

# Bond-selective chemical reactivity from first principles: methane on metallic surfaces

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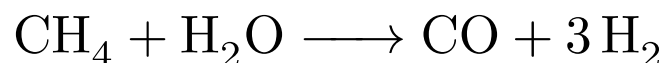
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# Reactivity of methane on metallic surfaces

## Motivation

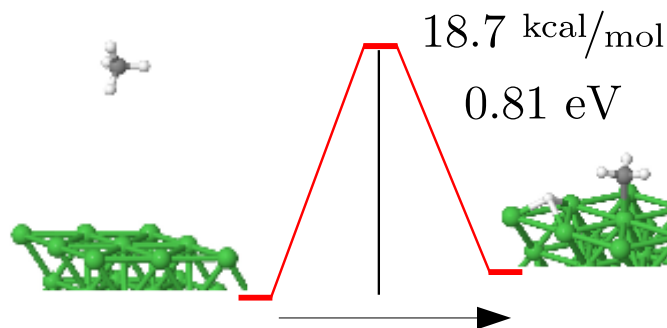
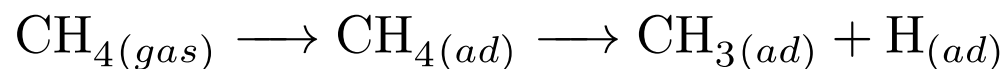
In many technologically relevant applications are involved chemical reactions of gases on metallic surfaces used as catalyst

- Catalytic hydrogen ( $\text{H}_2$ ) production from steam methane ( $\text{CH}_4$ ) reforming, (standard procedure for commercial hydrogen)



In the presence of a solid catalyst, full decomposition of the reactants on its surface and recombination of the products.

**Rate limiting step:** adsorption and cleavage of first C-H bond onto the metallic catalyst

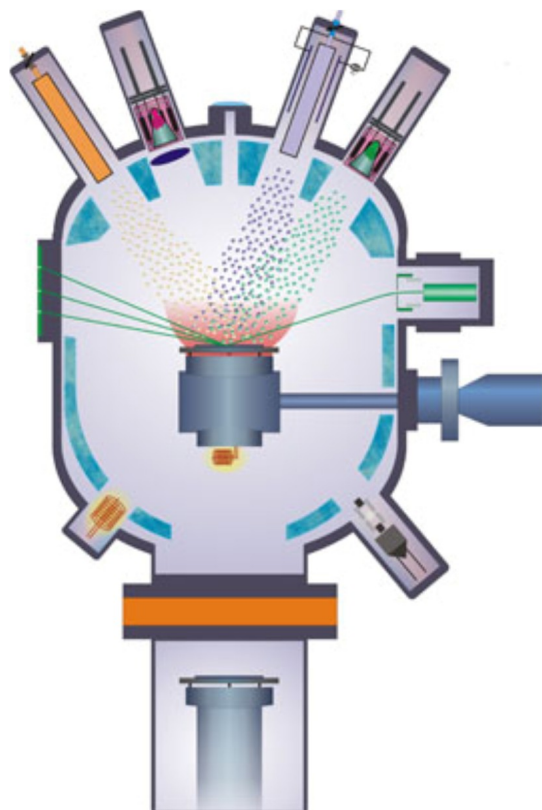
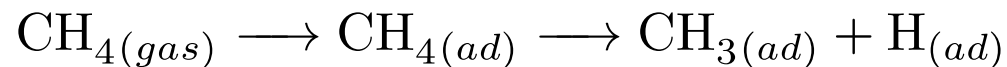


- The cleavage of the C-H bond in vacuum requires 4.5 eV for that reason catalysts are used!

# Reactivity of methane on metallic surfaces

## Molecular beam experiments

A lot of effort is made to elucidate mechanisms to enhance this elementary reaction



- Beam of molecules with highly controlled states:
  - Incidence direction
  - Initial kinetic energy  $E_i$
  - Initial vibrational state  $\nu_k$
  - Well characterized metallic surface
- Goal:
  - Rule out how initial conditions of the molecules affect reactivity
  - Find optimal conditions
  - Selectivity (in bond to break) and control the outcome of the reaction
- These highly controlled state-of-the-art experiments are a perfect suite for comparison with a theoretical treatment

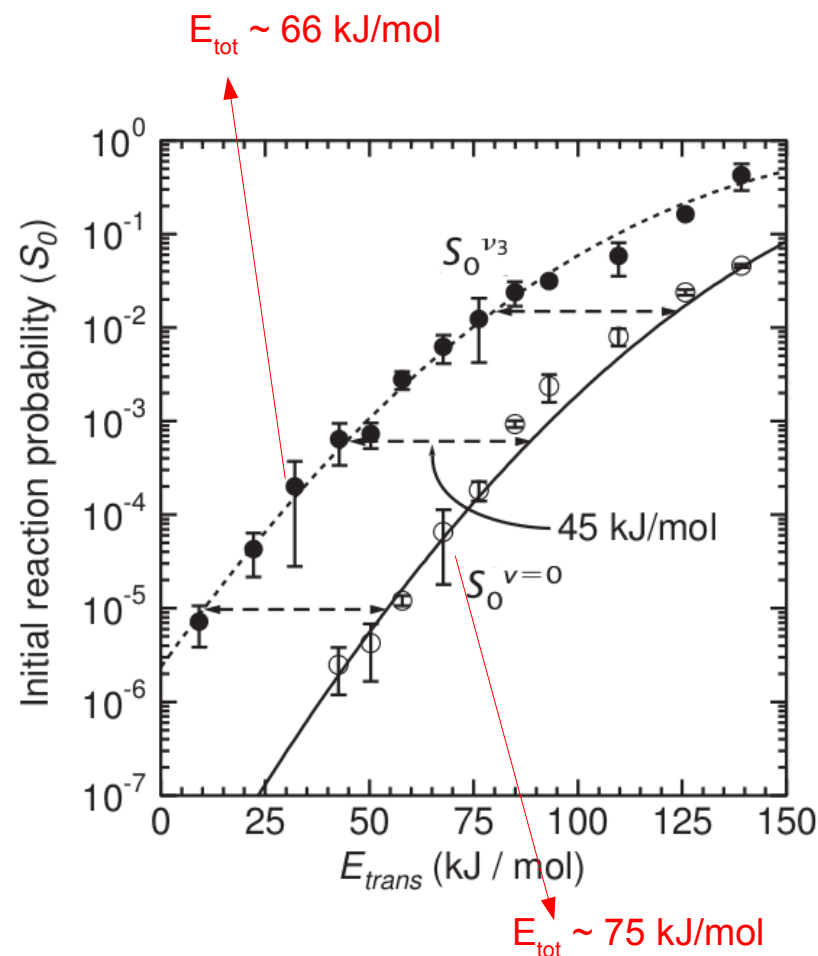
# Reactivity of methane on metallic surfaces

Molecular beam experiments: results for CH<sub>4</sub> in Ni(111)

## Preference for Vibrational over Translational Energy in a Gas-Surface Reaction

R. R. Smith, D. R. Killelea, D. F. DelSesto, A. L. Utz

State-resolved gas-surface reactivity measurements revealed that vibrational excitation of  $\nu_3$  (the antisymmetric C-H stretch) activates methane dissociation more efficiently than does translational energy. Methane molecules in the vibrational ground state require 45 kilojoules per mole (kJ/mol) of translational energy to attain the same reactivity enhancement provided by 36 kJ/mol of  $\nu_3$  excitation. **This result contradicts a key assumption underlying statistical theories of gas-surface reactivity** and provides direct experimental evidence of the central role that vibrational energy can play in activating gas-surface reactions.



