

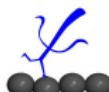
# Quantum dynamics of hydrogen atoms on graphene

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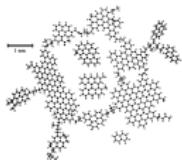
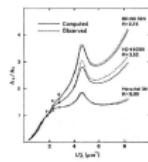
*Challenges in reaction dynamics of gas-surface interactions and methodological advances in dissipative and non-adiabatic processes*

Albi, June 25-29, 2017



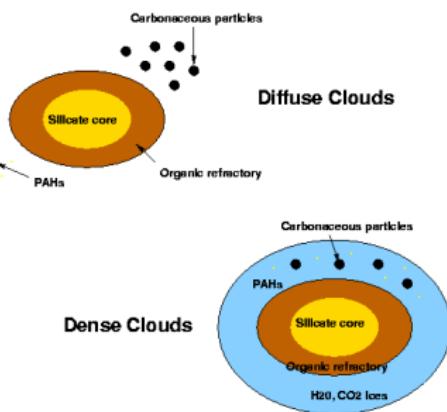
# H<sub>2</sub> in the ISM

- Hydrogen is the most abundant element of the Universe
- H<sub>2</sub> is formed on the surface of *dust grain*



Hydrogen-graphite is an important model for understanding H<sub>2</sub> formation in ISM

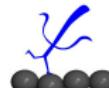
$$f_{\text{grain}} = n_{\text{grain}} / n_H \sim 10^{-12} \text{ i.e. } \sim 1\% \text{ of ISM mass}$$



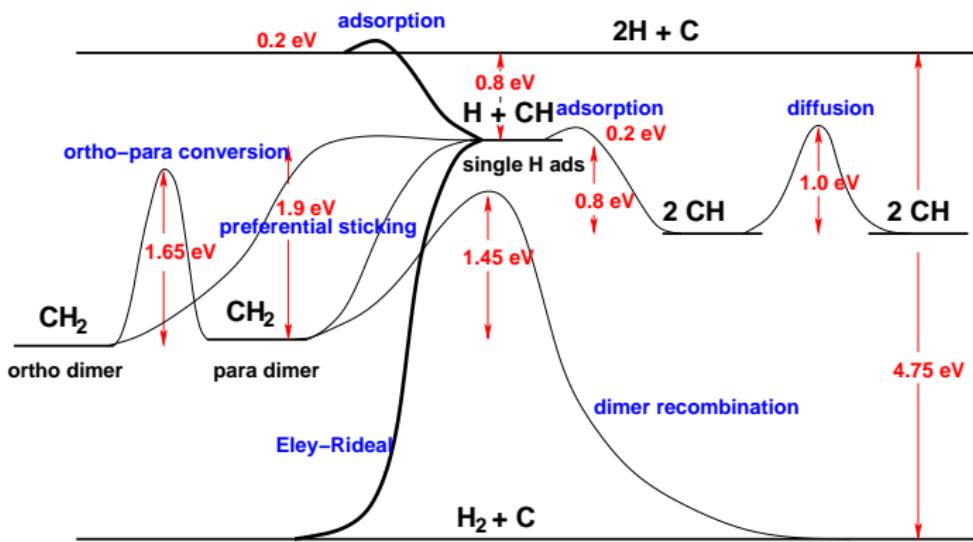
# Chemisorption and reaction

Stable (**chemisorbed**) hydrogens are needed to explain H<sub>2</sub> formation in different ISM environments..

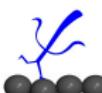
- Chemisorbed H atoms are **immobile**  
⇒ LH can be ruled out, **Eley-Rideal** is the main reactive pathway
- H atoms face an energy **barrier to stick**  
⇒ **Direct sticking** (Matteo's talk) and **phys-to-chem conversion**



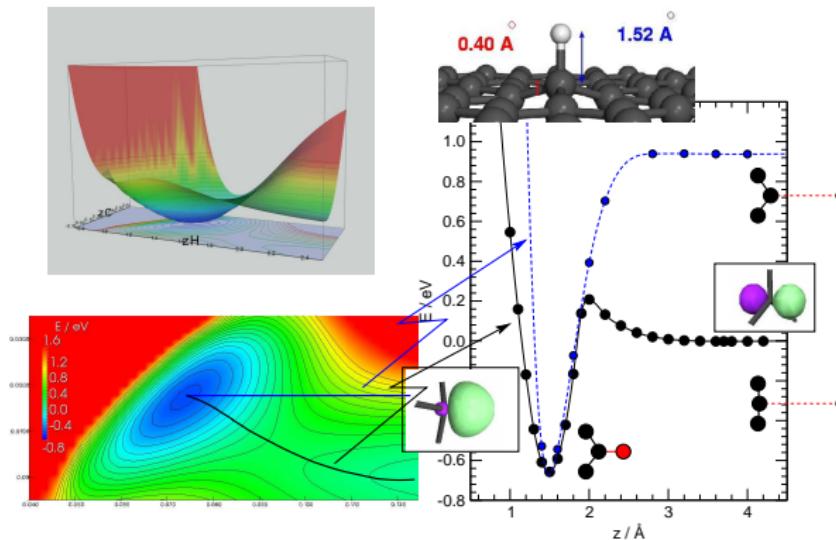
# Energy landscape



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

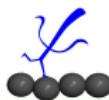


# Chemisorption of a H atom

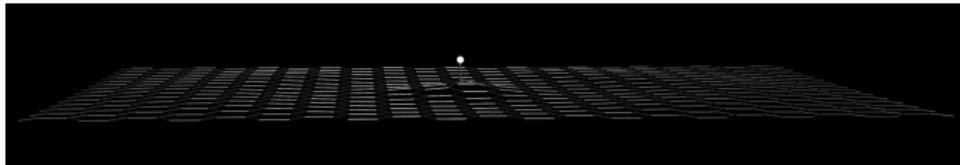


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)  
 X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

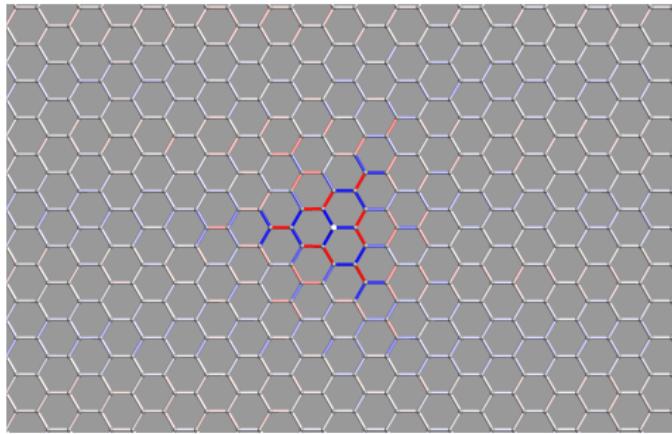
phys



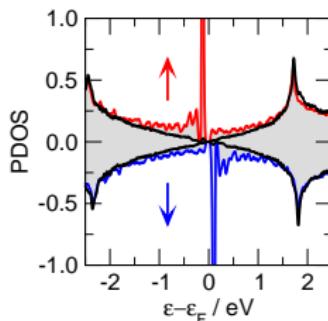
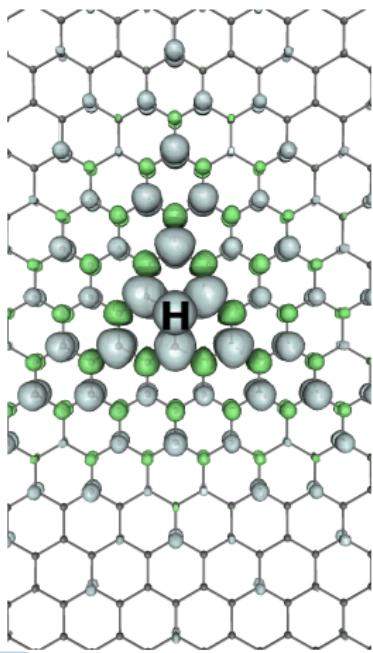
# Chemisorption of a H atom



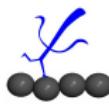
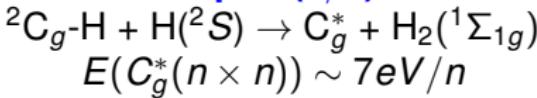
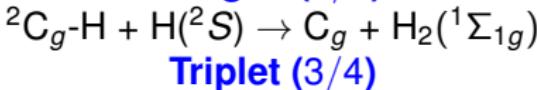
0.5% shorter -  $d_{CC}^0$  - 0.5% longer



# Midgap states



**Singlet (1/4)**



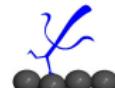
# Outline

## 1 Eley-Rideal reaction dynamics

- System-bath modeling
- Full quantum dynamics

## 2 Phys-to-Chem conversion

- Flux-side correlation function
- Quantum dynamics



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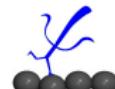
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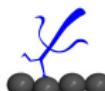
# Eley-Rideal

Several studies with notable differences in the detailed results, though all agree on

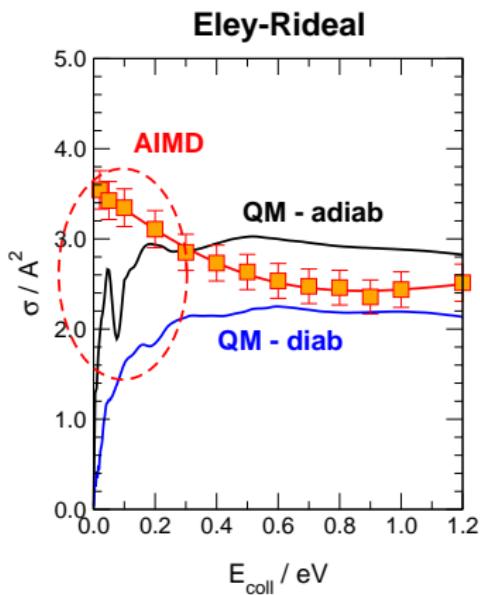
- the size of the cross-section
- the internal excitation of the nascent molecule

Only few of them addressed the issue of the lattice dynamics and dissipation, none in a full quantum dynamical setting..

