# Semi-tutorial on disentangling plasma-surface interactions through simulations

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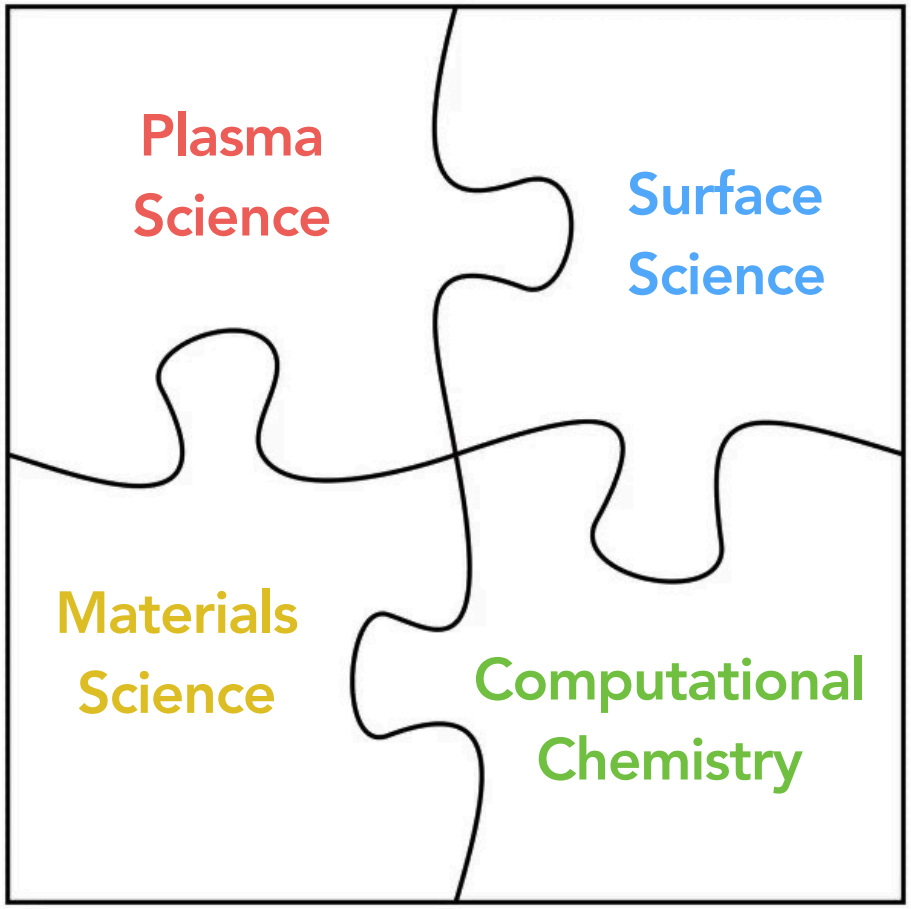
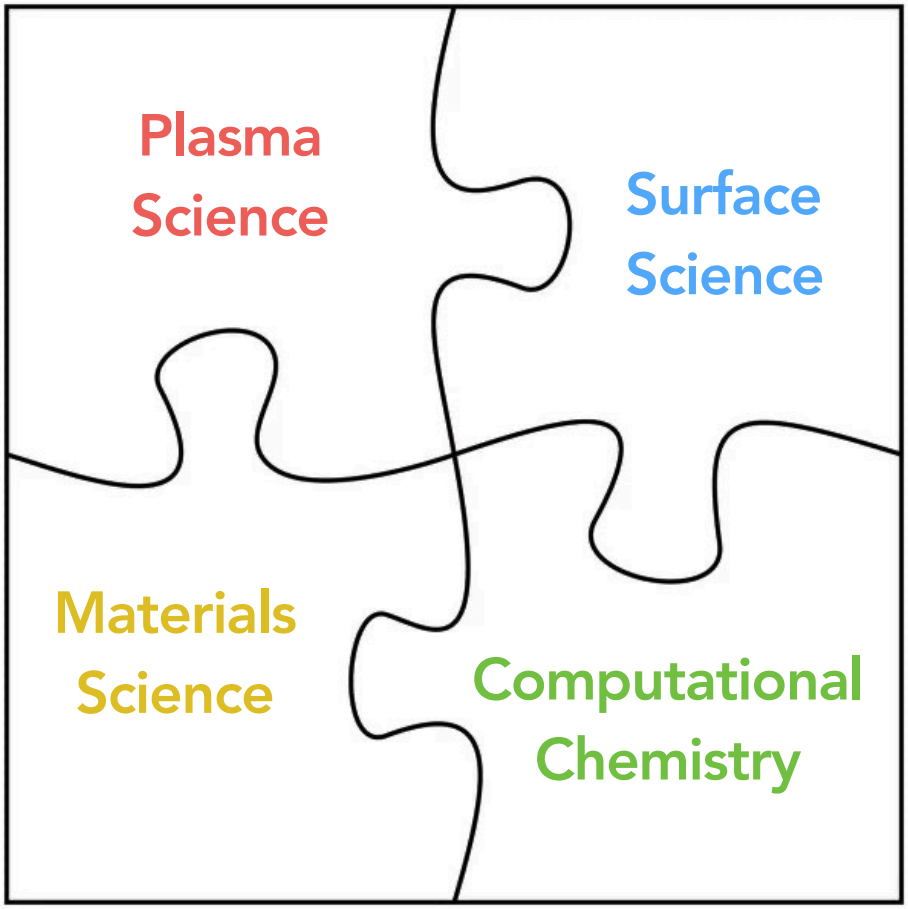
# Computational plasma-surface studies