- Sticking probability  $S_0$  resolved in initial kinetic energy and vibrational states

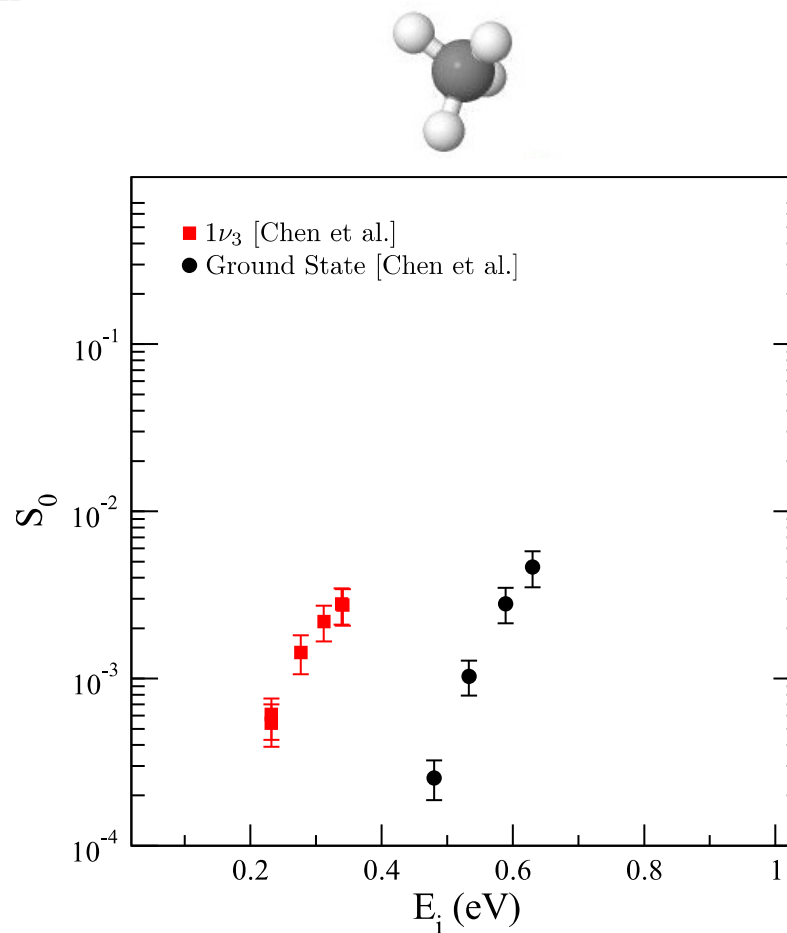
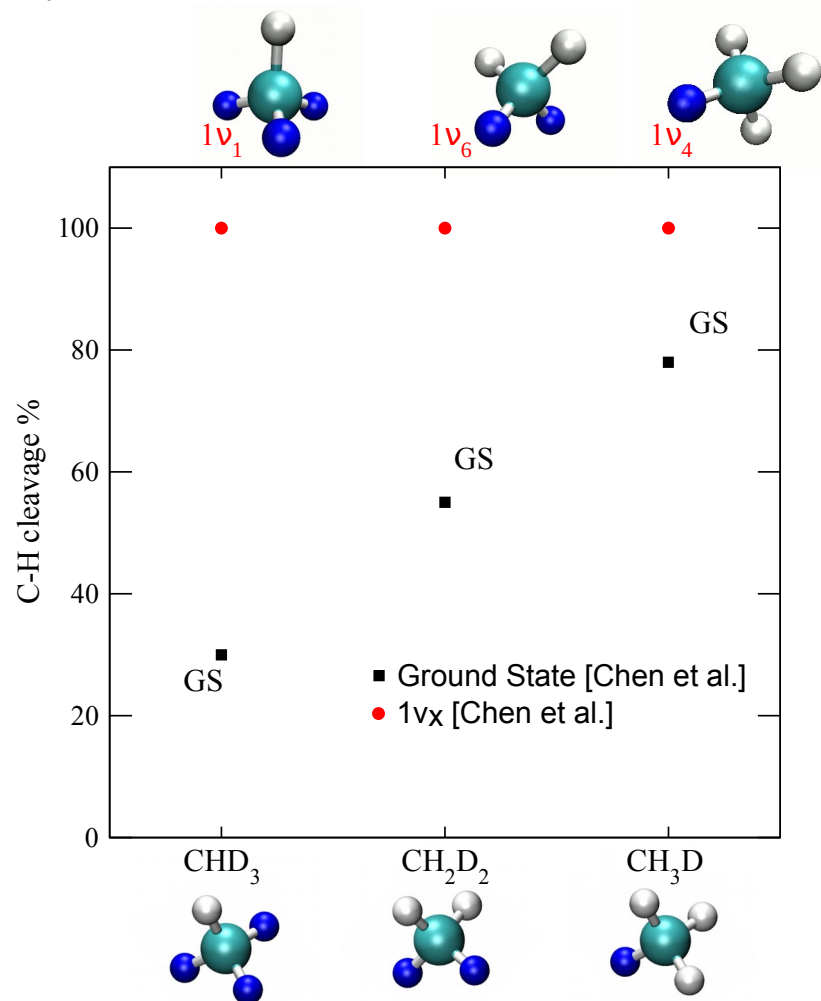
# Reactivity of methane on metallic surfaces

Molecular beam experiments: results for CH<sub>4</sub> on Pt(111)

## Vibrationally bond-selected chemisorption of methane isotopologues on Pt(111) studied by reflection absorption infrared spectroscopy†

Li Chen,<sup>a</sup> Hirokazu Ueta,<sup>a</sup> Régis Bisson<sup>b</sup> and Rainer D. Beck<sup>\*a</sup>

*Faraday Discuss.*, 2012, 157, 285–295



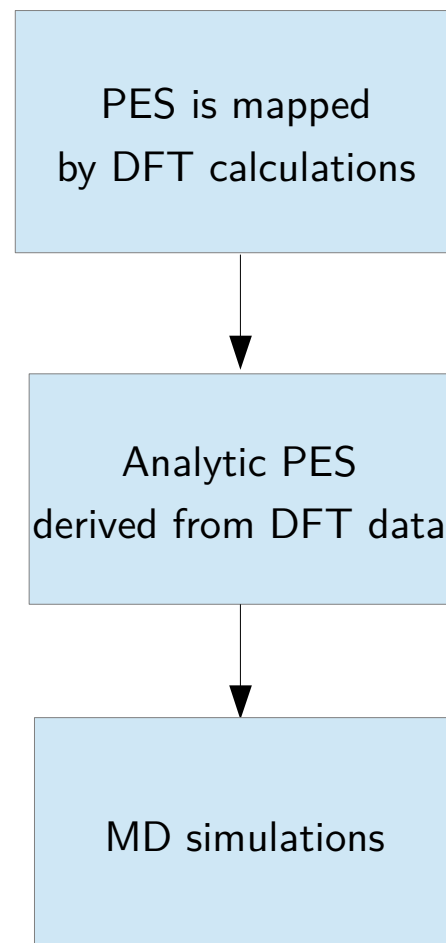
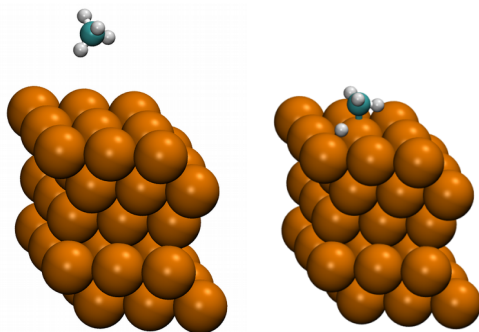
Chen et al., *Rev. Sci. Instrum.* **84**, pp. 053902 (2013)