- 
- 2001-05 A. J. Meijer *et al.*, JPC A 105, 2173 (2001); **M. Rutigliano, M. Cacciatore, and G. D. Billing, CPL 340, 13 (2001)**; X. Sha, B. Jackson and D. Lemoine, JCP 116, 7158 (2002); S. Morisset *et al.*, PCCP 5, 506 (2003); **S. Morisset *et al.*, CPL 378, 615 (2003)**; JPC A 108, 8571 (2004)
- 2006-10 R. Martinazzo and G.F. Tantardini, JPCA (Letter), 109 (2005) 9379; JCP 124, 124703 (2006); JCP 124, 124704 (2006); S. Casolo *et al.* JPCA A, 113 (2009) 14545; D. Bachellerie *et al.*, PCCP 11, 2715 (2009), M. Sizun *et al.* 498, 32 (2010)
- 2011-15 Bonfanti *et al.* PCCP, 13 (2011) 16680; **S. Casolo, G.F. Tantardini and R. Martinazzo, PNAS 110, 6674 (2013)**; JPCA A, 120, 5032 (2016)
- 2016- Pasquini *et al.* PCCP 18 (2016) 6607



# Eley-Rideal: AIMD xsections



Dynamical lattice,  
surface corrugation

..but classical dynamics

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



# Eley-Rideal: reduced-dimensional models

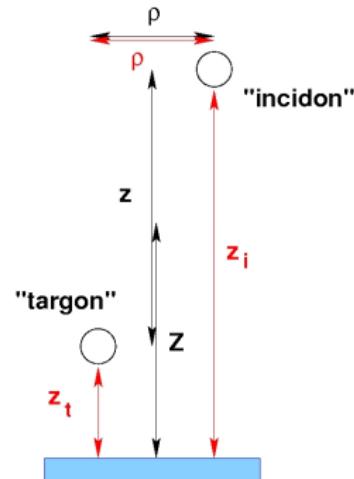
- **Rigid, flat** surface approximation<sup>1</sup>
- Substrate **diabatic** vs. **adiabatic** dynamics<sup>2</sup>

Diabatic limit  $E_{puck}$  is left on the surface, smaller xsections, smaller internal excitation

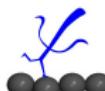
Adiabatic limit  $E_{puck}$  is made available to products, larger xsections, larger interal excitation

- **3D quantum dynamics** at both high and vanishing collision energies, for any isotope combination, etc.

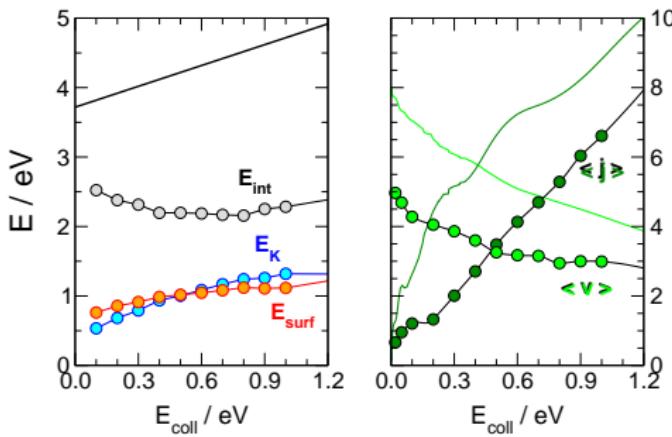
⇒ state-to-state, energy-resolved cross sections for ***all*** possible processes



- [1] M. Persson and B. Jackson, JCP 102, 1078 (1995); D. Lemoine and B. Jackson, CPC 137, 415 (2001)  
[2] X. Sha, B. Jackson and D. Lemoine, JCP 116, 7158 (2002)

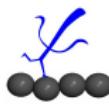


# Eley-Rideal: AIMD $E$ -partitioning

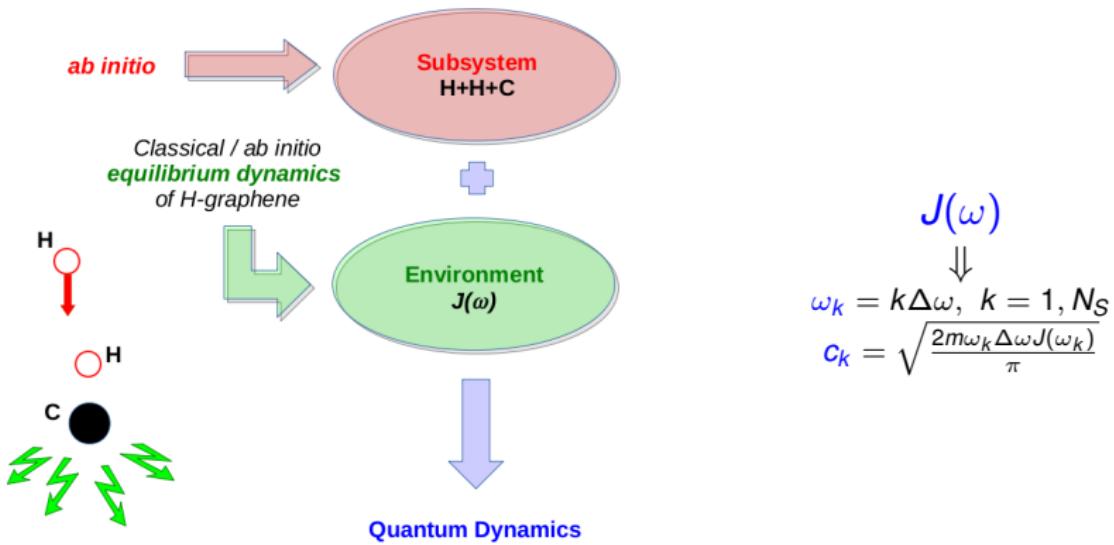


..most of energy is **internal**, but energy transfer to the surface is **considerable**

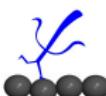
$E_{\text{surf}}$  compares well with  $\sim 0.8$  eV of the substrate diabatic picture



# System-bath modeling: our strategy

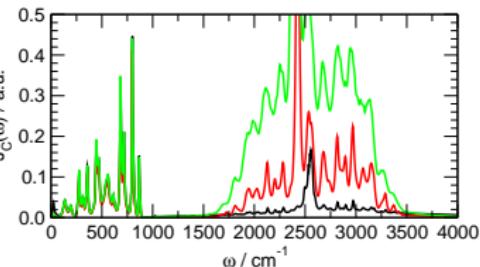
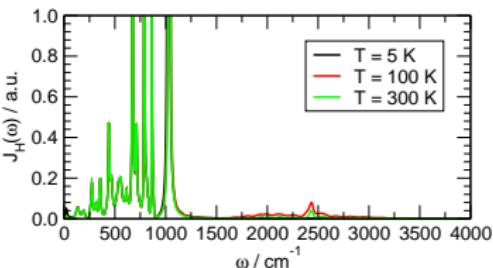
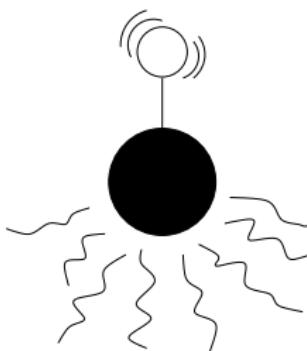
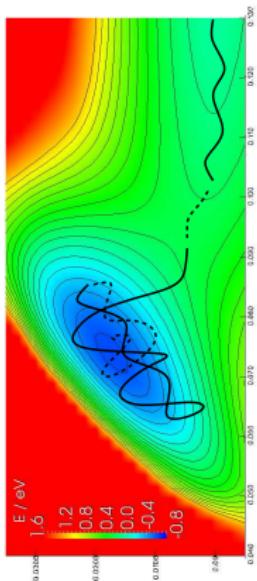


$$H = \frac{\mathbf{p}_i^2}{2m_i} + \frac{\mathbf{p}_t^2}{2m_t} + \frac{p_C^2}{2m_C} + V_{CH_2}(\mathbf{x}_i, \mathbf{x}_t, z_C) + \sum_k^{N_S} \left\{ \frac{p_k^2}{2m} + \frac{m\omega_k^2}{2} \left( x_k - \frac{c_k \delta z_C}{m\omega_k^2} \right)^2 \right\}$$

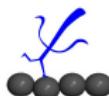


# Environment: $J(\omega)$

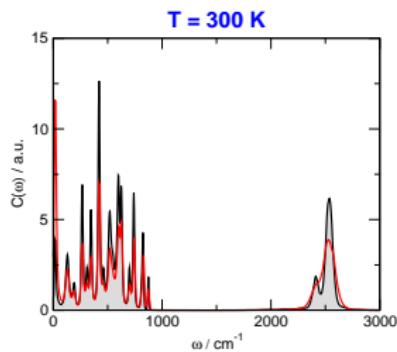
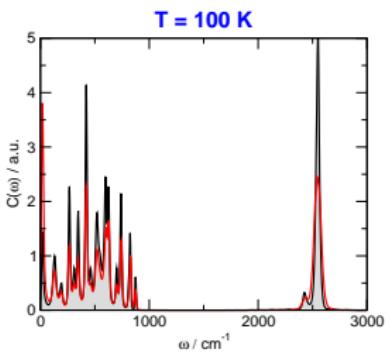
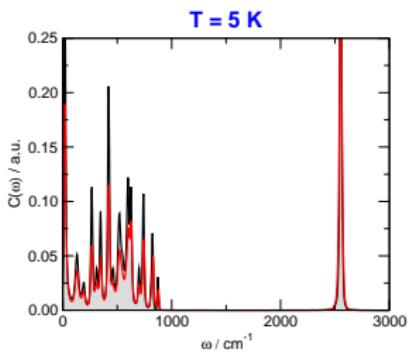
$$C_H(t) \rightarrow J_H(\omega) \rightarrow J_C(\omega)$$



