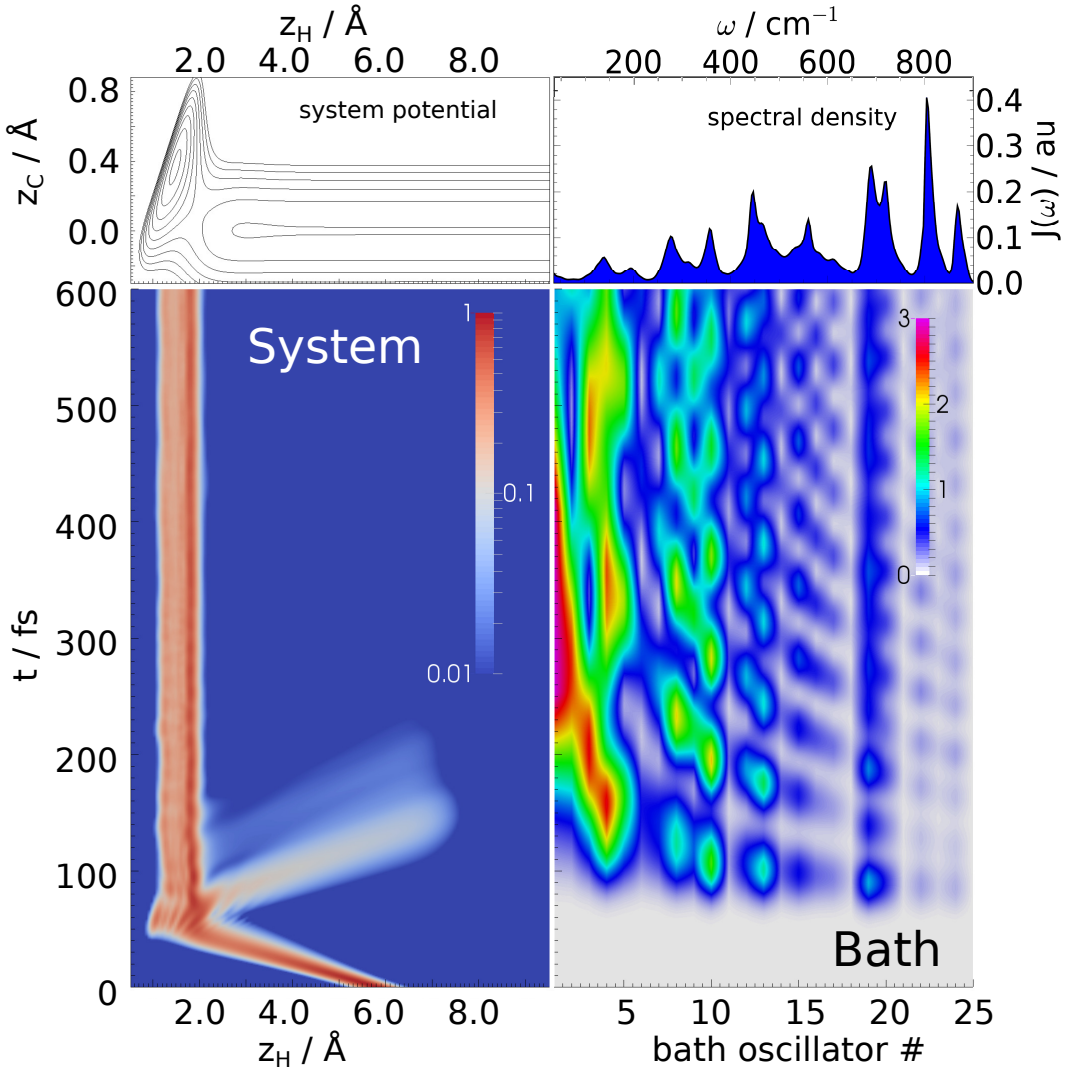
Average momentum (a_0^{-1})	3	4.5	5	7	8.5	10
z_H wavepacket width (a_0)	1.1	0.8	0.8	0.45	0.45	0.45
Final propagation time (fs)	1200.	900.	800.	600.	600.	600.
z_H grid minimum (a_0)	1.5	1.5	1.5	1.0	1.0	1.0
z_H grid maximum (a_0)	30.0	24.0	24.0	18.0	16.0	15.0
z_C grid minimum (a_0)	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
z_C grid maximum (a_0)	1.8	1.8	1.8	1.8	1.8	1.8
AP strength (E_h)	$1.4 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$	$1.62 \cdot 10^{-5}$	$8.97 \cdot 10^{-5}$	$4.174 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$
z_H of the flux line (a_0)	14.	14.	14.	11.	11.	11.