# Reactivity of methane on metallic surfaces

## Theoretical treatment

### Bottom-up approach

- DFT calculations to determine interatomic interactions  
Find minimum energy pathways connecting gas-phase CH<sub>4</sub> with dissociated species.  
Characterize the critical regions of the Potential Energy Surface (Transition States).
- Build a continuous representation of the PES  
Develop force field that describe bond breaking
- Run the reaction dynamics simulations



# Reactivity of methane on metallic surfaces

## DFT modelling: CH<sub>4</sub> on Pt(111)

- Calculations with VASP, plane waves basis DFT code.
- The system is treated with the supercell approach by periodically repeating a big unit cell in 3D
- An ideal Pt(111) surface is assumed

- Setup:

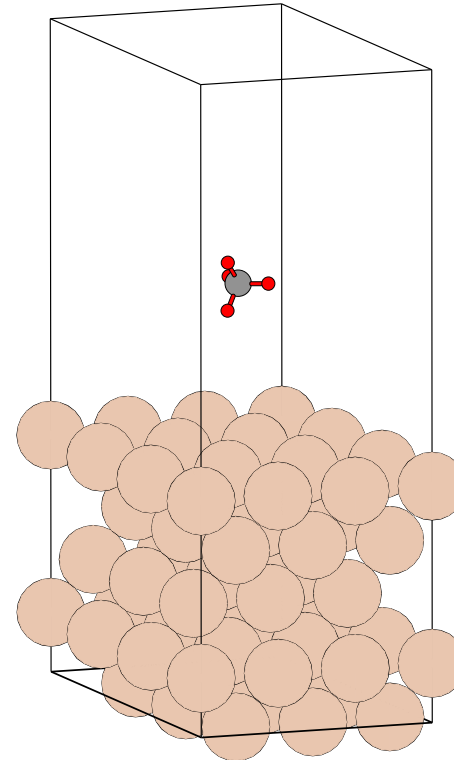
PBE GGA

PAW pseudopotentials

3 × 3 unit cell

Five layers of surface atoms

k-points sampling: 5×5×1



# Reactivity of methane on metallic surfaces

## Model for the PES

Challenge: we need a force field able to describe the bonded interactions but also allowing these bonds to be cleaved

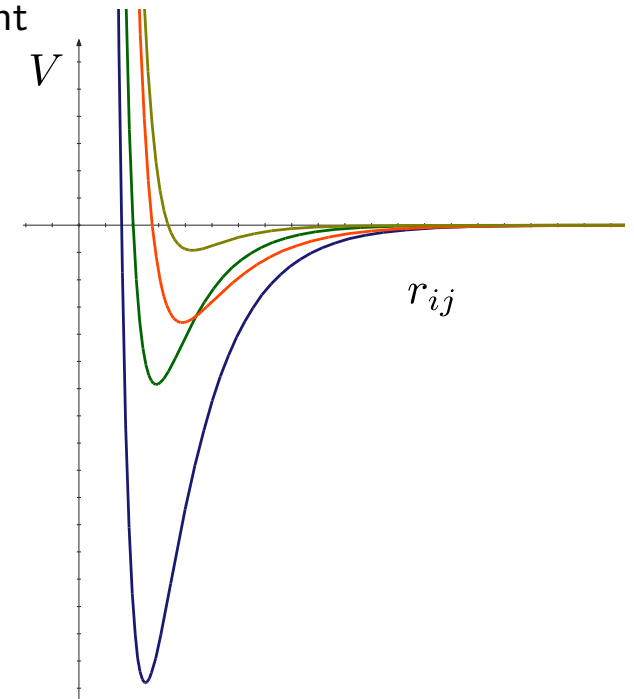
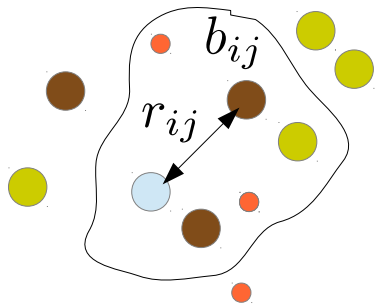
**Reactive force field** based on the Tersoff proposal [1]

- The bonding between two species is affected by its chemical environment

The more coordinated the less strong

Proper model for covalent and metallic bonding

$$V^{\text{RFF}} = \sum_{i,j} [V^R(r_{ij}) - b_{ij}V^A(r_{ij})]$$





# Reactivity of methane on metallic surfaces

## Model for the PES: potential development

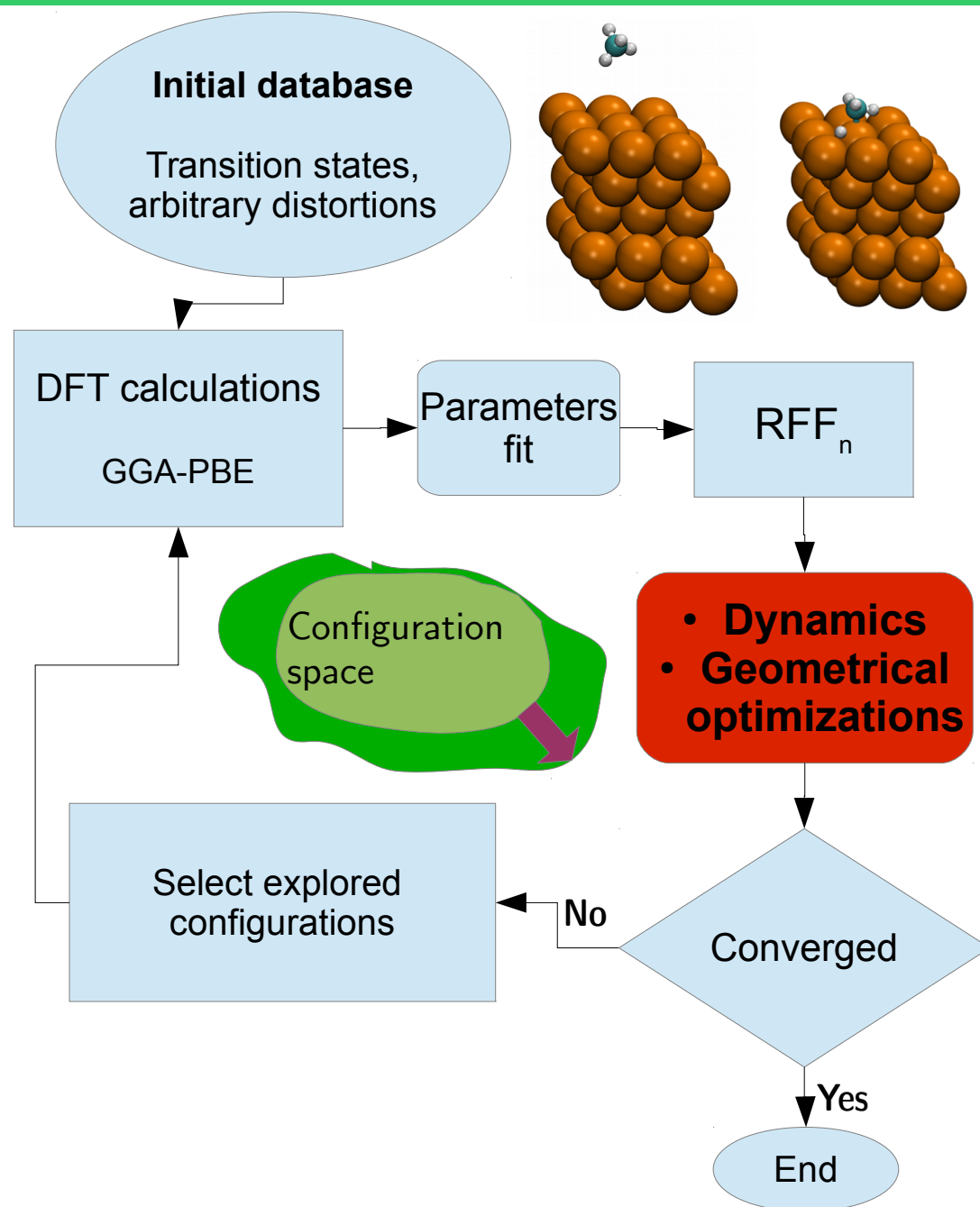
The analytic form of the RFF for the CH<sub>4</sub>/Pt(111) system presents 77 free parameters