High degree of complexity is to be expected

# Computational plasma-surface studies




Focus:
plasma catalysis & astrochemistry

Can models & simulations disentangle this complexity?

**High degree of complexity is to be expected**

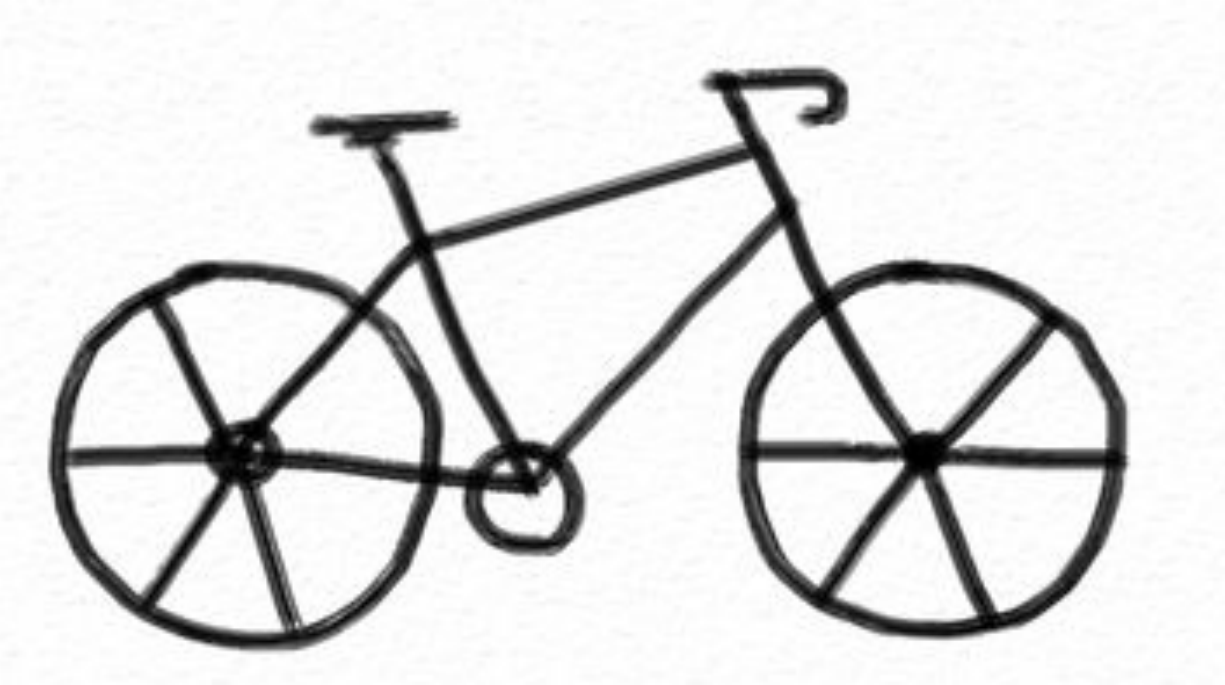
# Modelling

Complex system - can we model this?