Table: Grid and initial wavefunction parameters (system only)

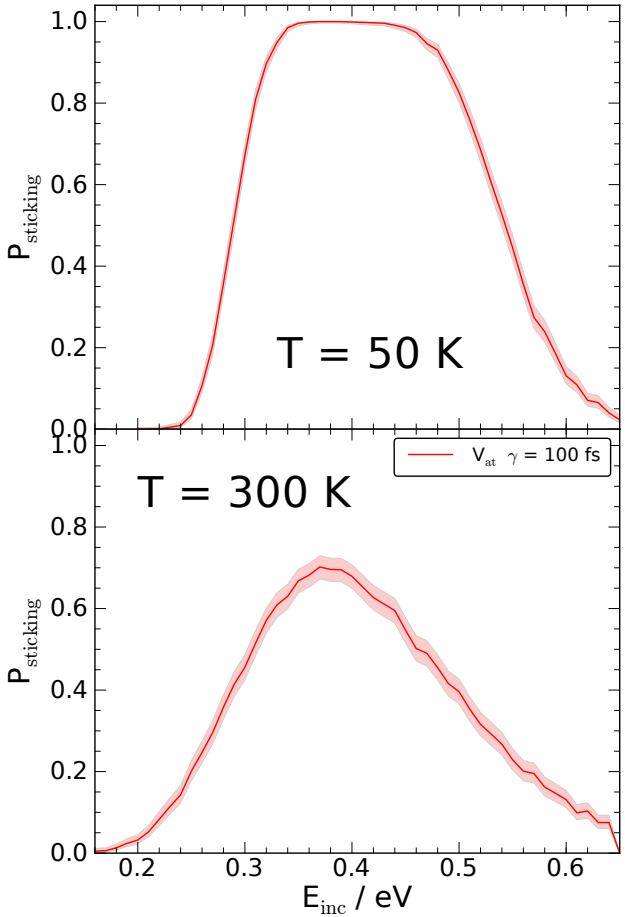
2D Sticking ($T_s = 0$ K) with MCTDH



2D Sticking ($T_s = 0$ K) with MCTDH



..insights from classical dynamics

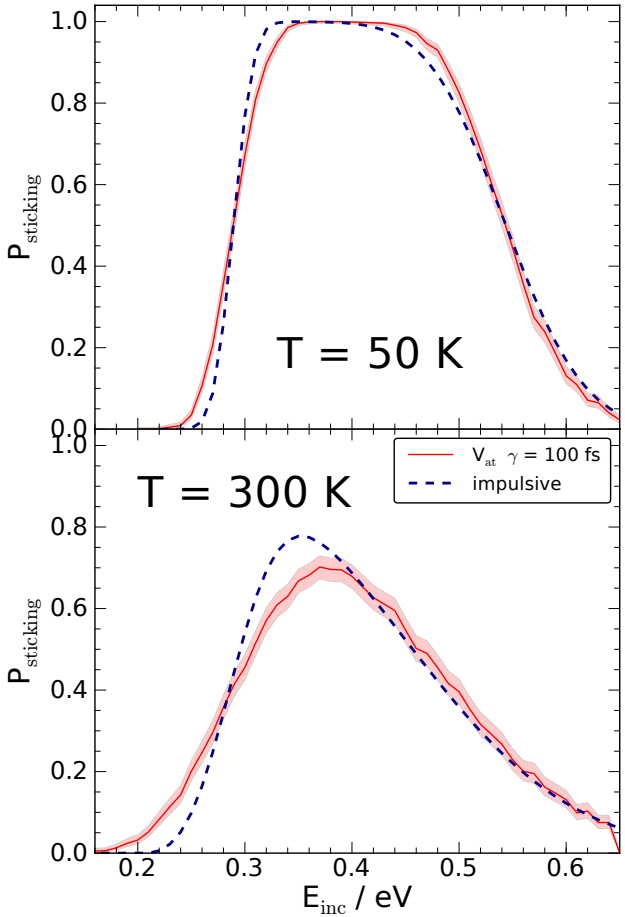


MD with the atomistic potential V_{at}

- Barrier-crossing at low energies
- Energy transfer at high energies

..both depend on the thermal agitation of the carbon atoms

..insights from classical dynamics

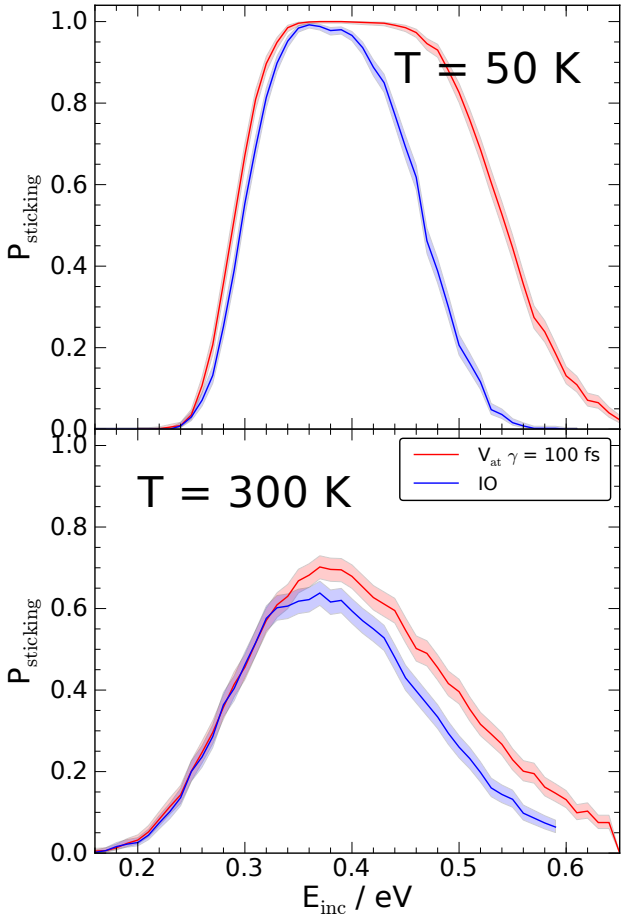


Simple, impulsive model:
barrier energy E_b, well depth D

- Barrier-crossing: $E_{rel} > E_b$
  $\Rightarrow v_C \in [-|v_H| + v_b, \infty)$
- Energy transfer: $\delta\epsilon > E - E_b$
  $\Rightarrow v_C \in [v_-, v_+]$
  $v_\pm(E) = -\frac{1-\chi}{2}|\tilde{v}_H| \pm \frac{1+\chi}{2} v_0$