Least squares fitting of total energies using a Levenberg-Marquardt algorithm

$$\chi^2(a, b, \dots) = \sum_i^{N_{\text{conf}}} \omega_j (V_j^{\text{DFT}} - V_j^{\text{RFF}})^2$$

It is controlled not just the least square deviation, but also to have a proper description of critical points of the PES (transition states, normal modes)

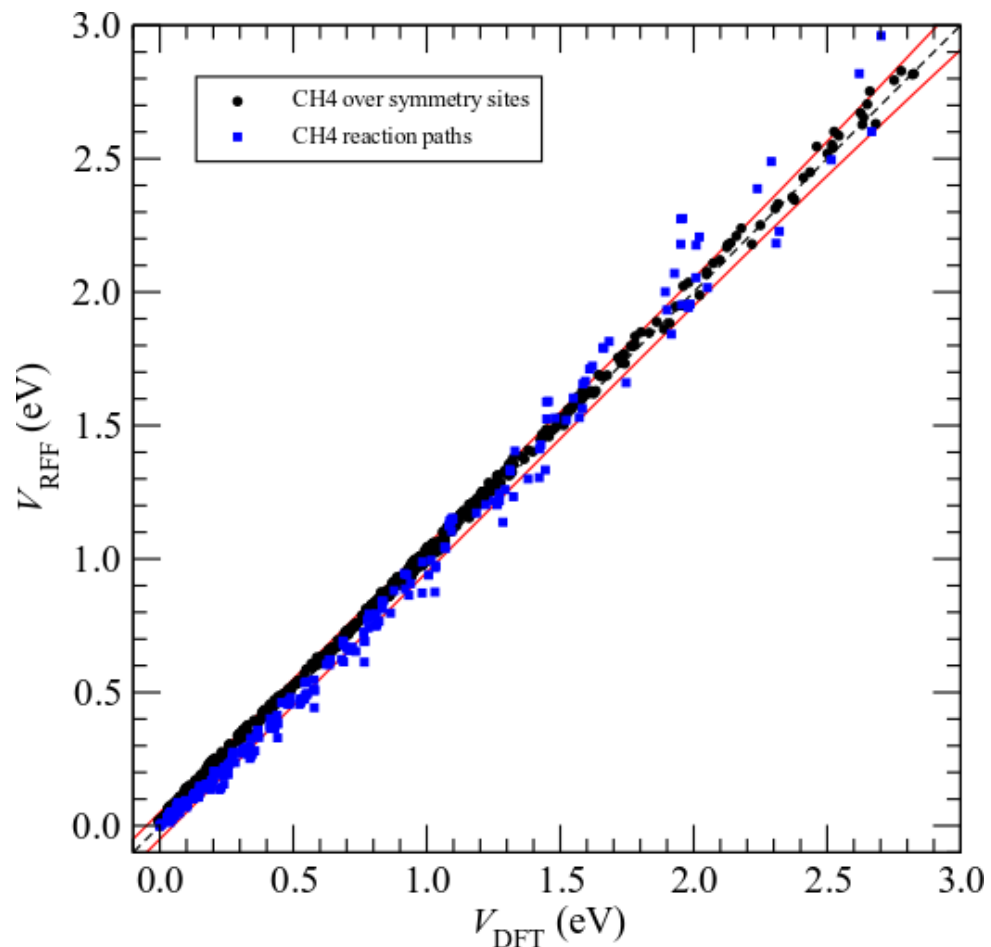
When the database grows is converged RFF vs. DFT differ in  $\approx 0.1 \text{ eV} = 2 \text{ kcal/mol}$



# Reactivity of methane on metallic surfaces

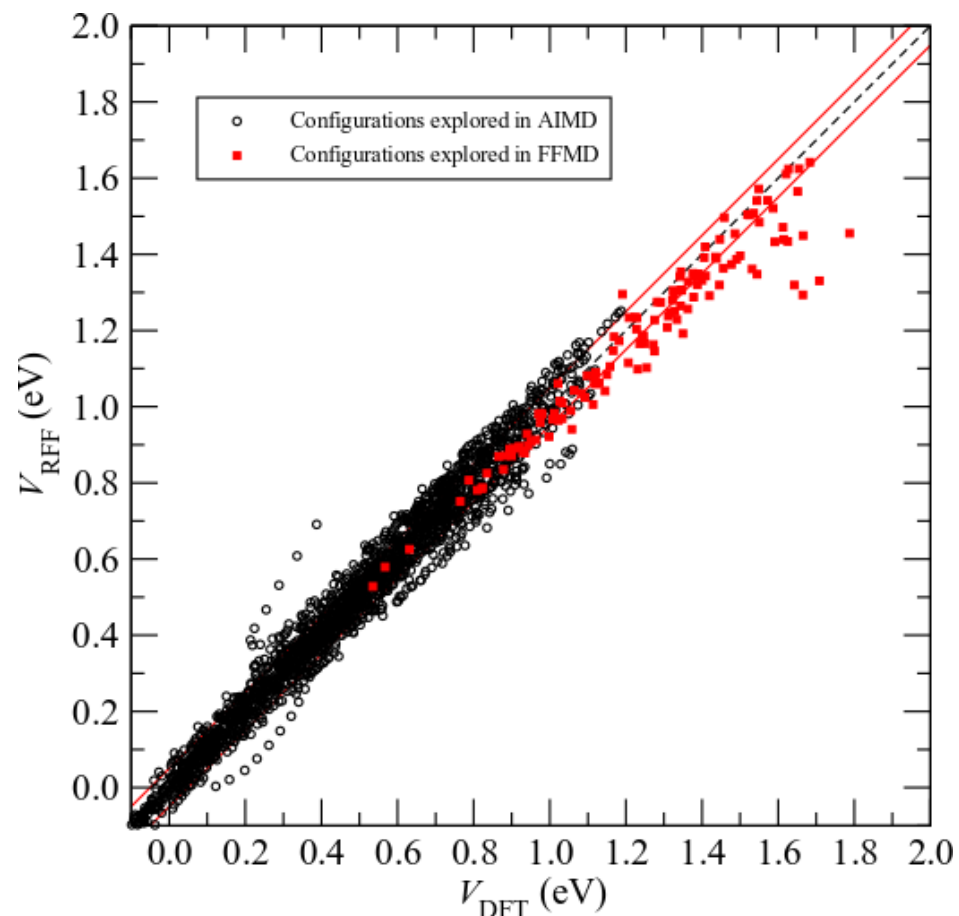
## Model for the PES: potential development