# Modelling: 1st attempt (top-down)

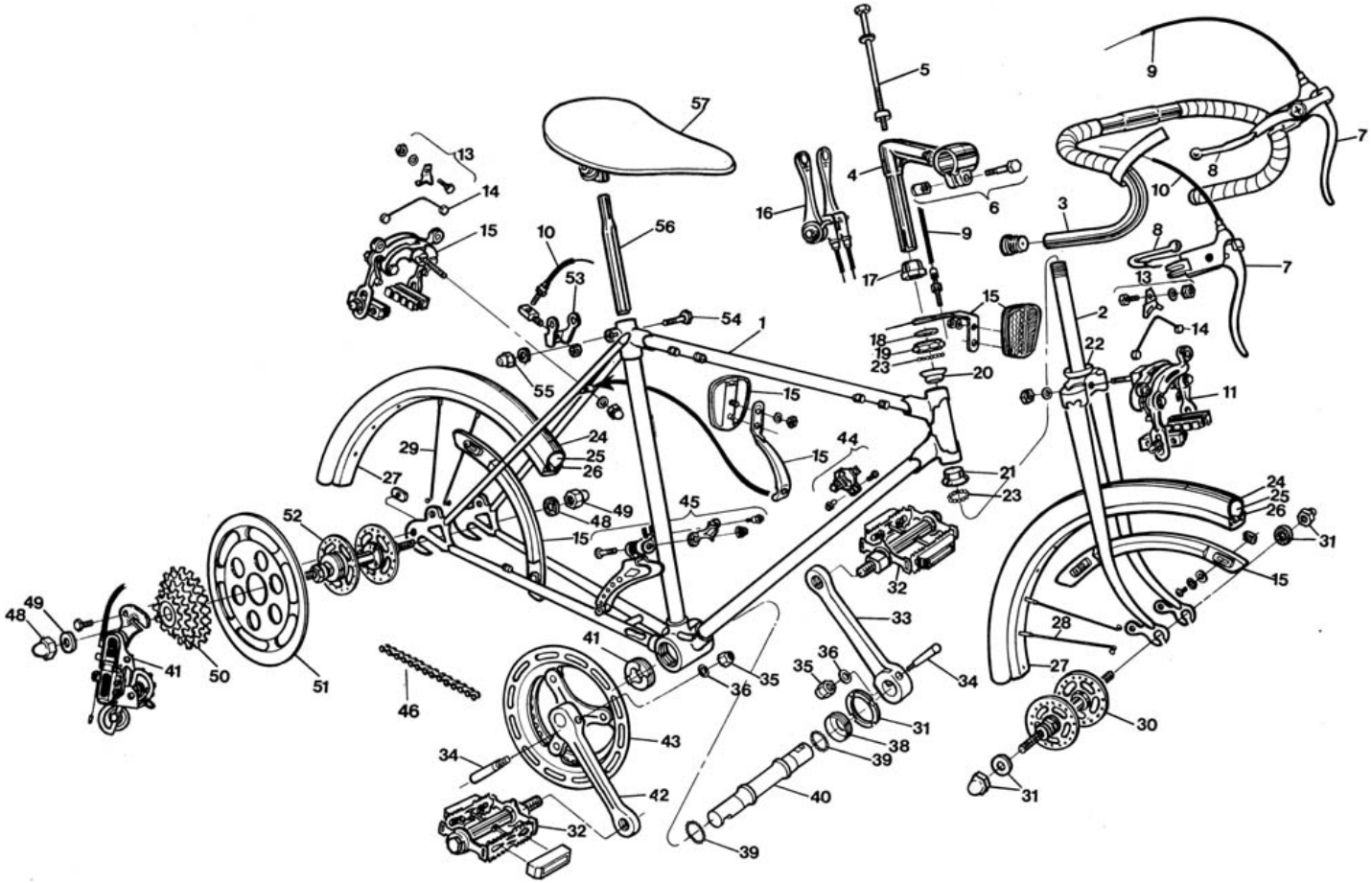
We probably need some improvements ...