$$P_s(E) = \int_{\Sigma(E)} g_{cl}(v)dv$$

..insights from classical dynamics

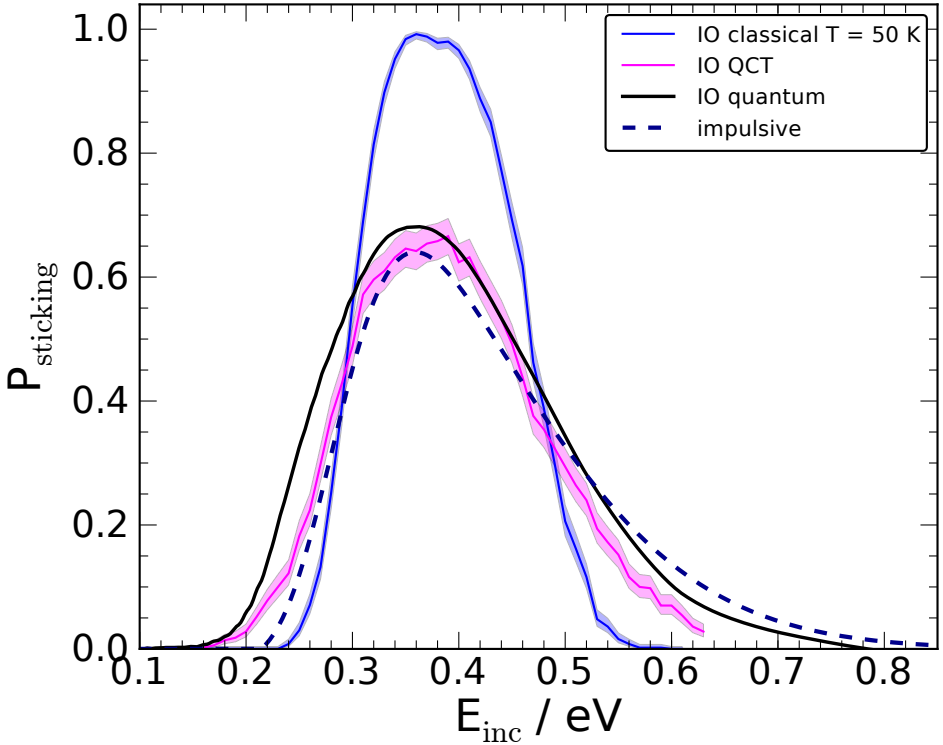


IO *vs.* lattice dynamics

- Good agreement at low energies
- not enough energy transfer at high energies

..the IO model is a good surrogate of the atomistic model in the region most interesting for quantum dynamics

..insights from classical dynamics



Impulsive model + quantum bath

$$g_{cl}(v) \Rightarrow g_q(v)$$

velocity distribution function
of the C atom oscillator coupled a bath

$$g_q(v) = \sqrt{\frac{m_c}{\pi\hbar\Omega_T}}\, e^{-\frac{m_c v^2}{\hbar\Omega_T}}$$

$$\Omega_T = \frac{\int_0^{+\infty} d\omega J_H(\omega)\omega^2 \coth\left(\frac{\hbar\omega}{2k_B T}\right)}{\int_0^{+\infty} d\omega J_H(\omega)\omega}$$