M. Bonfanti, B. Jackson, K.H. Hughes, I. Burghardt and R. Martinazzo, J. Chem. Phys. 143, 124703 (2016)



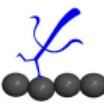
# Environment: $J(\omega)$



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

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

M. Bonfanti, B. Jackson, K.H. Hughes, I. Burghardt and R. Martinazzo, J. Chem. Phys. 143, 124703 (2016)



# Subsystem

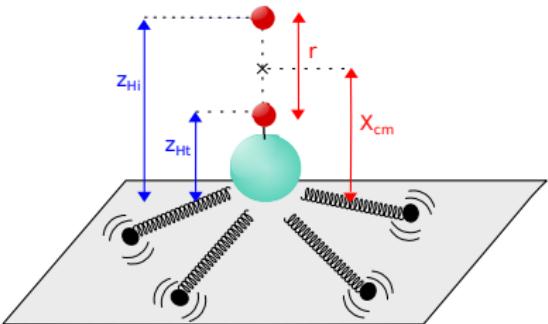
## SO-like model potential

### -H<sub>2</sub> system

Plane-wave DFT PW91 calculations fitted to a modified LEPS form<sup>[1]</sup>  $V_{LEPS}(z_i, z_t, \rho_{\parallel})$

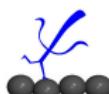
**N.B.:diabatic case**

### SO-like Coupling



$$\begin{aligned} V_{CH_2}(\mathbf{x}_i, \mathbf{x}_t, z_C) \\ \Downarrow \\ V_{LEPS}(z_i - z_C, z_t - z_C, \rho_{\parallel}) + \\ + V_{CH}(z_t, z_C) - V_t(z_t - z_C) \end{aligned}$$

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



# ER dynamics with ML-MCTDH

Hierarchical multi-configuration expansion of  $\Psi^{(0)}(x_1, x_2, \dots x_N)$

0<sup>th</sup> level: overall wavefunction and **mode grouping**  $\mathbf{x} \equiv (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_0})$

$$\Psi^{(0)}(\mathbf{x}) = \sum_{\mathbf{l}} A_{\mathbf{l}}^{(0)} \Psi_{i_1}^{(1)}(\mathbf{q}_1) \Psi_{i_2}^{(2)}(\mathbf{q}_2) \dots \Psi_{i_{N_0}}^{(N)}(\mathbf{q}_{N_0})$$

1<sup>st</sup> level: wavefunctions of mode ('node')  $\mathbf{q}_K \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots)$  are further expanded on (common) spf's..

$$\Psi_i^{(K)}(\mathbf{q}_K) = \sum_{\mathbf{l}} A_{\mathbf{l}}^{(K,i)} \Psi_{1,i_1}^{(K)}(\mathbf{r}_1) \Psi_{2,i_2}^{(K)}(\mathbf{r}_2) \dots \Psi_{N_k,i_{N_1}}^{(K)}(\mathbf{r}_{N_K})$$

...

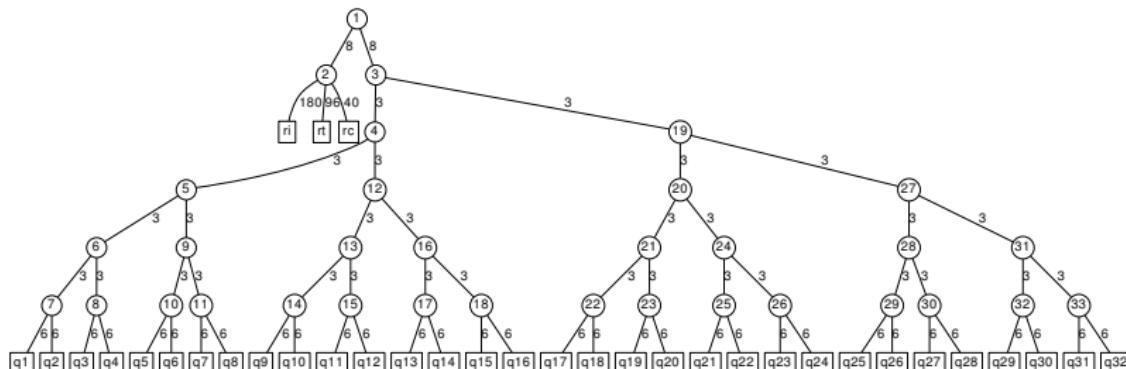
do until reach the **primitive level** where  $\mathbf{u}_L \equiv (x_1, x_2, \dots)$

$$\Psi_j^{(L)}(\mathbf{u}_L) = \sum_{\mathbf{l}} C_{\mathbf{l}}^{(L,j)} \chi_{i_1}^{(1)}(x_1) \chi_{i_2}^{(2)}(x_2) \dots$$



# ER dynamics with ML-MCTDH

**35D wavepacket dynamics:**  $\Psi(z_i, z_t, z_C, q_1, q_2, \dots q_{32}, t)$

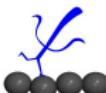


..

$$\Psi_j^{(20)}(\mathbf{Q}_{20}, t) = \sum_{i_1=1}^3 \sum_{i_2=1}^3 c_{i_1, i_2}^{(20, j)}(t) \Psi_{i_1}^{(21)}(\mathbf{Q}_{21}, t) \Psi_{i_2}^{(24)}(\mathbf{Q}_{24}, t)$$

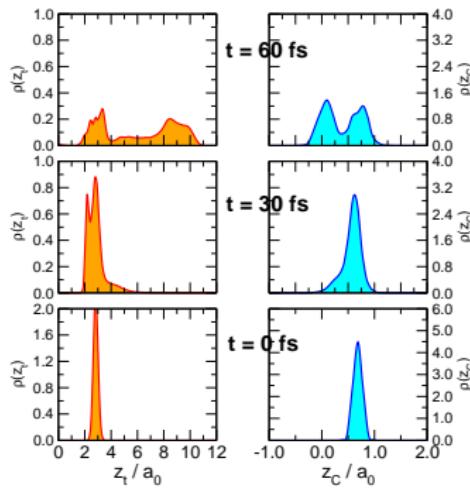
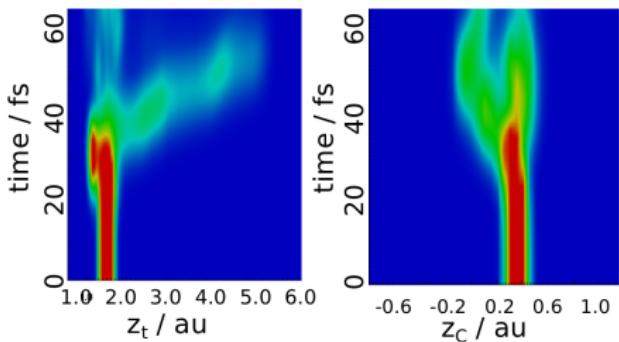
$$\Psi_j^{(21)}(\mathbf{Q}_{21}, t) = \sum_{i_1=1}^3 \sum_{i_2=1}^3 c_{i_1, i_2}^{(21, j)}(t) \Psi_{i_1}^{(22)}(\mathbf{Q}_{22}, t) \Psi_{i_2}^{(23)}(\mathbf{Q}_{23}, t)$$

$$\Psi_j^{(22)}(\mathbf{Q}_{22}, t) = \sum_{i_1=1}^6 \sum_{i_2=1}^6 a_{i_1, i_2}^{(22, j)}(t) \chi_{i_1}^{(17)}(q_{17}) \chi_{i_2}^{(18)}(q_{18})$$

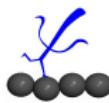


# ER dynamics with ML-MCTDH

$T_s = 0 \text{ K}$ ,  $E_{coll} = 1.0 \text{ eV}$



**N.B.:** APs are used at the grid edges

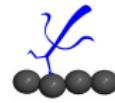
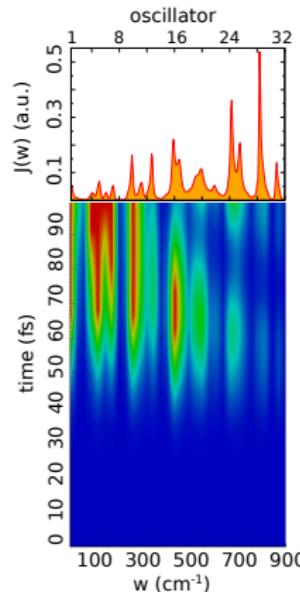


# ER dynamics with ML-MCTDH

$T_s = 0 \text{ K}$ ,  $E_{coll} = 1.0 \text{ eV}$

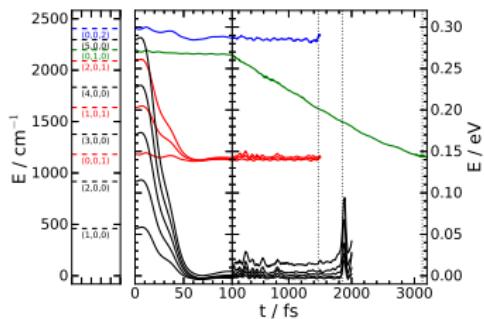
$$n(\omega_k, t) = \langle \Psi_t | a_k^\dagger a_k | \Psi_t \rangle$$

Surface ‘unpuckering’ is **strongly damped**..  
phonons form  $\sim 20 \text{ fs}$  after  $\text{H}_2$  formation