# Modelling: 2nd attempt (top-down)



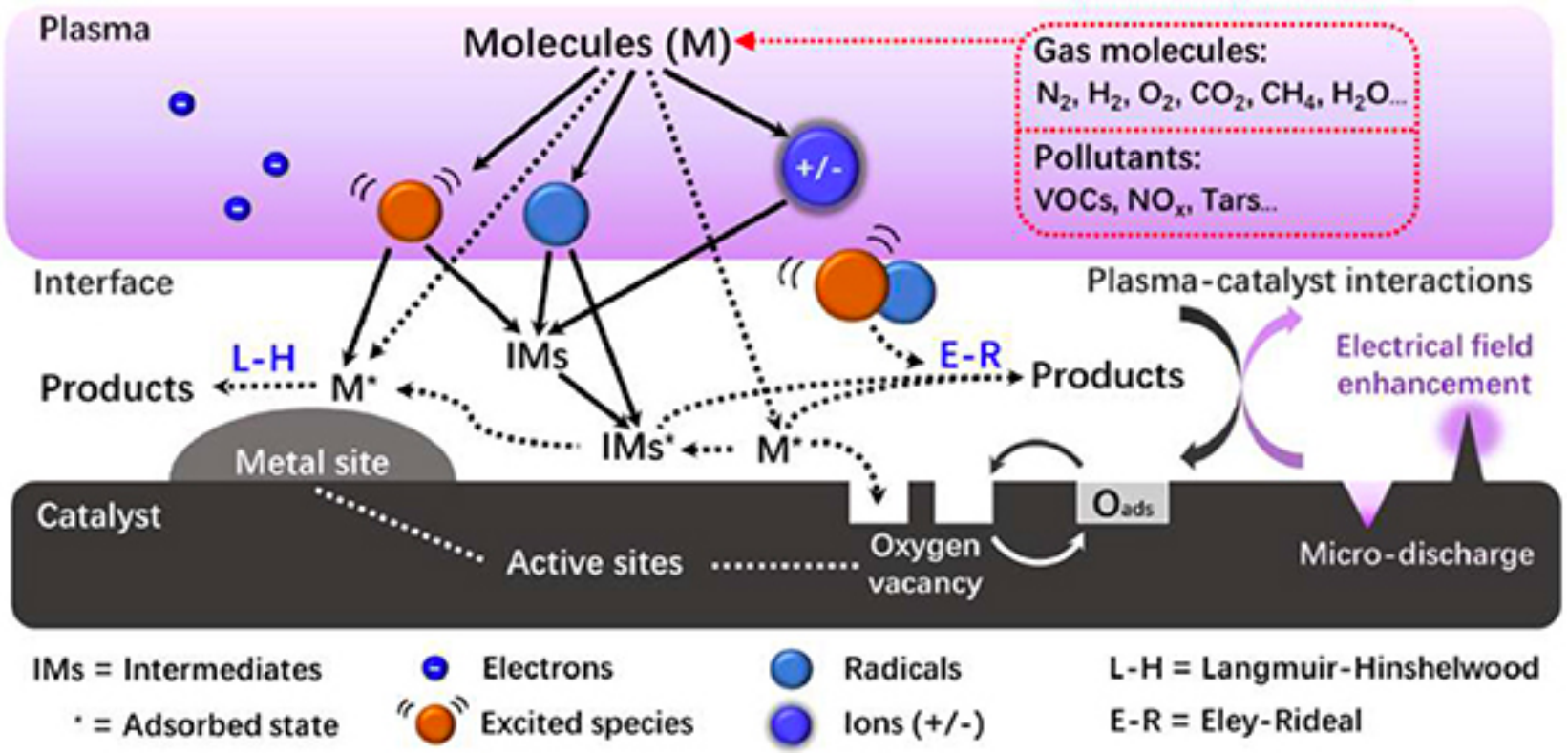
Is everything there that is important?