$$P_s(E) = \int_{\Sigma(E)} g_q(v)dv$$

gq

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

Bret Jackson

Keith Hughes

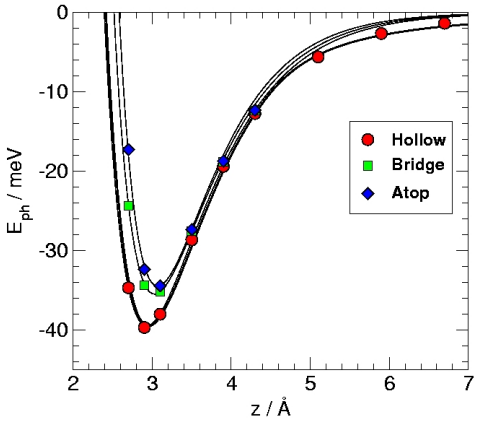
Irene Burghardt

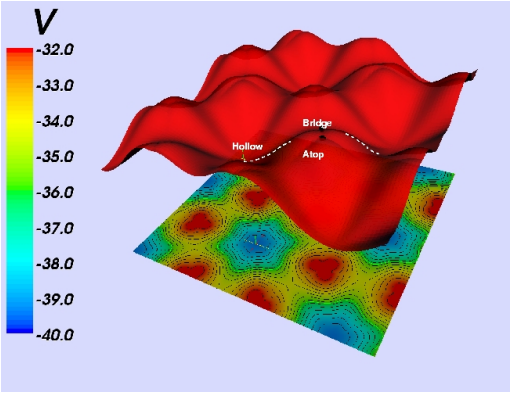
http://users.unimi.it/cdtg

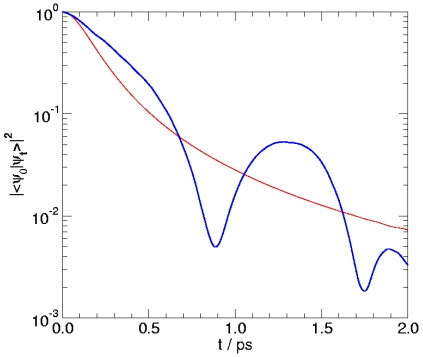
Acknowledgements

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$\pm$0.5 meV
- E_{barr} = 4.0 meV, $D_{T=0K}$ = 1.7 10^{-4} cm^2s^{-1}

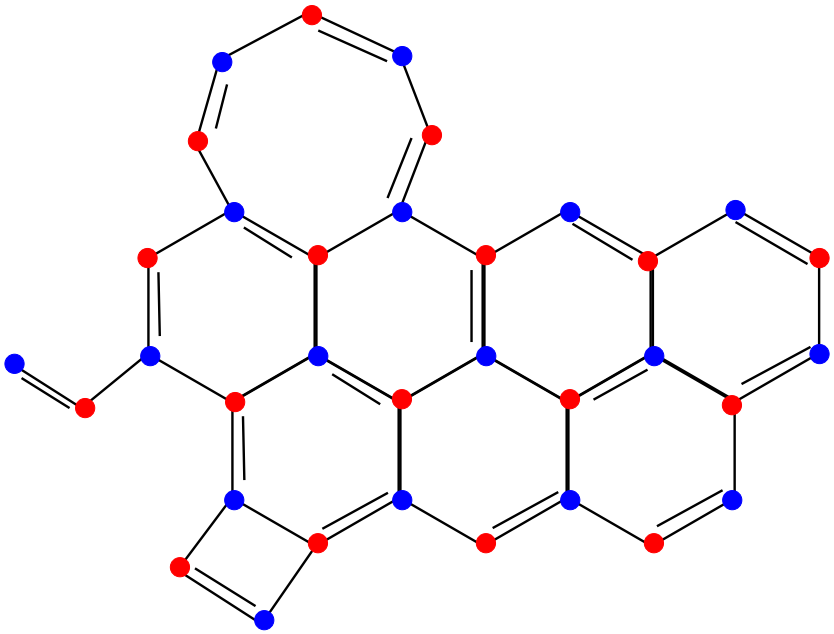
M. Bonfanti, R. Martinazzo, G.F. Tantardini and A. Ponti, *J. Phys. Chem. C*,**111**, 5825 (2007)