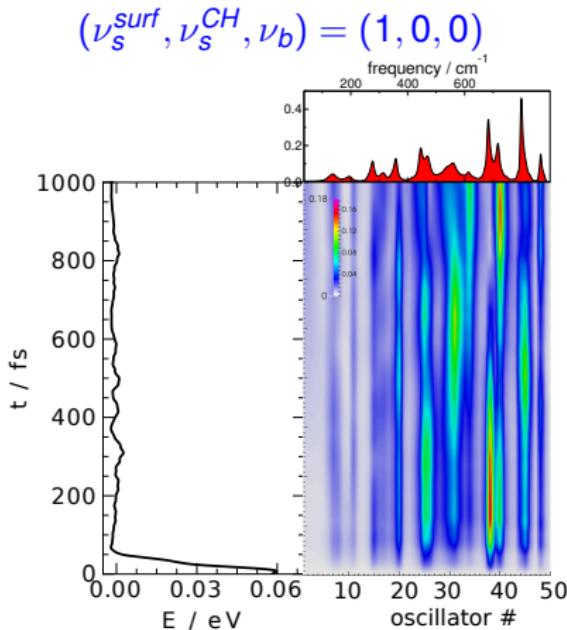


# Vibrational relaxation of CH

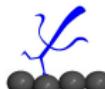
Relaxation from  $(\nu_s^{surf}, \nu_s^{CH}, \nu_b)$



$\nu_s^{surf}$  was found to relax in  $\sim 50$  fs

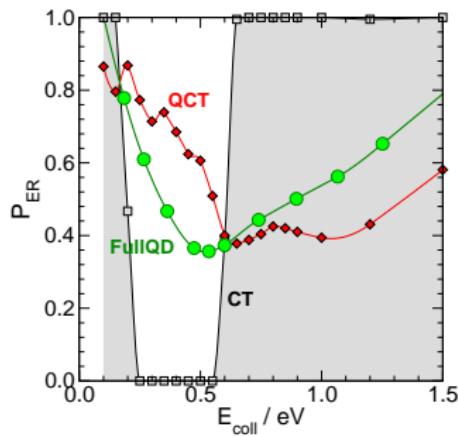


M. Bonfanti, B. Jackson, K.H. Hughes, I. Burghardt and R. Martinazzo, J. Chem. Phys. 143, 124703 (2016)

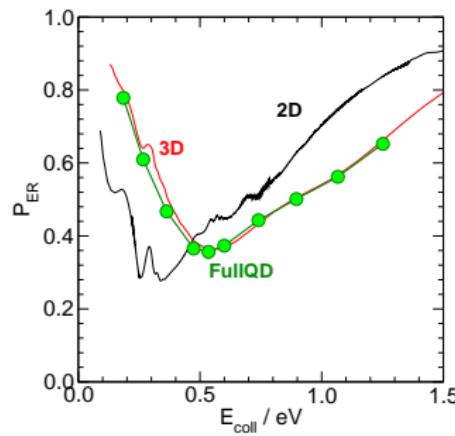


# ER dynamics: reaction probabilities

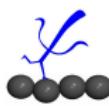
## Classical vs. Quantum



## Reduced vs. Full

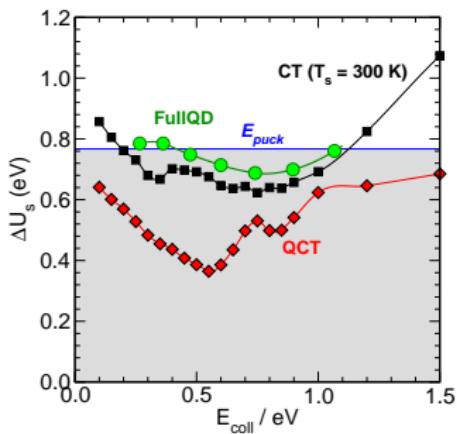


- ⇒ Initial state of the binding C atom plays a major role for  $P_{ER}$
- ⇒ Coupling to the bath plays a minor role for  $P_{ER}$

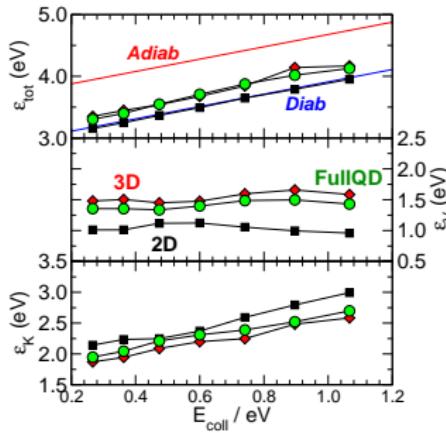


# ER dynamics: energy partitioning

**E transfer ( $U_{s,i} = E_{s,i} - E_{s,i}^0$ )**

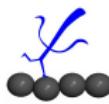


**H<sub>2</sub> partitioning**



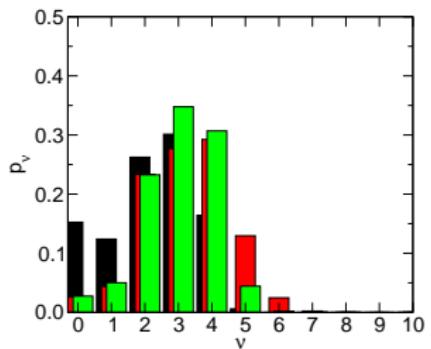
⇒ Puckering energy is left on the surface

⇒ H<sub>2</sub> energy partitioning is very close to the **diabatic** limit

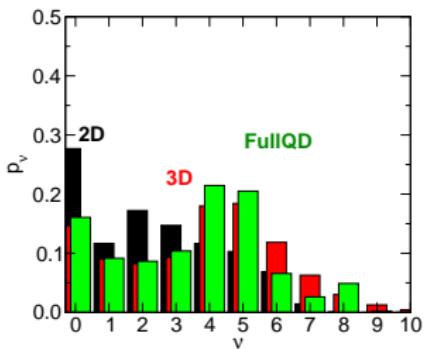


# ER dynamics: energy partitioning

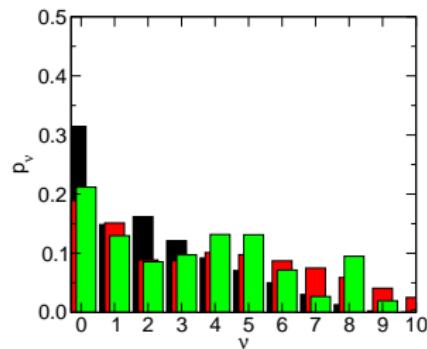
$E_{coll} = 0.27 \text{ eV}$



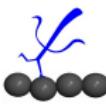
$E_{coll} = 0.74 \text{ eV}$



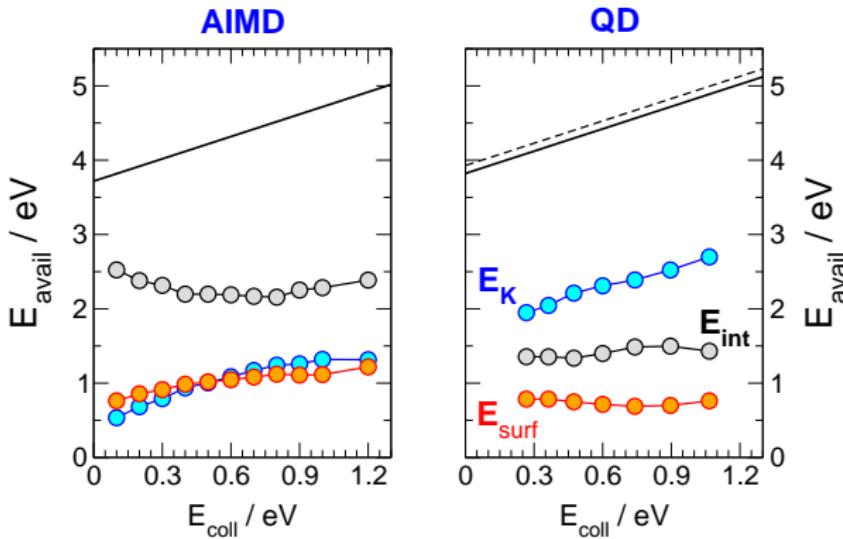
$E_{coll} = 1.07 \text{ eV}$



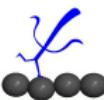
⇒ H<sub>2</sub> energy partitioning is very close to the **diabatic** limit



# ER dynamics: energy partitioning

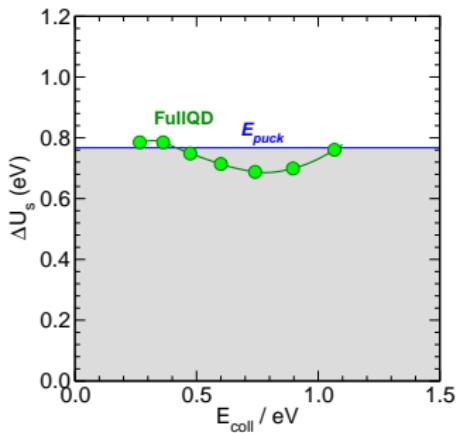


- ⇒ Non-collinear collisions and rotational excitation?
- ⇒ Correct initial state for the surface?
- ⇒ Interaction potential and electronic structure theory level?