# Modelling (bottom-up)



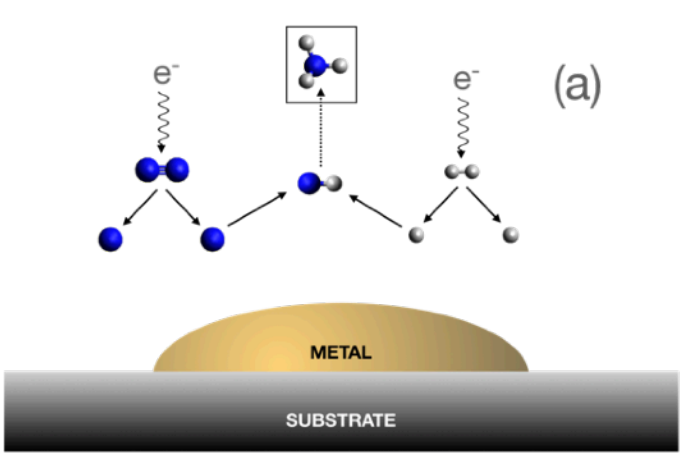
Let's hope this works the way it should ...

# Complexity abound

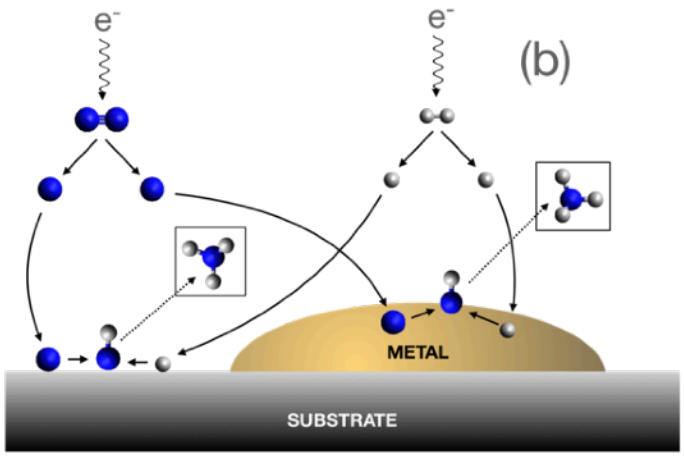



A. Bogaerts et al., J. Phys. D: Appl. Phys. **53** (2020) 443001

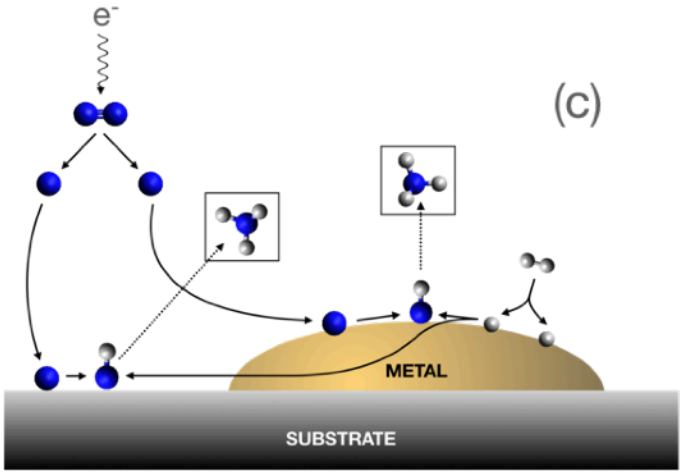
# Plasma catalysis ≠ plasma + catalysis



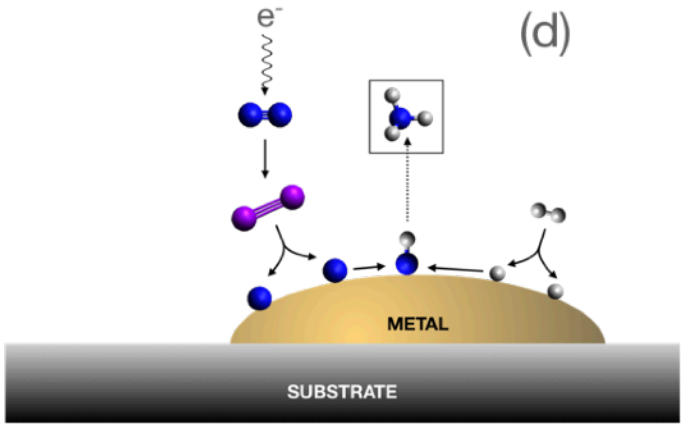

*gas-phase*




*surface-enhanced plasma-driven*




*plasma-enhanced, semi-catalytic*




*plasma-catalytic*

Bogaerts et al, 2022, Plasma Sources Sci. Technol. 31 053002

# Modelling: what to expect and what not

**In modelling,**

we try to gain fundamental understanding

complementary to experiments

by capturing the essential physics & chemistry

(and hope that everything plays out as it does in reality)