Total energies with the final potential vs DFT ( $\sim 10000$  configurations in the final database)



- CH4 approaching the surface on different sites
- CH4 reaction pathways on the top site

Red lines  $\pm 0.05$  eV

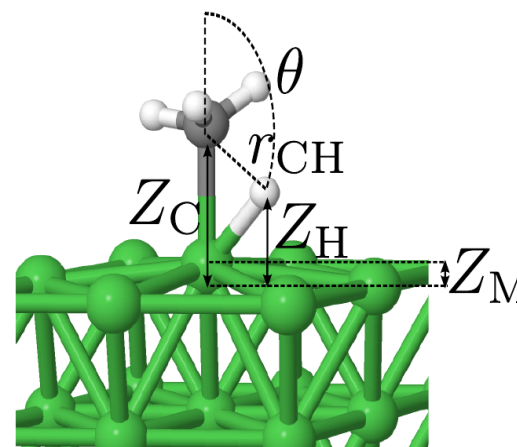
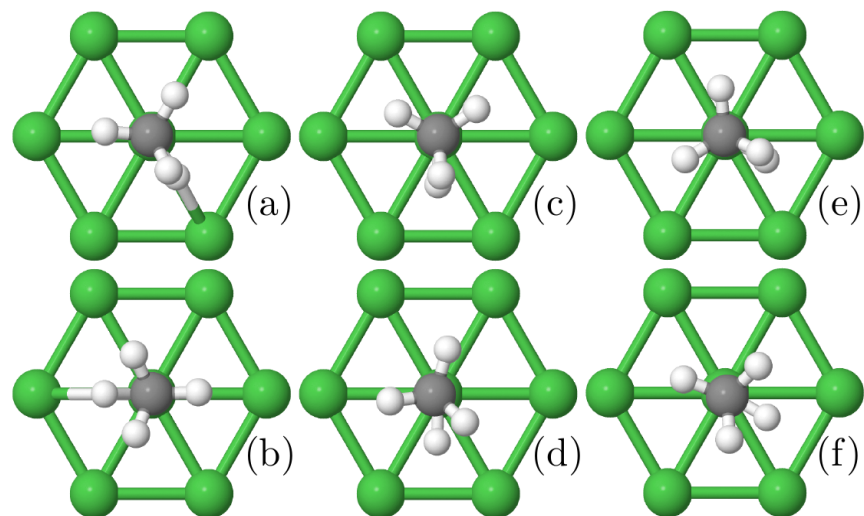


- Configurations explored with AIMD
- Configurations explored with preliminaries RFF

# Reactivity of methane on metallic surfaces

## Model for the PES: potential development

Transition states: Critical points of PES



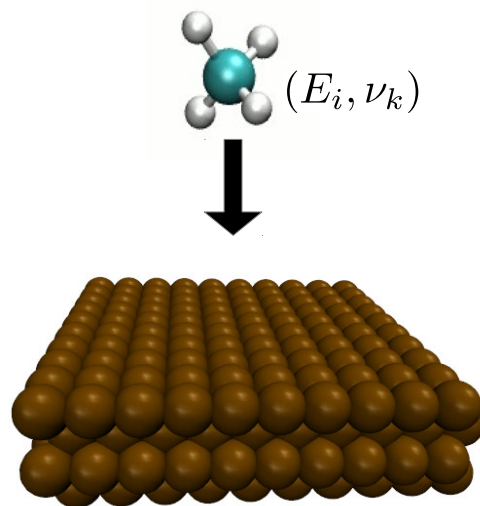
	DFT					RFF					$\Delta E_b^{\text{rel}}$ (eV)
	$d_{\text{CM}}$ (Å)	$r_{\text{CH}}$ (Å)	$\theta$ (°)	$\Delta Z_{\text{M}}$ (Å)	$E_b$ (eV)	$d_{\text{CM}}$ (Å)	$r_{\text{CH}}$ (Å)	$\theta$ (°)	$\Delta Z_{\text{M}}$ (Å)	$E_b$ (eV)	
a	2.21	1.50	131	0.17	0.68	2.19	1.46	132	0.18	0.62	0.06
b	2.23	1.47	132	0.16	0.69	2.22	1.38	134	0.16	0.63	0.06
c	2.20	1.52	132	0.17	0.71	2.21	1.42	133	0.16	0.63	0.08
d	2.22	1.50	133	0.18	0.72	2.22	1.40	133	0.16	0.65	0.07
e	2.21	1.51	133	0.17	0.69	2.20	1.45	132	0.18	0.62	0.07
f	2.23	1.48	135	0.16	0.71	2.22	1.42	131	0.19	0.63	0.08

# Reactivity of methane on metallic surfaces

## Simulations of reaction dynamics

### Quasiclassical approach [1]

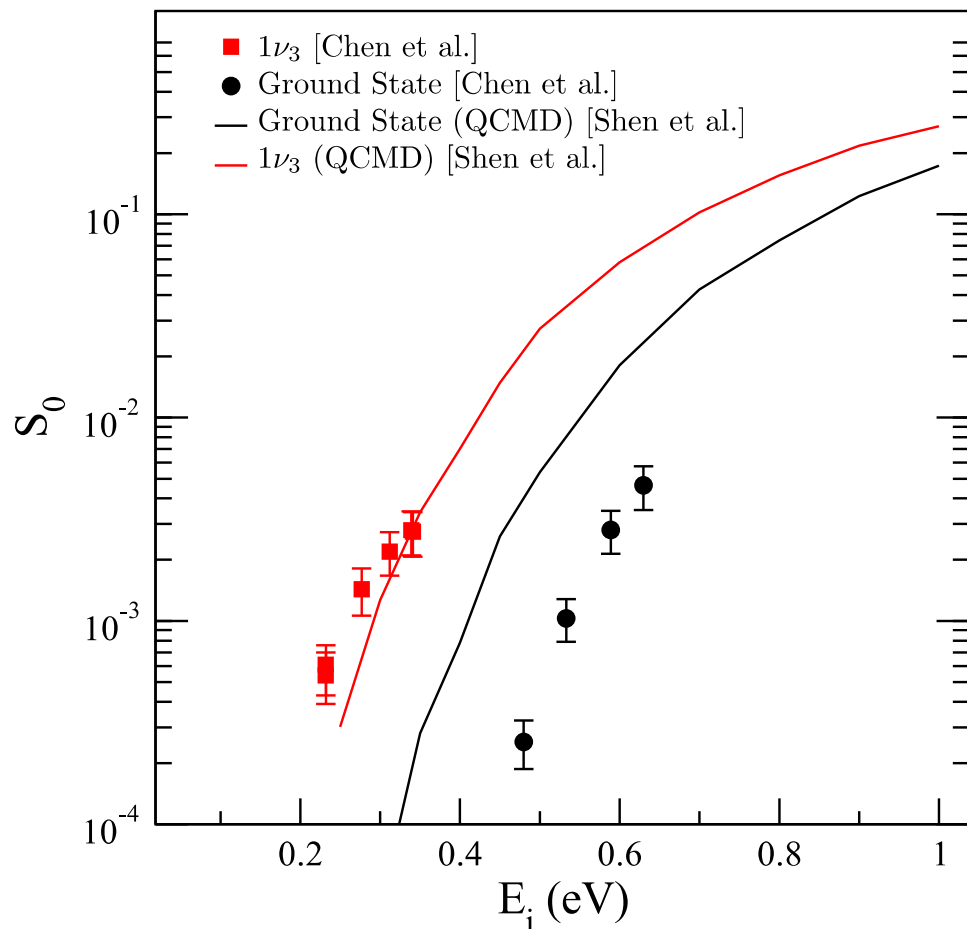
- Nuclei assumed to behave as classical particles, integration of the Newton equations
- The quantum Zero Point Energy and vibrational excited states energies are included.
- All the non controlled initial conditions are randomly tossed (impact site, orientation)
- $N$  trajectories are integrated for a given  $E_i$  and  $\nu_k$  and then  $S_0 = \frac{N_{\text{react}}}{N_{\text{tot}}}$   
( $\sim 10^5$  per initial condition)