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

$$b_i \to -b_i \Longrightarrow H_e^{\pi} \to -H_e^{\pi}$$

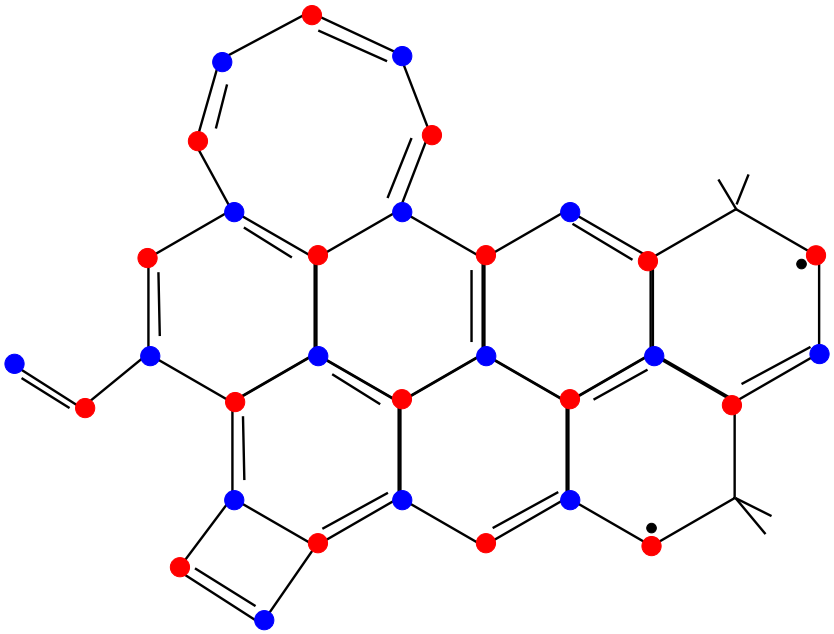
$$\epsilon_i, |\psi_i^{(+)}\rangle = \sum_k \alpha_k |a_k\rangle + \sum_j \beta_i |b_j\rangle$$

$$\Downarrow$$

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

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

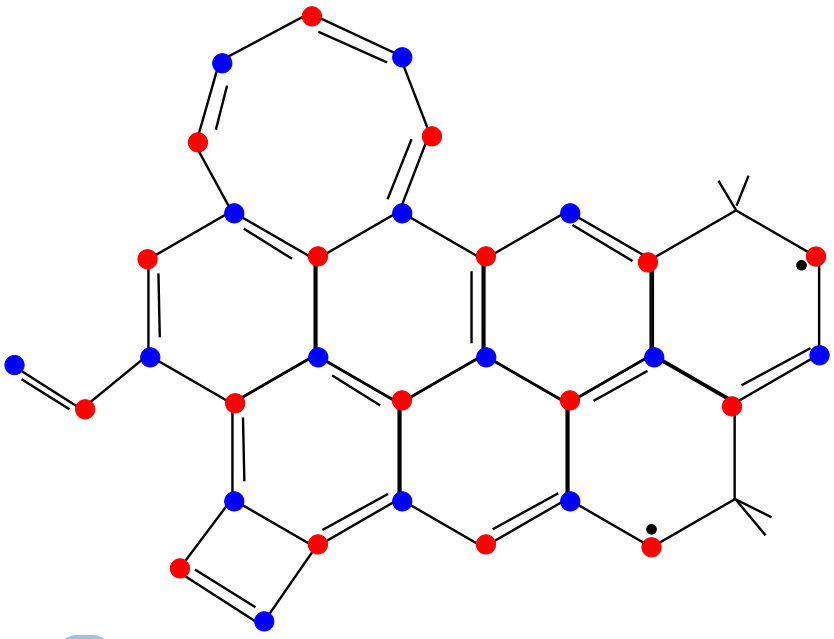
Let $n_A > n_B$, $\mathbf{T}(n_B x n_A)$

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

$\Longrightarrow \mathbf{T}\alpha = \mathbf{0}$ 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)

Two-wavepacket approach

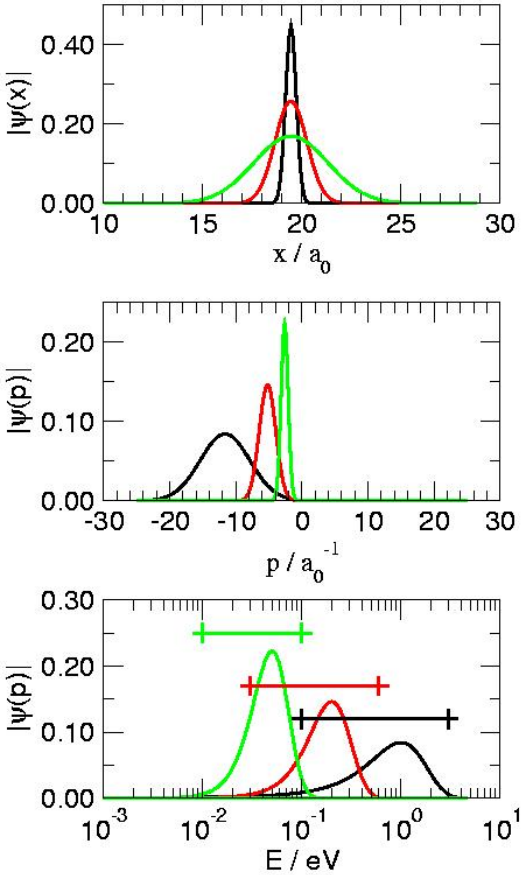
1WP asymptotic conditions:

(i) $|\Psi_0\rangle = |\psi_0\rangle\,|\alpha\rangle$ localized in the asymptotic region
(ii) $|\Psi_0\rangle$ with incoming p components only

for **x** everywhere except in the reagent channel..

$$\int_0^\infty e^{iEt}\,\langle \mathbf{x}\,|\,\Psi_t\rangle\,dt \sim \int_{-\infty}^{\infty} e^{iEt}\,\langle \mathbf{x}\,|\,\Psi_t\rangle\,dt$$
$$= 2\pi\,\langle \mathbf{x}\,|\,\delta(E-H)\,|\,\Psi_0\rangle$$

$$2\pi\,\langle \mathbf{x}\,|\,\delta(E-H)\,|\,\Psi_0\rangle = 2\pi\sum_\beta \langle \mathbf{x}|E\beta+\rangle\,\langle E\beta+|\Psi_0\rangle$$
$$\sim 2\pi\,\langle \mathbf{x}|E\alpha+\rangle\,\langle E\alpha|\Psi_0\rangle$$



Two-wavepacket approach

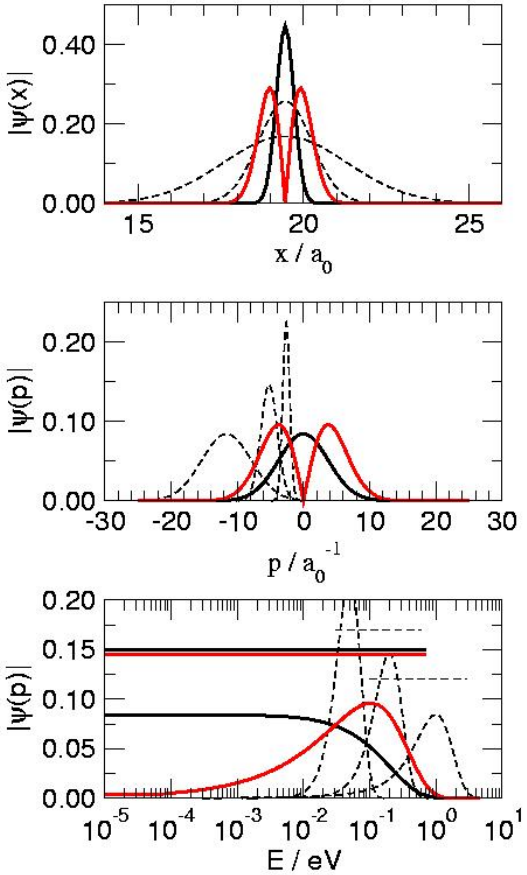
2WP asymptotic conditions:

(i) $|\Psi_i\rangle = |\psi_i\rangle\,|\alpha\rangle$ (i=1,2) localized in the asymptotic region

for **x** everywhere..

$$\int_{-\infty}^{\infty} e^{iEt}\,\langle \mathbf{x}\,|\,\Psi_t\rangle\,dt = 2\pi\,\langle \mathbf{x}\,|\,\delta(E-H)\,|\,\Psi_0\rangle$$

$$2\pi\,\langle \mathbf{x}\,|\,\delta(E-H)\,|\,\Psi_i\rangle = \frac{2\pi}{\sqrt{\bar{v}}}\left\{\langle \mathbf{x}|E\alpha+\rangle\,\psi_i(-\bar{p}) - \sum_{\beta} S^*_{\alpha\beta}(E)\,\langle \mathbf{x}|E\beta+\rangle\,\psi_i(\bar{p})\right\}$$



Two-wavepacket approach

Solve the 2x2 system for the unknown $X = \langle \mathbf{x} | E\alpha+ \rangle$..

$$\begin{aligned}\langle \mathbf{x} | E\alpha+ \rangle =& \frac{1}{2\pi} \frac{\sqrt{\bar{v}}}{\psi_1(-\bar{p})\psi_2(\bar{p}) - \psi_1(\bar{p})\psi_2(-\bar{p})} \\ & \{\psi_2(\bar{p}) 2\pi \langle \mathbf{x} \,|\, \delta(E-H) \,|\, \Psi_1 \rangle \\ & - \psi_1(\bar{p}) 2\pi \langle \mathbf{x} \,|\, \delta(E-H) \,|\, \Psi_2 \rangle\}\end{aligned}$$

..and exploit time-reversal symmetry to get rid of the backward propagation

$$\begin{aligned}\langle \mathbf{x} | E\alpha+ \rangle =& \frac{1}{2\pi} \frac{\sqrt{\bar{v}}}{i \mathrm{Im}(\psi_1^*(\bar{p})\psi_2(\bar{p}))} \\ & \left\{ \psi_2(\bar{p}) \mathrm{Re} \int_0^\infty e^{iEt} \langle \mathbf{x} \,|\, \Psi_{1,t} \rangle \, dt \right. \\ & \left. - \psi_1(\bar{p}) \mathrm{Re} \int_0^\infty e^{iEt} \langle \mathbf{x} \,|\, \Psi_{2,t} \rangle \, dt \right\}\end{aligned}$$