**In modelling,**

we typically cannot replicate or reproduce experiments

do not necessarily aim for (or even desire) quantitative agreement

# Connecting experiments to models

## or experimentalists to modellers

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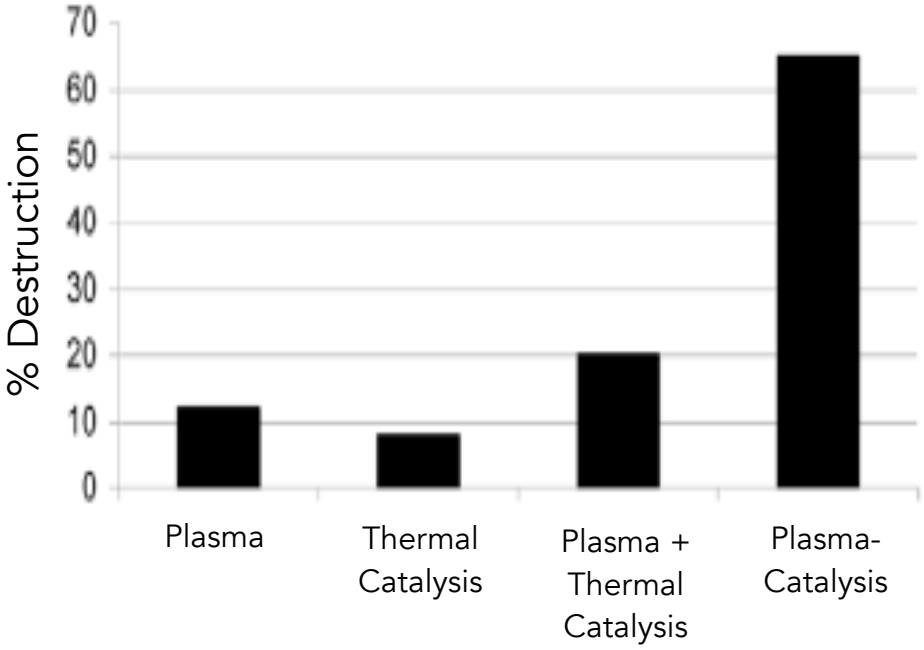
# Experimental input