- All the molecular dynamics simulations were carried out with an in-house developed code

# Reactivity of methane on metallic surfaces

## Simulations of reaction dynamics: comparison to experiments



- Correct qualitative description of the sticking curves
- Description of the reactivity enhancement with  $1\nu_3$
- Overestimation of the sticking for the vibrational groundstate

¿Problem with the PES or the treatment of the vibrations?

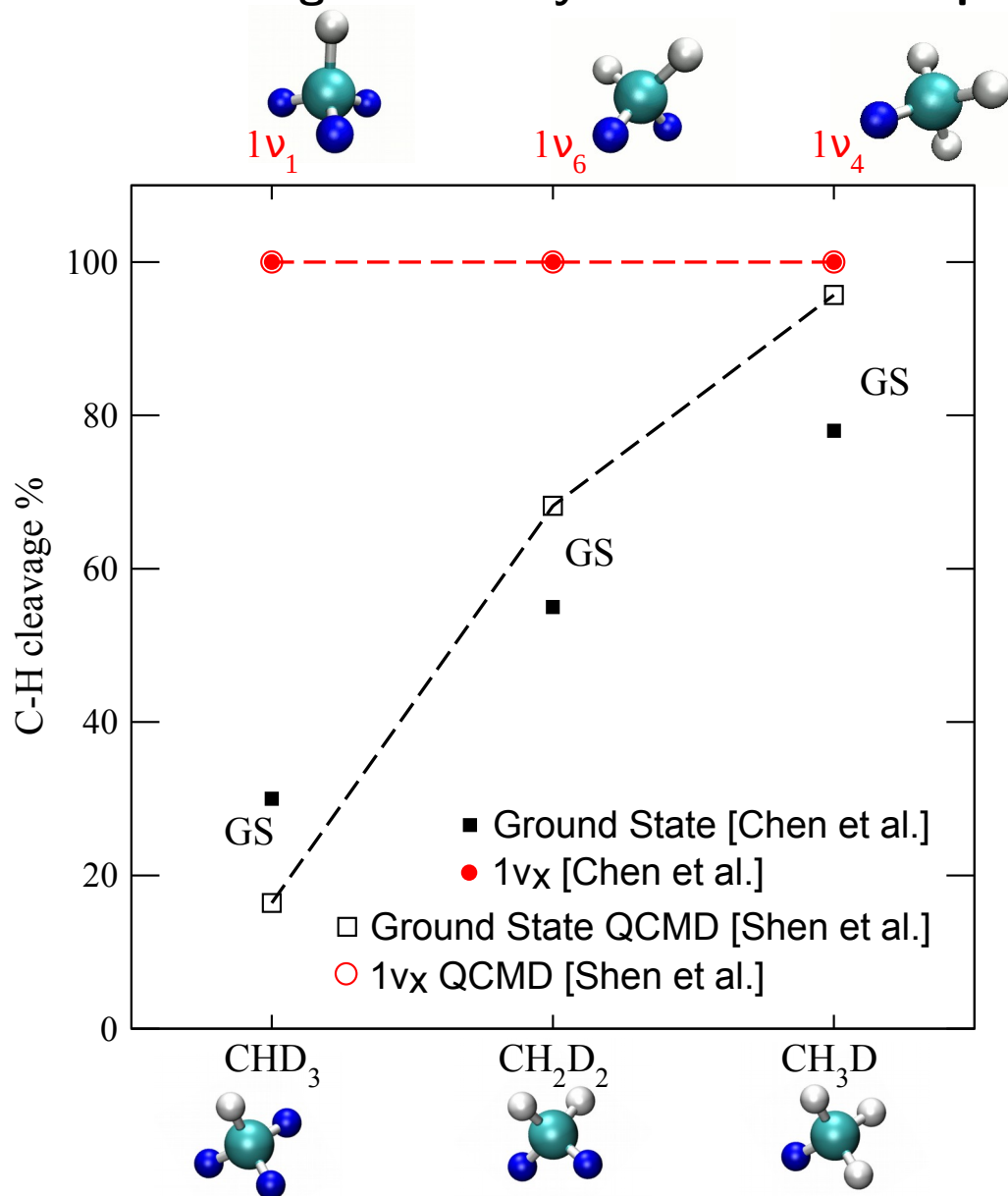


Quantum dynamics of the nuclei are required to rule out quasiclassical approach shortcomings

# Reactivity of methane on metallic surfaces

## Simulations of reaction dynamics: comparison to experiments

### Bond cleavage selectivity in methane isotopologes $\text{CH}_x\text{D}_x$



In the experiments are able to control the bond to break by vibrational preexcitation