# ER dynamics: energy partitioning

**E transfer ( $U_{s,i} = E_{s,i} - E_{s,i}^0$ )**



**Surface Heating..**

$$c_v \approx \frac{12\pi^4}{5} n k_B \left( \frac{T}{\Theta_D} \right)^3$$

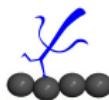
$$\Theta_D \approx 400 \text{ K}$$

$$n = \frac{4}{35.3} \times 10^{12} \mu\text{m}^{-3}$$



$$\Delta T \sim 0.2 \text{ mK}$$

for each  $\text{H}_2$  molecule formed  
on a typical  $\mu\text{m}$ -sized grain at  
 $T = 5 \text{ K}$



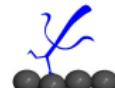
# Outline

## 1 Eley-Rideal reaction dynamics

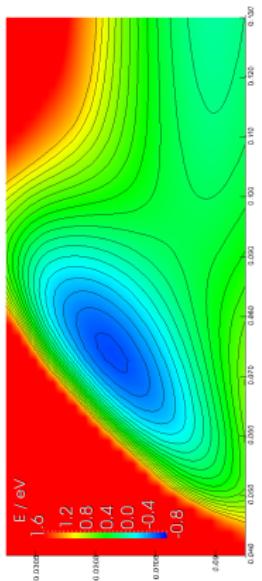
- System-bath modeling
- Full quantum dynamics

## 2 Phys-to-Chem conversion

- Flux-side correlation function
- Quantum dynamics



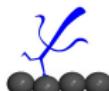
## $H_{phys} \rightarrow H_{chem}$

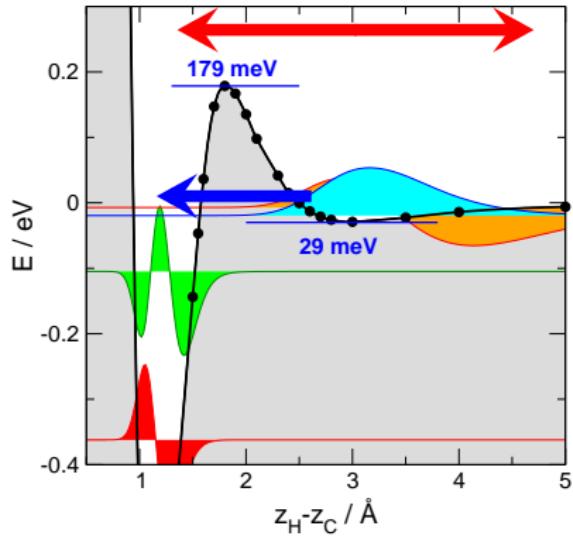


Reaction time  $k^{-1}$  may be very large ( $\sim s$ ) but..

- time scale of **cloud evolution** is extremely large
- might be comparable with the **time between arrivals** of H on grains, i.e.  $(dN/dt)^{-1} = (P_s v_H n_H \Sigma)^{-1} \sim 10^2 s$

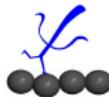
..physisorbed H atoms might find their time to convert into stable species



$H_{phys} \rightarrow H_{chem}$ 


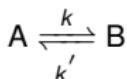
The mechanism is relevant in the **quantum regime** only.. since **desorption** would be highly favoured otherwise

$\Rightarrow k(T)$  is extremely sensitive to **dissipation** (coupling to phonons)



# Flux-side correlation function

Reaction times  $1/k$  can be very long..



**However,** if a kinetic description is possible, one only needs the dynamics up to a time  $t_P \ll k^{-1}$  when kinetic behaviour sets in..

Provided  $P_A(0) = 1$

$$\frac{dP_B}{dt}(t_P) = kP_A - k'P_B \sim k$$

i.e.  $t_P$  is the **plateau time** of

$$k(t) = \frac{dP_B}{dt}(t) = \text{Tr}(\dot{\rho}_A(0)h(t))$$

where ***h*** is the **product projection operator**



# Flux-side correlation function

The common choice

$$\rho_A = \frac{e^{-\frac{\beta H}{2}}(1-h)e^{-\frac{\beta H}{2}}}{Z_A}$$

leads to

Reactive Flux

$$k(t) = \frac{1}{Z_A} \text{Tr}(F_\beta h(t)) = \frac{1}{Z_A} C_{fs}^\beta(t)$$

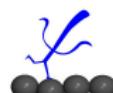
where

- $F_\beta = e^{-\frac{\beta H}{2}} F e^{-\frac{\beta H}{2}}$  is the **Boltzmannized flux operator** and  $F = \dot{h}$
- $Z_A$  is the **reagent partition function**,  $Z_A = \text{Tr}(e^{-\beta H}(1-h))$

**N.B.** When relaxing the above assumptions..

Improved Reactive Flux

$$k(t) = \frac{1}{Z_A} \frac{C_{fs}^\beta(t)}{P_A(0)+(P_A(0)-1)\frac{Z_A}{Z_B}-\left(\frac{1}{Z_A}+\frac{1}{Z_B}\right) \int_0^t C_{fs}^\beta(t') dt'}$$



# Flux-side correlation function

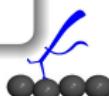
$$C_{fs}^{\beta}(t) = \text{Tr} \left( F_{\beta} e^{+i \frac{Ht}{\hbar}} h e^{-i \frac{Ht}{\hbar}} \right)$$

- $F$  is a **manageable** ('system' only) operator,  $F = \sum_{\nu} \nu | \nu \rangle \langle \nu |$
- **stochastic sampling** is possible for simple (HO-like) environments



## Boltzmann Sampling

- 1 pick up an appropriate (flux-related) **system** state  $| \nu \rangle$
- 2 pick up a **bath** state  $| \mathbf{N} \rangle = | n_1, n_2, \dots, n_k, \dots \rangle$  from  $p_{\mathbf{N}} = Z_0^{-1} e^{-\beta \hbar \sum_k n_k \omega_k}$
- 3 **build** the **initial wavepacket**  $| \nu, \mathbf{N} \rangle$  of the whole system
- 4 **propagate**  $| \nu, \mathbf{N} \rangle$  in both **imaginary** ( $\hbar \beta / 2$ ) and **real** ( $t$ ) time
- 5 compute expectation values of  $h$  over times  $t$  and **average** over the realizations



# Flux-side correlation function

$$C_{fs}^{\beta}(t) = \text{Tr} \left( F_{\beta} e^{+i \frac{Ht}{\hbar}} h e^{-i \frac{Ht}{\hbar}} \right)$$

$$F = e^{+\frac{\beta H_S}{2}} \left( \sum_v v_{\beta} |v_{\beta}^S\rangle \langle v_{\beta}^S| \right) e^{+\frac{\beta H_S}{2}} \equiv \sum_v w_v^{\beta} |v\rangle \langle v|$$

$$P_{v,\mathbf{N}}^{\beta}(t) = \langle v, \mathbf{N} | \mathcal{V}_{\tau}^{\dagger} h \mathcal{V}_{\tau} | v, \mathbf{N} \rangle \quad \tau = t - i\hbar\beta/2$$

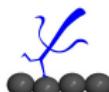
Boltzmann Sampling

$$C_{fs}^{\beta}(t) = Z_0 \sum_v w_v^{\beta} \langle\langle W_{v,\mathbf{N}}^{\beta} P_{v,\mathbf{N}}^{\beta}(t) \rangle\rangle$$

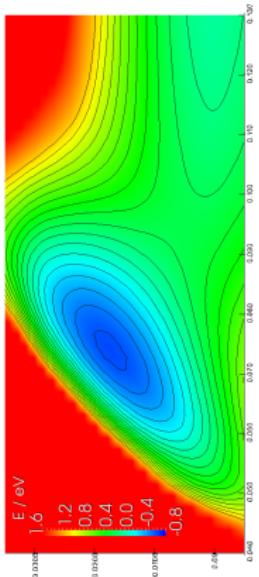
where

- $w_v^{\beta}$  are **flux weights**
- $\mathcal{V}_{\tau}$  is a **unitary** propagator in **complex time**  $\tau$
- $W_{v,\mathbf{N}}^{\beta}$  are **thermal factors** enforcing unitarity of  $\mathcal{V}_{\tau}$
- $\langle\langle .. \rangle\rangle$  is the Monte-Carlo average over  $\mathbf{N}$

MC



# The model



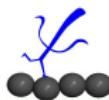
**2D reaction system coupled to a heat bath**

**Refined CH sticking potential**

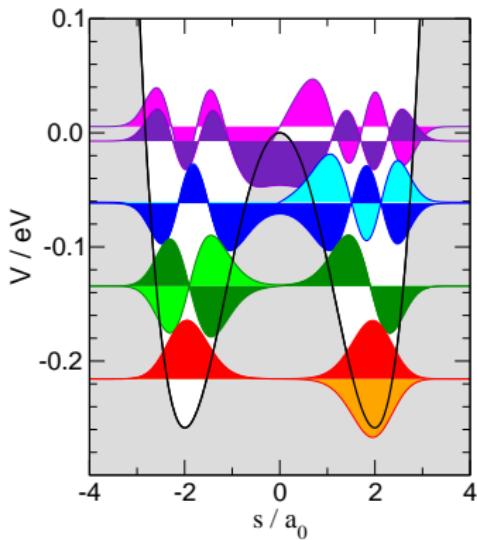
vdW-inclusive DFT calculations that reproduce the shallow physisorption well

**Coupling to the lattice via C only**  
 $J_C(\omega)$

$$H = \frac{p_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V_{CH}(z_H, z_C) + \sum_k^{N_S} \left\{ \frac{p_k^2}{2m} + \frac{m\omega_k^2}{2} \left( x_k - \frac{c_k \delta z_C}{m\omega_k^2} \right)^2 \right\}$$



# The ‘toy’ model



**1D reaction system coupled to a heat bath**

**Double well potential**

$$V_{DW}(s) = -\frac{m_H \omega_b^2}{2} s^2 + \frac{m_H^2 \omega_b^4}{16 E_b} s^4$$

$$\omega_b = 500 \text{ cm}^{-1}, E_b = 0.2585 \text{ eV}$$

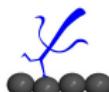
$$\Delta E_0 = 0.00108 \text{ cm}^{-1} \quad \tau_0 = \frac{\pi \hbar}{\Delta E_0} = 15.4 \text{ ns}$$