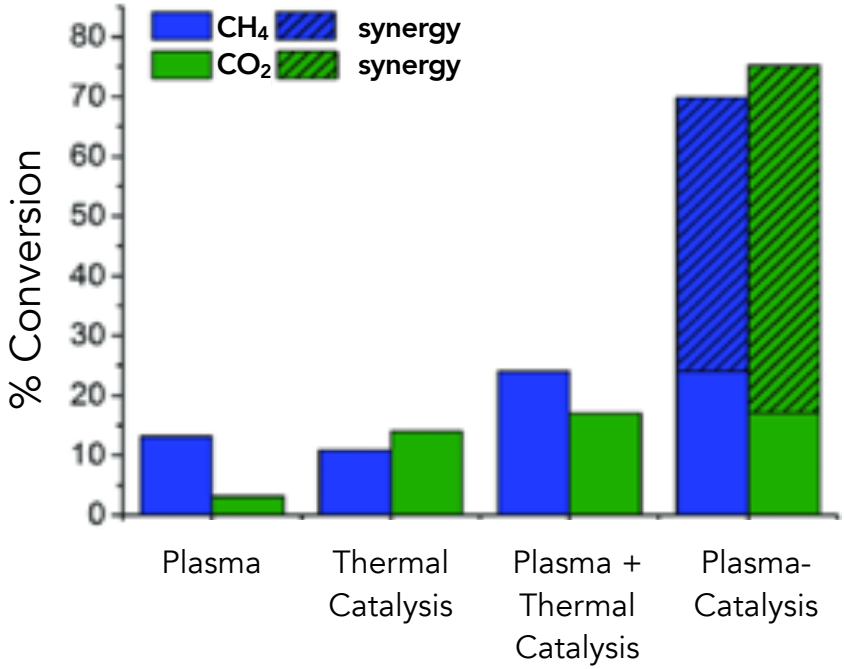
**Gas cleaning:**

Toluene decomposition




**Gas conversion:**

$CH_4$ / $CO_2$ reforming



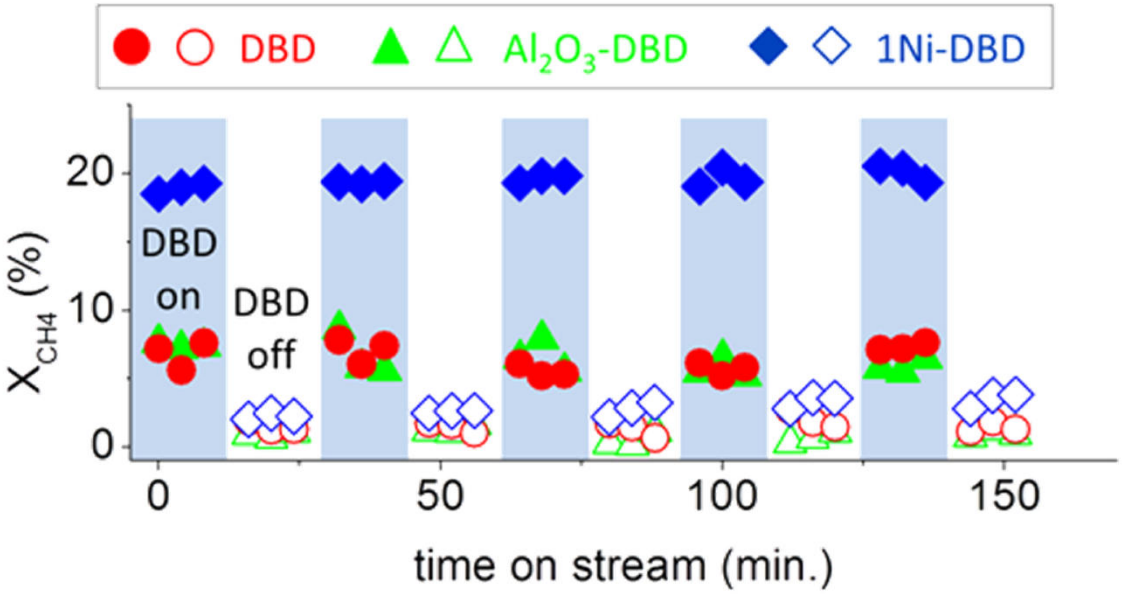

Clear interplay of catalyst and plasma

**Mechanism?**

C. Whitehead, Pure Appl. Chem. **82** (2010) 1329

A. Zhang et al, Chem. Eng. J.**156** (2010) 601

# Experimental input

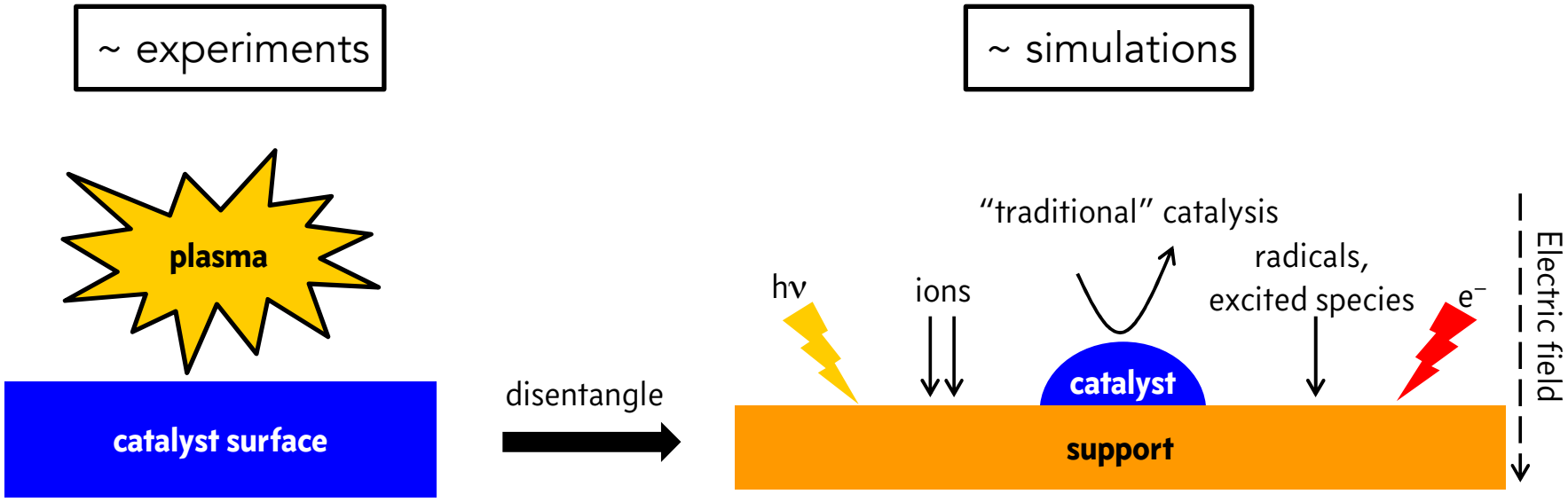