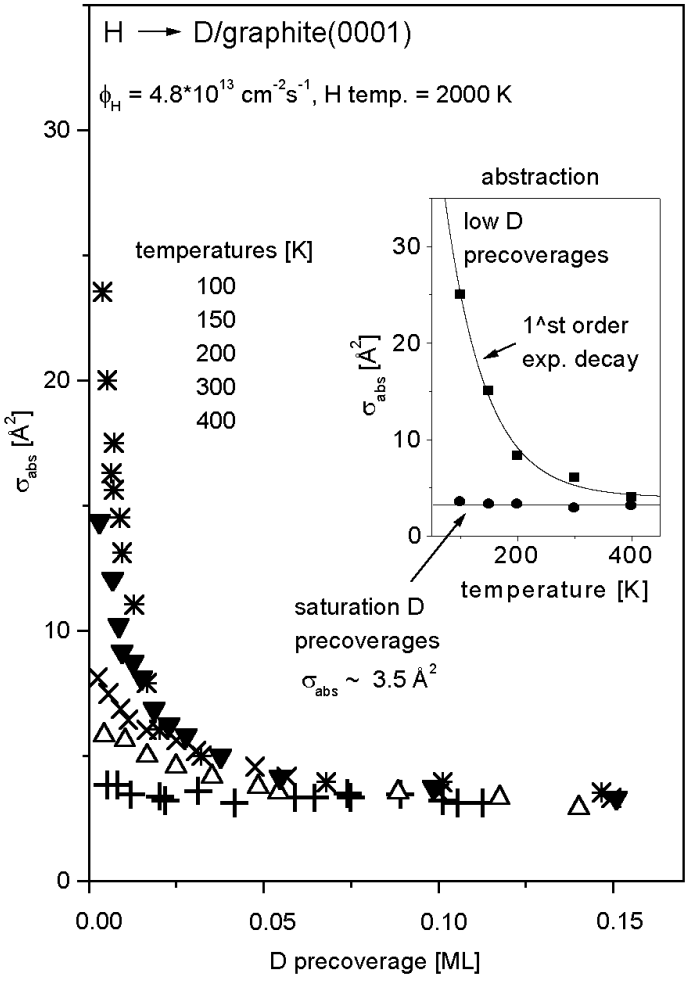
Two-wavepacket approach

Further simplifications arise from the use of 'even' and 'odd' momentum wavepackets..

$$\langle \mathbf{x} | E\alpha + \rangle = \frac{1}{2\pi}\sqrt{\bar{v}}e^{-i\bar{p}x_0} \left\{ \frac{1}{\phi_g(\bar{p})}\mathrm{Re}\int_0^\infty e^{iEt}\left\langle \mathbf{x} \,\middle|\, \Psi_{g,t}\right\rangle dt - \frac{i}{\phi_u(\bar{p})}\mathrm{Re}\int_0^\infty e^{iEt}\left\langle \mathbf{x} \,\middle|\, \Psi_{u,t}\right\rangle dt \right\}$$

	1WP	2WP
$\psi_0(x)$	$\psi_0(x) = (2\pi\delta^2)^{-1/4}e^{-(x-x_0)^2/4\delta^2}e^{-ip_0(x-x_0)}$	$\psi_g(x) = (2\pi\delta^2)^{-1/4}e^{-(x-x_0)^2/4\delta^2}$ $\psi_u(x) = (6\pi\delta^2)^{-1/4}e^{-(x-x_0)^2/12\delta^2}(x-x_0)/\sqrt{3}\delta$
$g(E)$	$\sqrt{8\pi}\delta mm' e^{-2\delta^2(p-p_0)^2}/p$	$2^{5/2}\,3^{3/4}\,\sqrt{\pi}\delta^2 mm' e^{-4\delta^2 p}$
$\phi_\beta^\infty(E)$	$\phi_\beta^\infty(E) = \int_0^\infty e^{iEt}\langle R_\infty\beta\|\Psi_t\rangle\, dt$	$\phi_\beta^\infty(E) = \mathrm{Re}\int_0^\infty e^{iEt}\langle R_\infty\beta\|\Psi_{g,t}\rangle\, dt +$ $-i\mathrm{Re}\int_0^\infty e^{iEt}\langle R_\infty\beta\|\Psi_{u,t}\rangle\, dt$