**(Quasi) Ohmic damping**

$$J(\omega) = m \omega \gamma e^{-\omega/\omega_c}$$

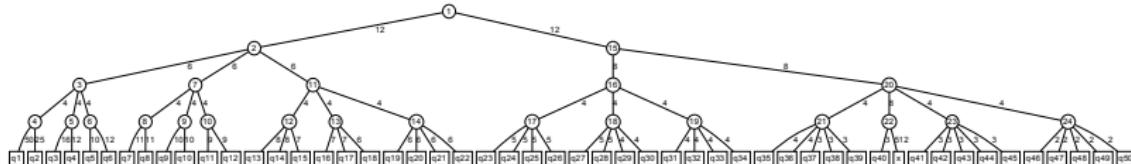
$$\gamma = 0.01 - 2.0 \omega_b$$

$$H = \frac{p^2}{2m_H} + V_{DW}(s) + \sum_k^N \left\{ \frac{p_k^2}{2m} + \frac{m\omega_k^2}{2} \left( x_k - \frac{c_k s}{m\omega_k^2} \right)^2 \right\}$$



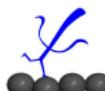
# Monte Carlo ML-MCTDH

Reasonable set-up which guarantees  $\sim 1 - 2\%$  accuracy over a wide range of temperatures and coupling strengths<sup>†</sup>



- $N = 50$  bath DoF were found sufficient for convergence w.r.t. bath size
- Number of MC realizations ( $N_{MC}$ ) range between **208** (2x8 core-Intel Xeon 2630 v3 @2.4GHz) and **1088** (on 68 core-Intel Xeon Phi7250@1.4GHz)
- $> 10,000$  wavepacket runs

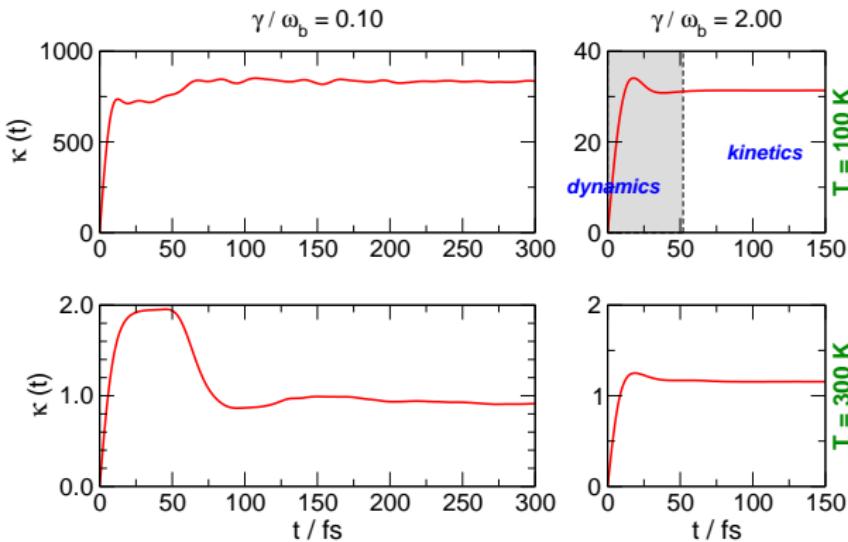
<sup>†</sup> cf. QUAPI results by M. Topaler and N. Makri, J. Chem. Phys. 101, 7500 (1994)





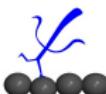
## Flux-side correlator

$C_{fs}^\beta(t)$  is **odd** and **continuous**, very short time is 'ballistic'..



$C_{fs}^\beta(t)$  does reach a **plateau** in **100-1000 fs**..  
 $t_P$  **increases** with **decreasing**  $\gamma$

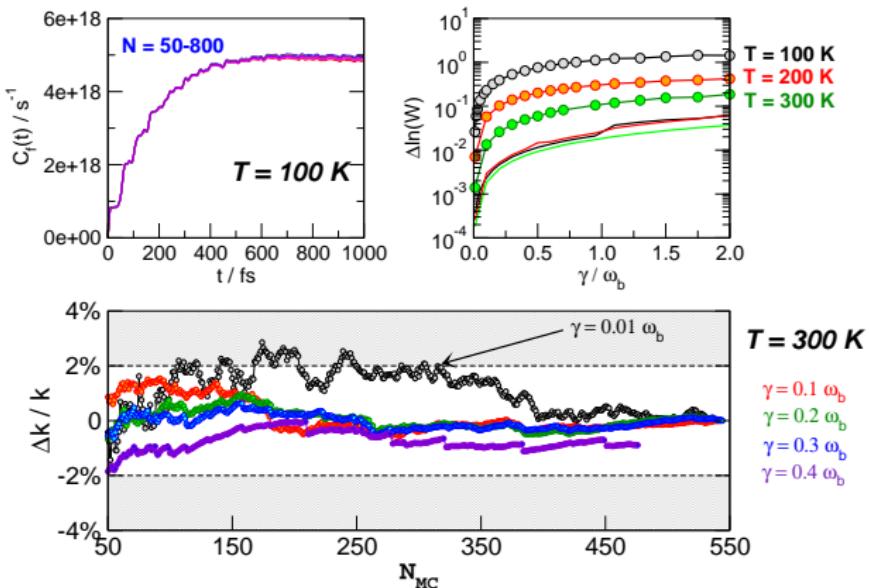
N.B.  $\kappa(t) = k(t)/k_{TST}$



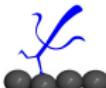
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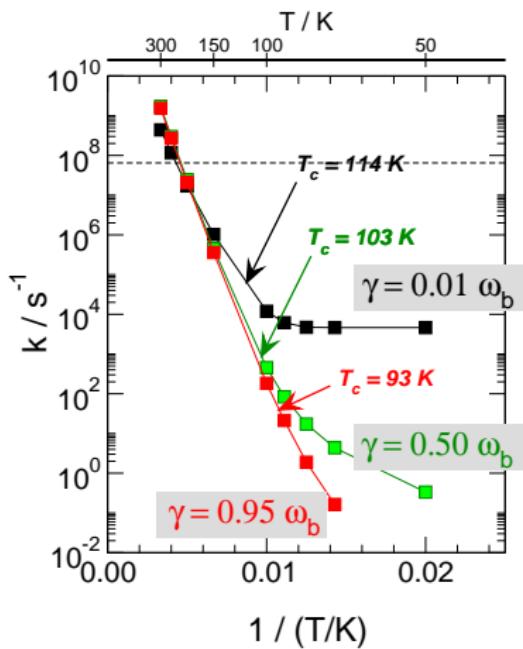
# Monte Carlo sampling



MC convergence is **uniform** over time and rather **fast**  
 MC sampling gets harder at...**low temperature**



# Temperature



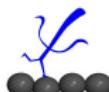
- **Cross-over temperature**  $T_c$  depends on coupling strength, roughly as†

$$T_c \sim \frac{\hbar \tilde{\omega}_b}{2\pi k_B} \quad (\nu_\beta \tilde{\tau}_b \sim \lambda_\beta)$$

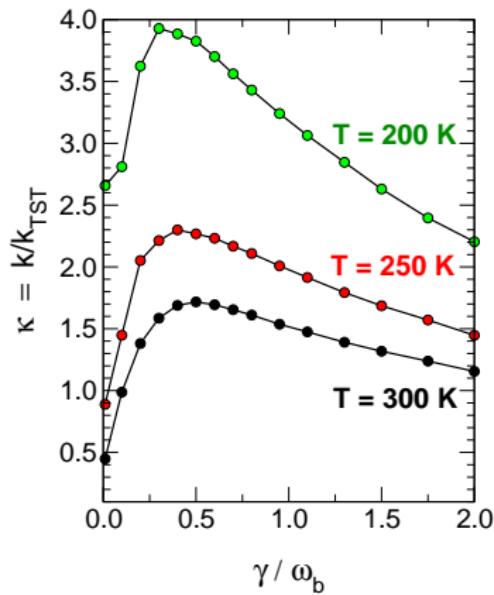
$\tilde{\omega}_b$ : frequency of the unstable mode in the coupled system

- **Low  $T$**  results are extremely sensitive to damping
- **High  $T$**  results have non-trivial dependence on  $\gamma$

† P. Hanggi, H. Grabert, G.-L. Ingold, and U. Weiss, Phys. Rev. Lett. 55, 761 (1985); H. Grabert and U. Weiss, Phys. Rev. Lett. 53, 1787 (1984)

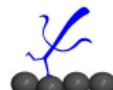


# Kramers' turnover

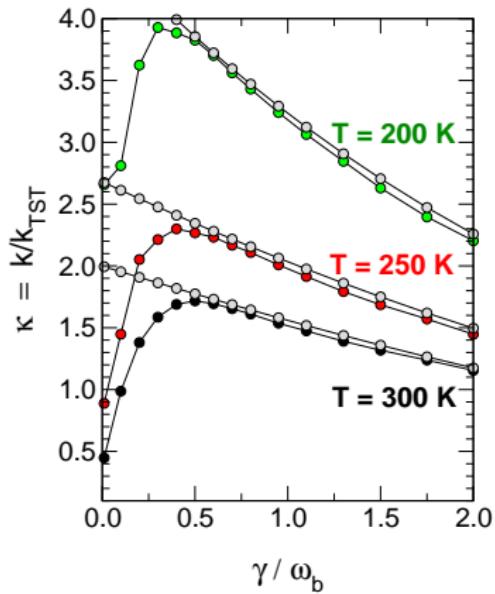


## Classical (activated) dynamics

- Energy diffusion at small friction
- Spatial diffusion at large friction
- Turnover friction decreases with decreasing  $T$