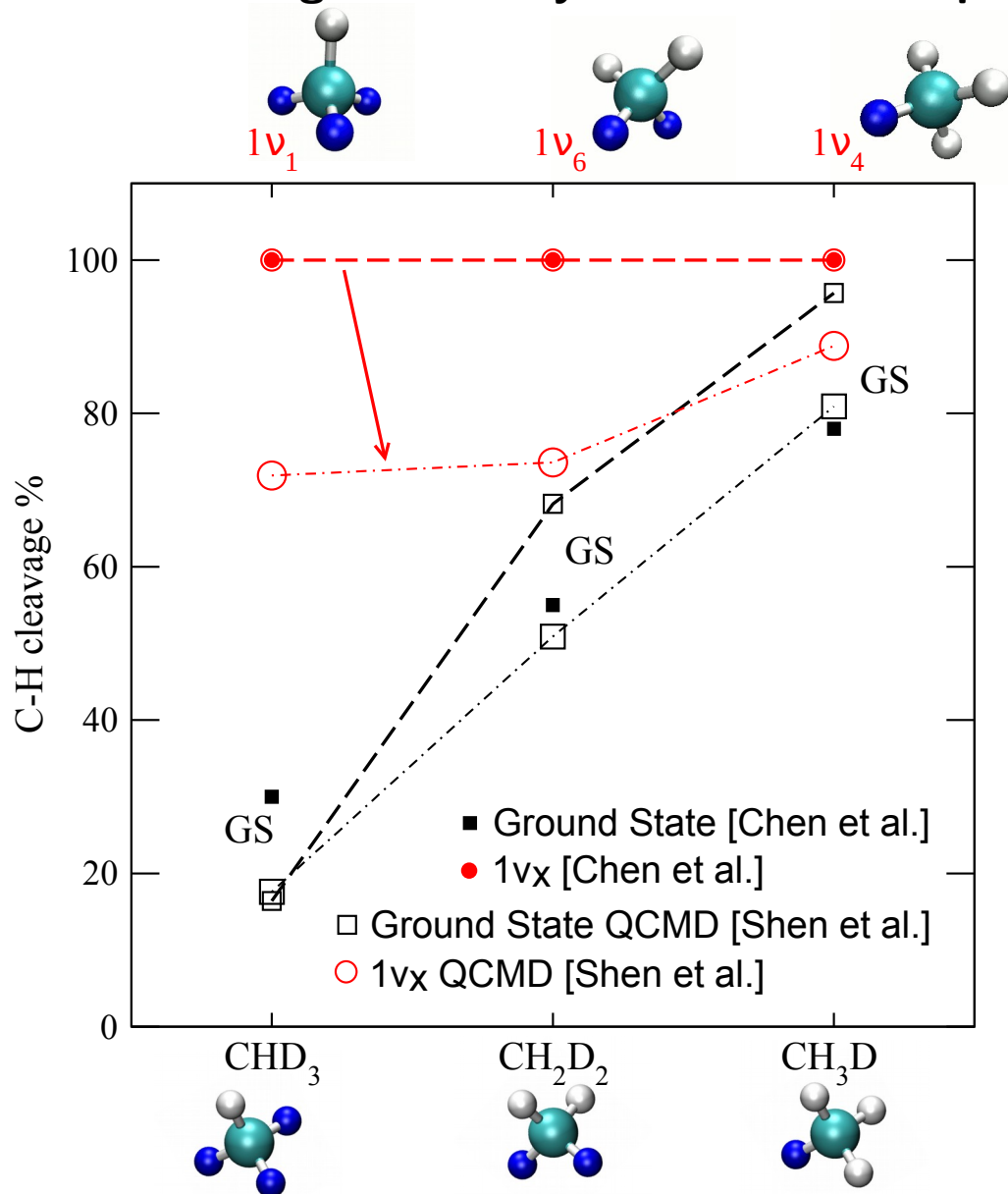
Initial total energy maintained constant  $\approx 0.55$  eV

Theoretical results describes all the trends properly and they account for the observed selectivity

# Reactivity of methane on metallic surfaces

## Simulations of reaction dynamics: comparison to experiments

### Bond cleavage selectivity in methane isotopologes $\text{CH}_x\text{D}_x$



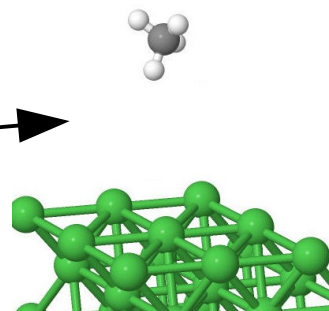
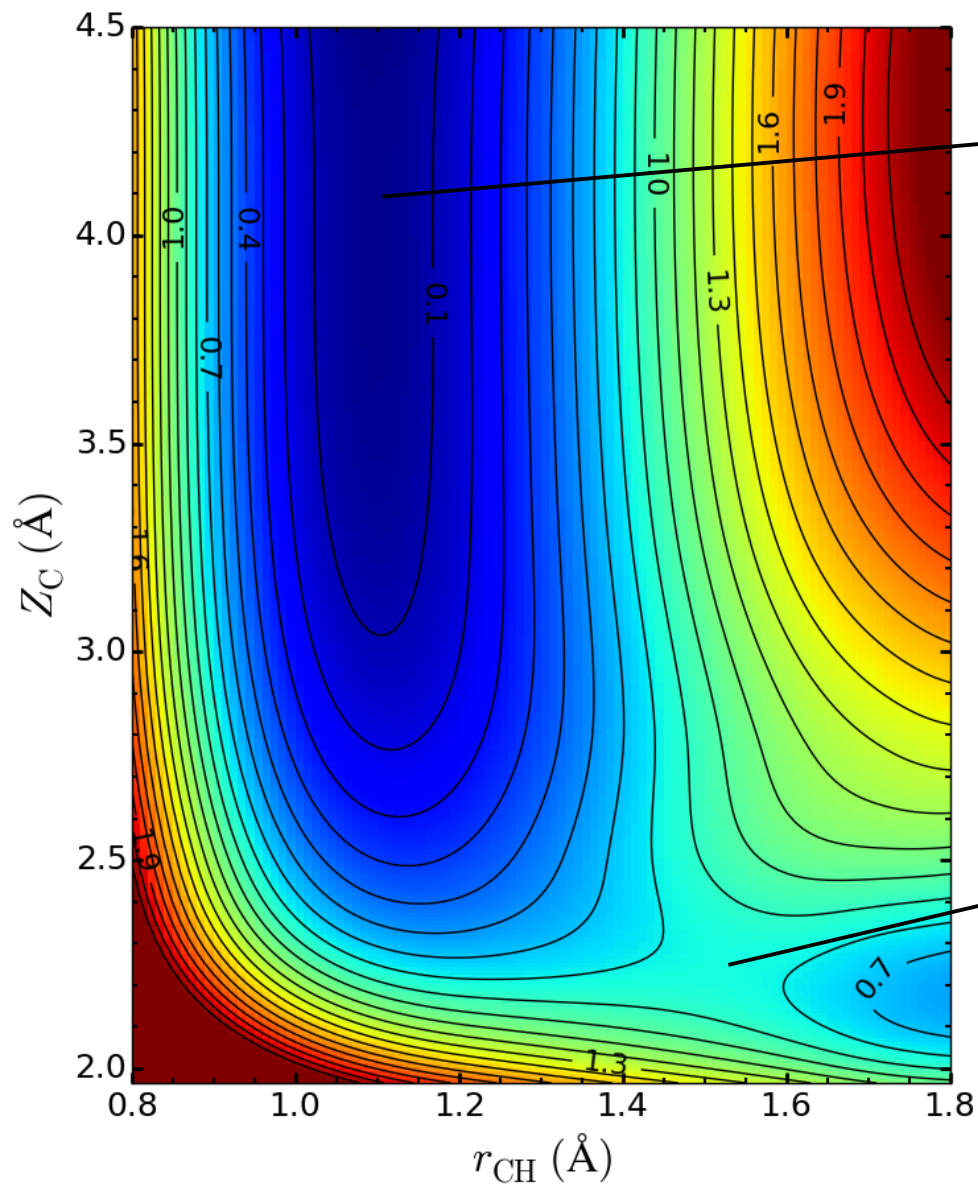
Theoretical prediction

When increasing the initial kinetic energy with an extra 0.5 eV it is observed a selectivity loss for the initially excited modes.