Zecho's kinetic experiments



System-bath

..choosing the system potential

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

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

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

$$\Downarrow$$

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

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

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

System-bath modeling: our strategy

$$\ddot{z}(t) + \int_{-\infty}^{+\infty} \gamma(t-\tau)\dot{z}(\tau)d\tau + \omega_0^2 z(t) = \xi(t)/m$$

$$\Downarrow$$

$$\delta\tilde{z}(\omega) = \frac{1}{m}\frac{\tilde{\xi}(\omega)}{\omega_0^2 - \omega^2 - i\omega\tilde{\gamma}(\omega)}$$

$$\Downarrow$$

$$\frac{1}{2}\omega\tilde{C}(\omega) = \frac{k_B T}{m}\,\mathrm{Im}\left(\frac{1}{\omega_0^2 - \omega^2 - i\omega\tilde{\gamma}(\omega)}\right)$$

$$\Downarrow$$

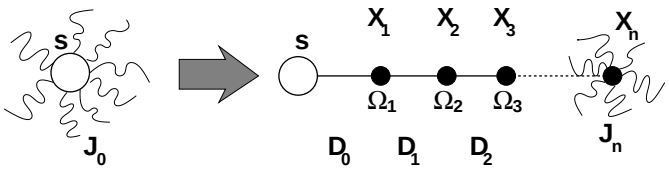
$$S(z) = iz\tilde{C}^{>}(z) + C(0) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\omega\tilde{C}(\omega)/2}{\omega - z}d\omega$$

$$\Downarrow$$

$$S(z) \equiv \frac{k_B T}{m}\frac{1}{\omega_0^2 - z^2 - iz\tilde{\gamma}(z)}$$

$$\Downarrow$$

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



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

$$W_H(z) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{J_H(\omega)}{\omega - z}d\omega$$

$$W_H^+(\omega) = \lim_{\epsilon\to 0^+} W_H(\omega + i\epsilon)$$

$$\Downarrow$$

$$J_C(\omega) = \frac{D_C^2 J_H(\omega)}{|W_H^+(\omega)|^2}$$

*

Quantum bath

$$\hat{\rho}(\xi) = \langle e^{i\xi p_0} \rangle, p_0 = \sum_k U_{0k} P_k \Rightarrow \hat{\rho}(\xi) = \prod_k \hat{\phi}_k(U_{0k}\xi), \;\; \hat{\phi}_k(\xi) \equiv \exp\left(-\frac{m\hbar\Omega_k}{4} \coth\left(\frac{\hbar\Omega_k}{2k_B T}\right)\xi^2\right)$$

$$\Omega_T = \sum_k |U_{0k}|^2 \Omega_k \coth\left(\frac{\hbar\Omega_k}{2k_B T}\right) \qquad \rho(p) = \frac{1}{\sqrt{\pi m\hbar\Omega_T}} e^{-\frac{p^2}{m\hbar\Omega_T}}$$

$$L = \frac{m}{2}\dot{\mathbf{x}}^t\dot{\mathbf{x}} - \frac{m}{2}\mathbf{x}^t\mathbf{V}\mathbf{x}$$

$$\mathbf{V}_{00} = \omega_0^2, \; \mathbf{V}_{0k} = \mathbf{V}_{k0} = -\frac{c_k}{m}, \;\; \mathbf{V}_{kl} = \delta_{kl}\omega_k^2$$

Simple: $|U_{0k}|^2 = \left(1 + \sum_{l=1}^{N-1} \frac{c_l^2}{(\omega_l^2 - \Omega_k^2)^2}\right)^{-1}$ ..but we need to know the eigenfrequencies Ω_k

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$$|\psi\rangle = x_0 |0\rangle + \int d\omega x(\omega) |\omega\rangle$$

$$L[\psi, \dot{\psi}] = \frac{m}{2} \langle\psi|\psi\rangle - \frac{m}{2} \langle\psi|V|\psi\rangle$$

$$V = \omega_0^2 |0\rangle\langle 0| - |\zeta\rangle\langle 0| - |0\rangle\langle\zeta| + \int d\omega\omega^2 |\omega\rangle\langle\omega| \text{ where } |\zeta\rangle = \frac{1}{m}\int d\omega c(\omega) |\omega\rangle$$

$$|U_{0k}|^2 \to -\frac{1}{\pi} \lim_{\epsilon\to 0^+} G_{00}(y + i\epsilon) \;\; (y \in \mathbb{R})$$

$$\Rightarrow G_{00}(z) = \frac{1}{z - \omega_0^2 - \frac{2}{\pi}\int_0^\infty \frac{J_C(\omega)\omega}{z-\omega^2} d\omega} \text{ or } W(z) \equiv \frac{1}{\omega_0^2 - z^2 - \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{J_C(\omega)}{\omega - z} d\omega}$$

$$\Im W^+(\omega) = \frac{\pi J_H(\omega)}{2\int_0^\infty J_H(\omega)\omega d\omega} \sum_k |U_{0k}|^2(..) \to \int d(\omega^2) \frac{\Im W^+(\omega)}{\pi}(..)$$

$$\Omega_T = \frac{\int_0^\infty \omega^2 \coth\left(\frac{\hbar\omega}{2k_B T}\right) J_H(\omega) d\omega}{\int_0^\infty \omega J_H(\omega) d\omega}$$