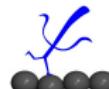
# Kramers' turnover



## Classical (activated) dynamics

Multidimensional transition state theory with  
**quantum corrections**<sup>†</sup>  
 ('quantum Grote-Hynes theory')  
 works fine in the **spatial diffusion** regime

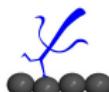
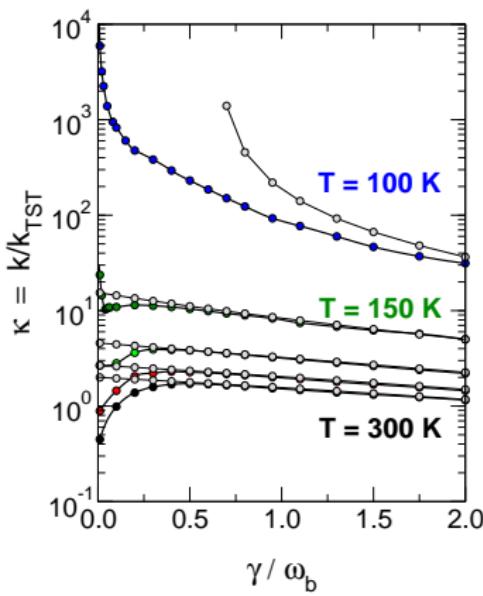
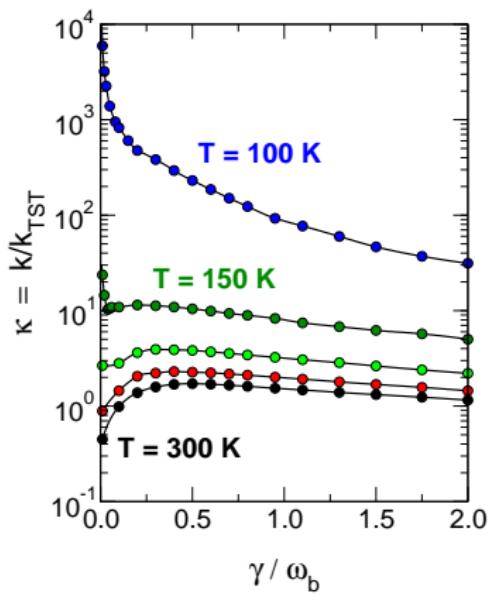
<sup>†</sup>P. G. Wolynes, Phys. Rev. Lett. 47, 968 (1981)



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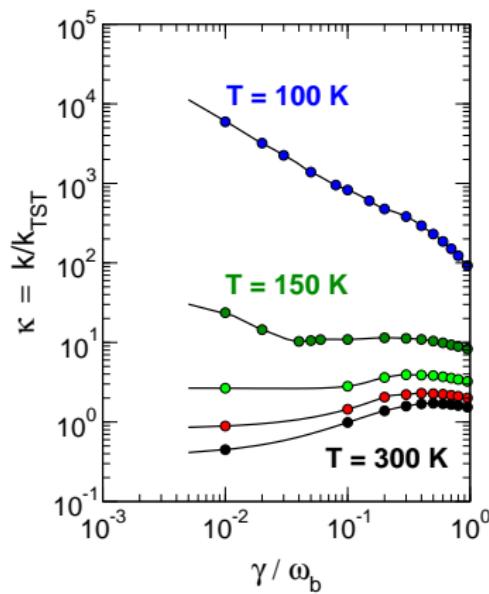
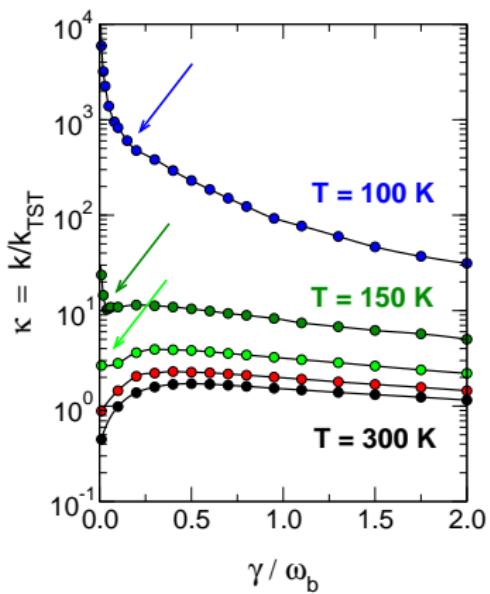
# Beyond Kramers' turnover



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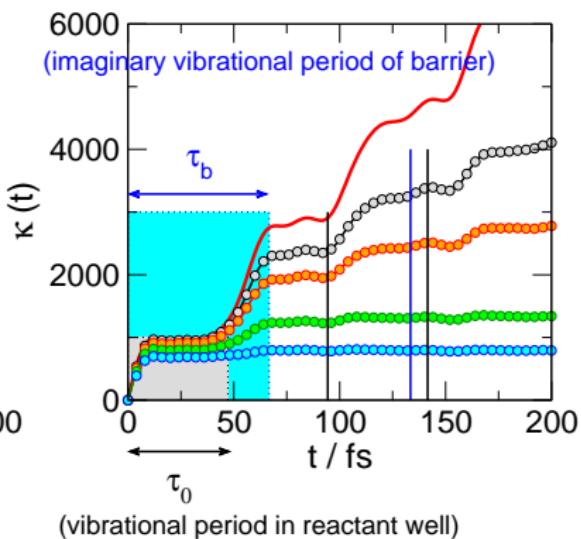
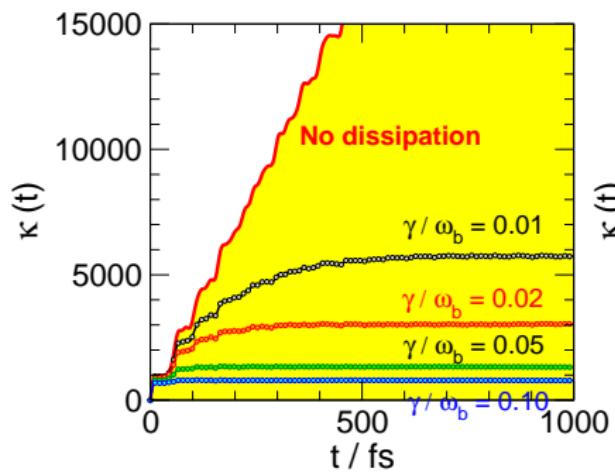
# Beyond Kramers' turnover



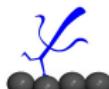
Low  $T$ -weak coupling regime..and emergence of quantum behaviour



# Beyond Kramers' turnover

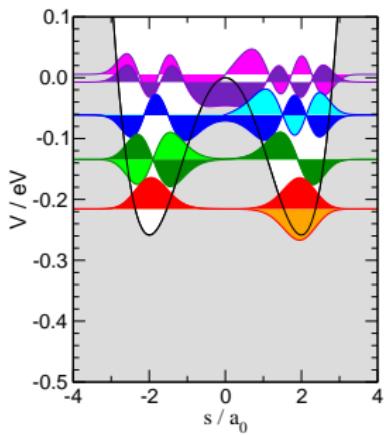


Low  $T$ -weak coupling regime..and emergence of rate dynamics

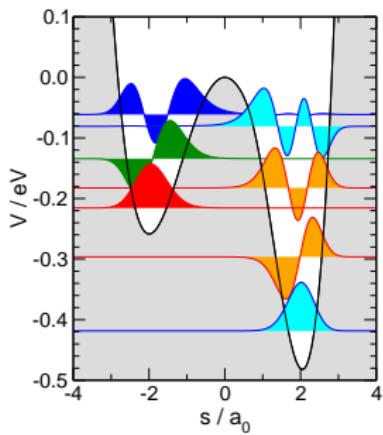


# Outlook

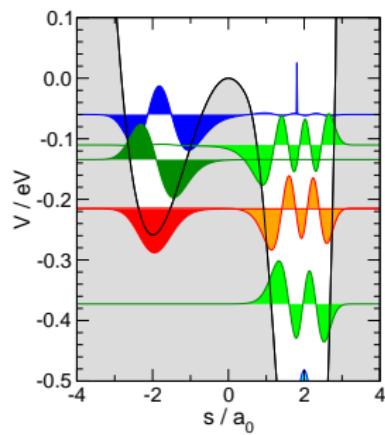
**Resonant**



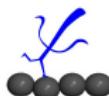
**Off-resonant**



**Quasi-resonant**



..for a given barrier ( $E_b, \omega_b$ ) and well ( $\omega_0$ ) dynamics



# Outlook

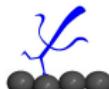
## Random Phase Wavefunctions

Proved to be very good for computing **averages**.

For **trace expressions** ..