# Reactivity of methane on metallic surfaces

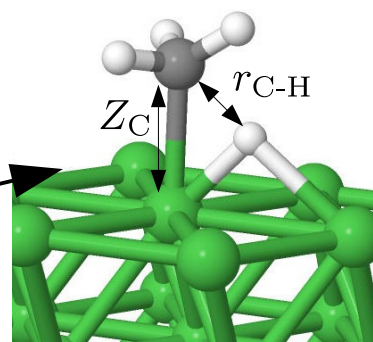
## Simulations of reaction dynamics

Selectivity as a function of impact energy: explanation



2D cut of the PES spanning heights of the carbon atom over the surface  $Z_C$  and C-H internuclear distances  $r_{C-H}$

At every point of the 2D cut all the rest of the coordinates are optimized

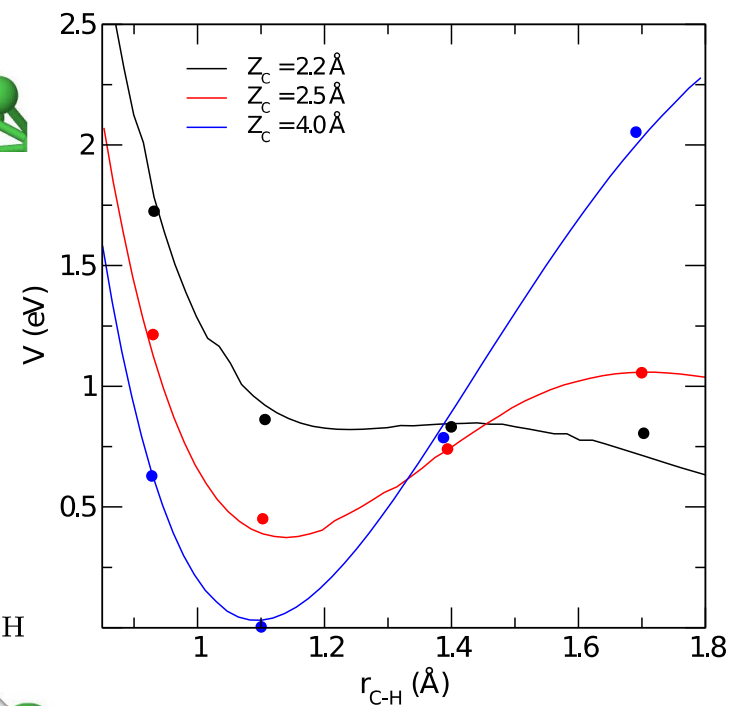
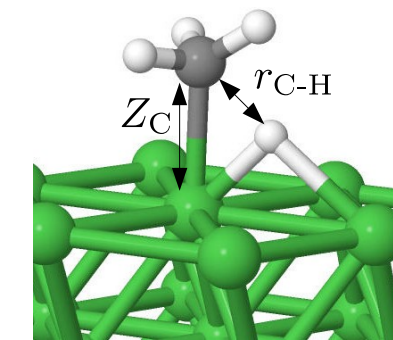
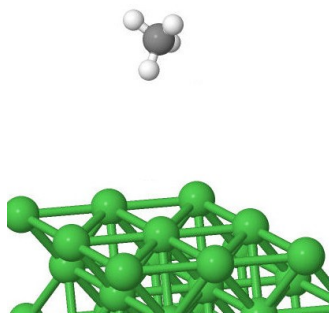
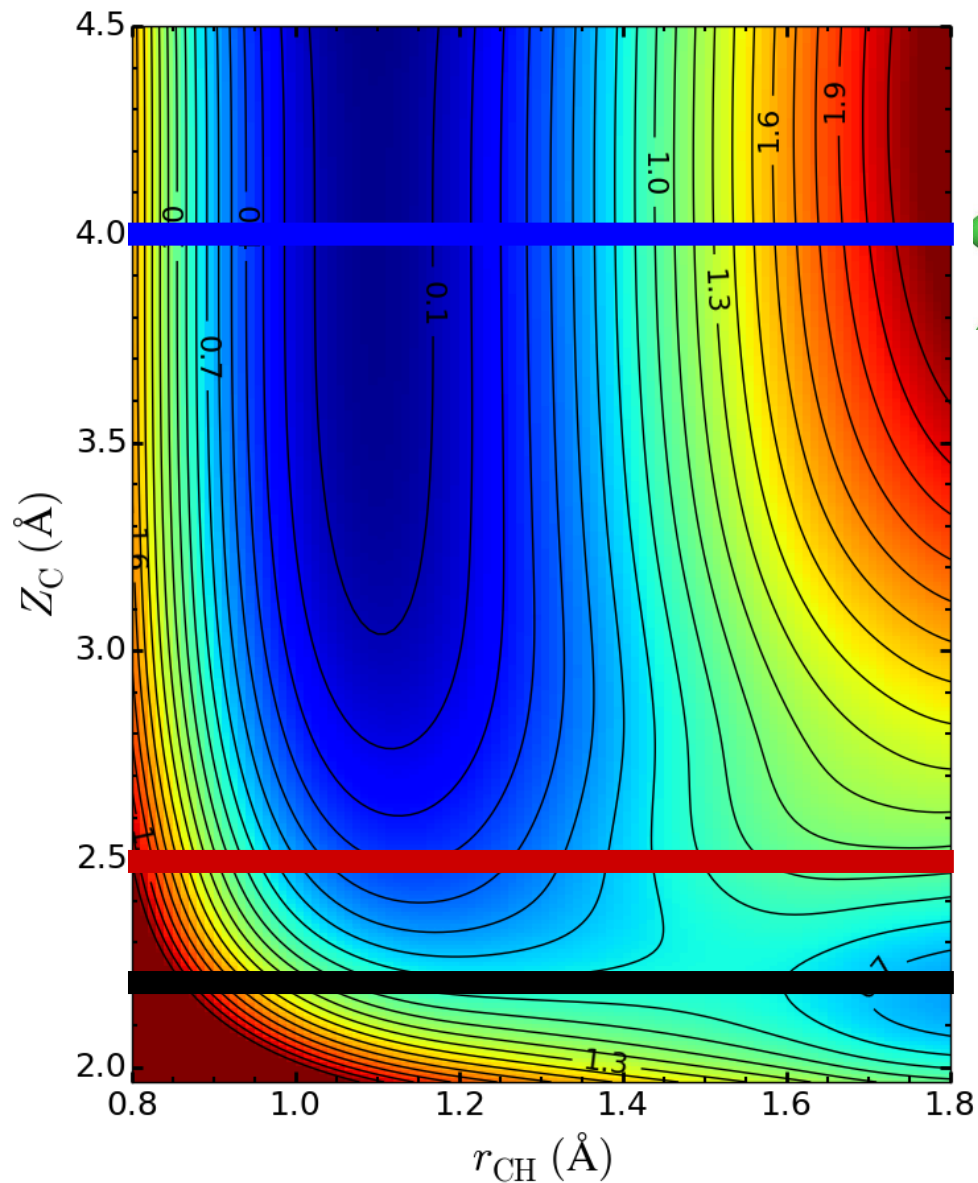




# Reactivity of methane on metallic surfaces

## Simulations of reaction dynamics

Examples of the approach for other systems



# Reactivity of methane on metallic surfaces

## Conclusions

**The approach of developing potentials with Reactive Force Fields proposals fitted to DFT data, seems promising if the fitting is performed for the specific system to be studied.**

**The developed potentials were able to account for all the experimental trends observed.**

**The current results show that selectivity experimentally observed for methane isotopologues will decrease when increasing the initial translational energy.**

▪

**Thanks for your attention**