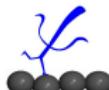
$$\begin{aligned}\text{Tr}(A) &= \sum_k \langle \Phi_k | A | \Phi_k \rangle \\ |\Psi(\theta_1, \theta_2, \dots, \theta_k, \dots)\rangle &= \sum_k e^{i\theta_k} |\Phi_k\rangle \\ \langle \Psi(\Theta) | A | \Psi(\Theta) \rangle &= \sum_{k,k'} e^{i(\theta_k - \theta_{k'})} \langle \Phi_{k'} | A | \Phi_k \rangle \\ &\quad \Downarrow \text{av. over } \Theta \\ \overline{\langle \Psi(\Theta) | A | \Psi(\Theta) \rangle} &\equiv \text{Tr}(A)\end{aligned}$$

- ⇒ The accuracy is determined by the length of the CI expansion
- ⇒ ML-MCDTH tree needs to be unreasonably large from the beginning
- ..better **combining** MC sampling with RPWs



# Summary

- **Lattice motion** can be described in a **full quantum** dynamical setting, provided it takes a simple (HO-like) form
- **System-bath partitioning** is crucial to have a reasonable (state-independent) memory kernel
- **Eley-Rideal**  $\text{H}_2$  formation is close to the **diabatic** limit and **heats up** the grain
- **Surface temperature** and **dissipative** effects in **reaction rates** can be investigated with efficient **stochastic sampling** schemes at a **full quantum** level



# Acknowledgements

**Marta Pasquini**



Simone Casolo



**Matteo Bonfanti**



<http://users.unimi.it/cdtg>

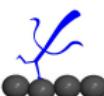
**Didier Lemoine**

**Bret Jackson**

**Irene Burghardt**

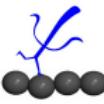
**Keith Hughes**

**Peter Saalfrank**

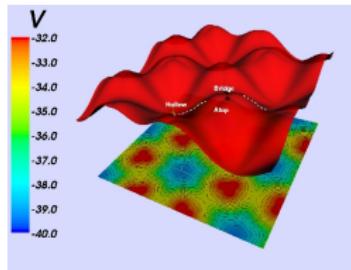
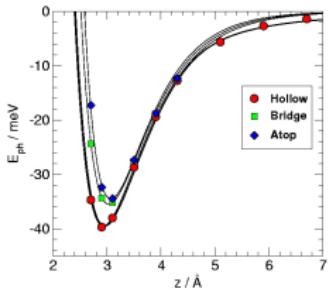


# Acknowledgements

**Thank you for your attention!**



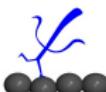
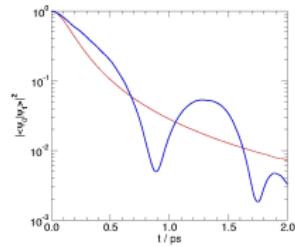
# Physisorption



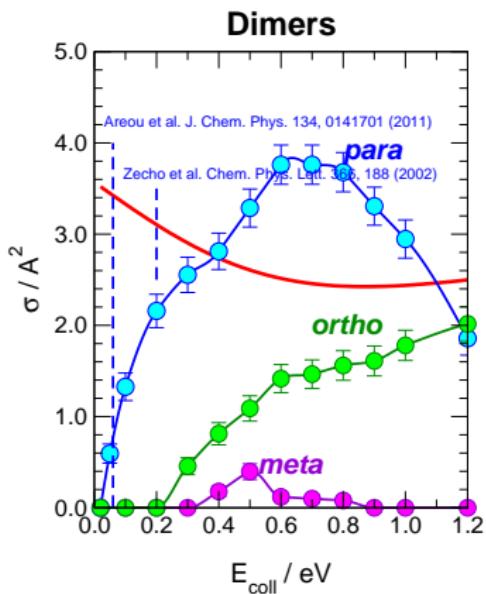
- HF-MP2 / aug-cc-pVDZ + BFs / CP-BSSE
- $D_e = 39.5 \text{ meV}$  vs  $D_e(\text{exp}) = 39.2 \pm 0.5 \text{ meV}$
- $E_{barr} = 4.0 \text{ meV}$ ,  $D_{T=0K} = 1.7 \cdot 10^{-4} \text{ cm}^2 \text{s}^{-1}$

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)



# Eley-Rideal: AIMD

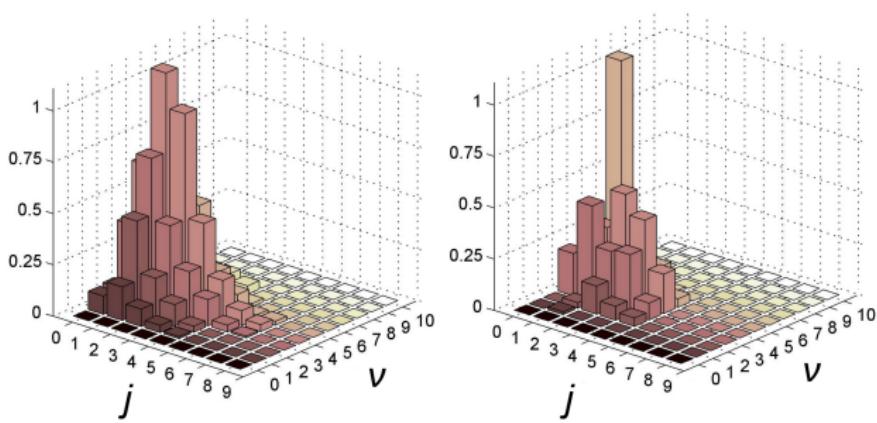


- Competition between reaction and *para*-dimer formation
- Dynamic threshold to *ortho*-dimer formation

..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)

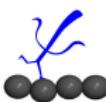
# Eley-Rideal: AIMD



$T_g = 300K, T_s = 15K$

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

AIMD for H/D @ 0.025 eV



# System-bath modeling: our strategy

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

↓

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

↓

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

↓

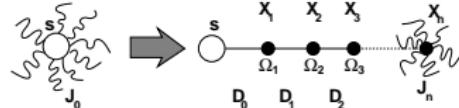
$$S(z) = iz\tilde{C}^>(z) + C(0) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\omega \tilde{C}(\omega)/2}{\omega - z} d\omega$$

↓

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

↓

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

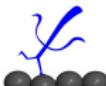


$$D_C^2 = \frac{2m_C}{\pi} \int_0^\infty J_H(\omega) \omega d\omega$$

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

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

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



# Quantum bath

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

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

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

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

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  $\Omega_k$

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

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

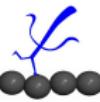
$$V = \omega_0^2 |0\rangle \langle 0| - |\zeta\rangle \langle 0| - |0\rangle \langle \zeta| + \int d\omega \omega^2 |\omega\rangle \langle \omega| \text{ where } |\zeta\rangle = \frac{1}{m} \int d\omega c(\omega) |\omega\rangle$$

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

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

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

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



# Monte Carlo sampling

$$F = e^{+\frac{\beta H_S}{2}} \left( \sum_v v_\beta |v_\beta^S\rangle \langle v_\beta^S| \right) e^{+\frac{\beta H_S}{2}} \equiv \sum_v w_v^\beta |v\rangle \langle v|$$

$$C_{fs}^\beta(t) = \sum_{v,\mathbf{N}} w_v^\beta \langle v, \mathbf{N} | e^{-\frac{\beta H}{2}} e^{+i\frac{Ht}{\hbar}} h e^{-i\frac{Ht}{\hbar}} e^{-\frac{\beta H}{2}} |v, \mathbf{N}\rangle$$



$$e^{-\frac{\beta H}{2}} |v, \mathbf{N}\rangle = e^{-\int_0^{\beta/2} \epsilon(\lambda) d\lambda} |\phi_{v,\mathbf{N}}(\beta/2)\rangle \quad |\Psi_{v,\mathbf{N}}^{t,\beta}\rangle = e^{-i\frac{Ht}{\hbar}} |\phi_{v,\mathbf{N}}(\beta/2)\rangle$$

$$\left[ -\frac{d|\phi\rangle(\lambda)}{d\lambda} = (H - \epsilon_\lambda) |\phi(\lambda)\rangle \quad \epsilon_\lambda = \frac{\langle \phi | H \phi \rangle}{\langle \phi | \phi \rangle} \right]$$

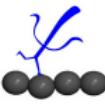
$$W_{v\mathbf{N}}^\beta = e^{-2 \int_0^{\beta/2} \epsilon(\lambda) d\lambda + \beta E_{\mathbf{N}}}$$



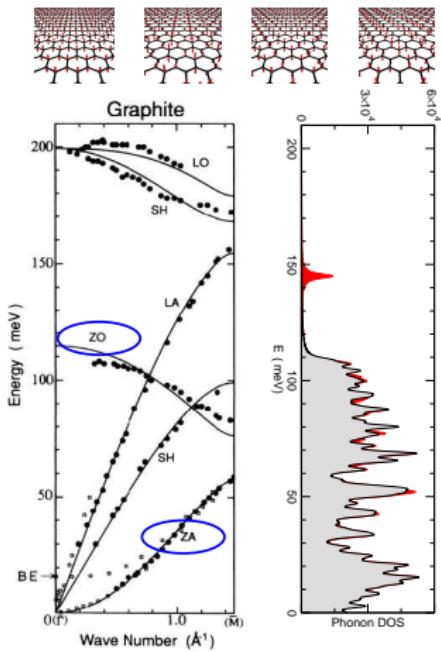
$$C_{fs}^\beta(t) = Z_0 \sum_{v,\mathbf{N}} \frac{e^{-\beta E_{\mathbf{N}}}}{Z_0} w_v^\beta W_{v,\mathbf{N}}^\beta \langle \Psi_{v,\mathbf{N}}^{t,\beta} | h | \Psi_{v,\mathbf{N}}^{t,\beta} \rangle$$



$$C_{fs}^\beta(t) = Z_0 \sum_v w_v^\beta \langle\langle W_{v,\mathbf{N}}^\beta P_{v,\mathbf{N}}^\beta(t) \rangle\rangle$$



# Environment: $J(\omega)$



## CH atomistic model for MD<sup>[1]</sup> CH system

Plane-wave DFT PW91 on a dense  $x_H, z_C$  grid<sup>[2]</sup>

### Lattice

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

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

### SO-like Coupling

$$\begin{aligned} V_{CH}(x_H, z_C, q^{eq}) &\Rightarrow \\ V_{CH}(x_H, y_H, z_H - Q, z_C - Q, q^{eq}) - \frac{k_C}{2}(z_C - Q)^2 \\ Q &= (z_1 + z_2 + z_3)/3 \end{aligned}$$

[1]J. Kerwin and B. Jackson, *J. Chem. Phys.* 128, 084702 (2008)  
[2]J. Kerwin, X. Sha and B. Jackson, *J. Phys. Chem. B*, 110, 18811 (2006)

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