Clear *reversible* interplay of catalyst and plasma

**Mechanism?**

J. Kim, ACS Energy Lett. **1** (2016) 96

# From experiment to modeling

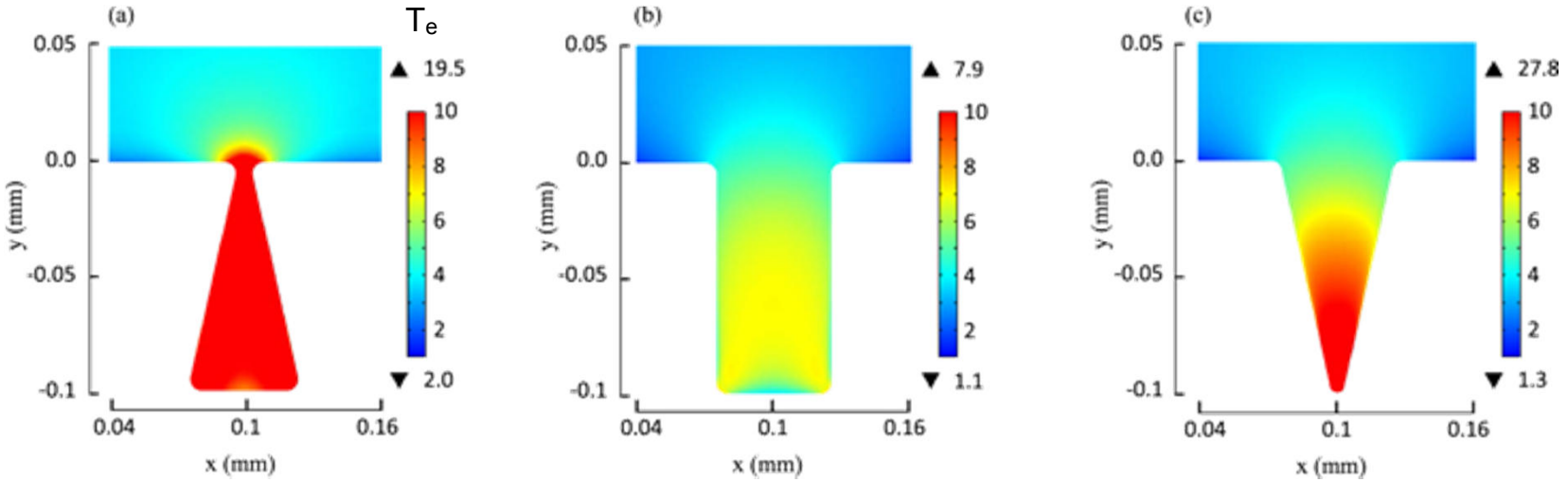



Modeling allows a bottom-up approach
to disentangle the process

**Typical:** Start off with plasma, then add catalyst

**Proposal:** Start off with thermal catalysis,
add plasma-factors one by one

# Macroscale modeling



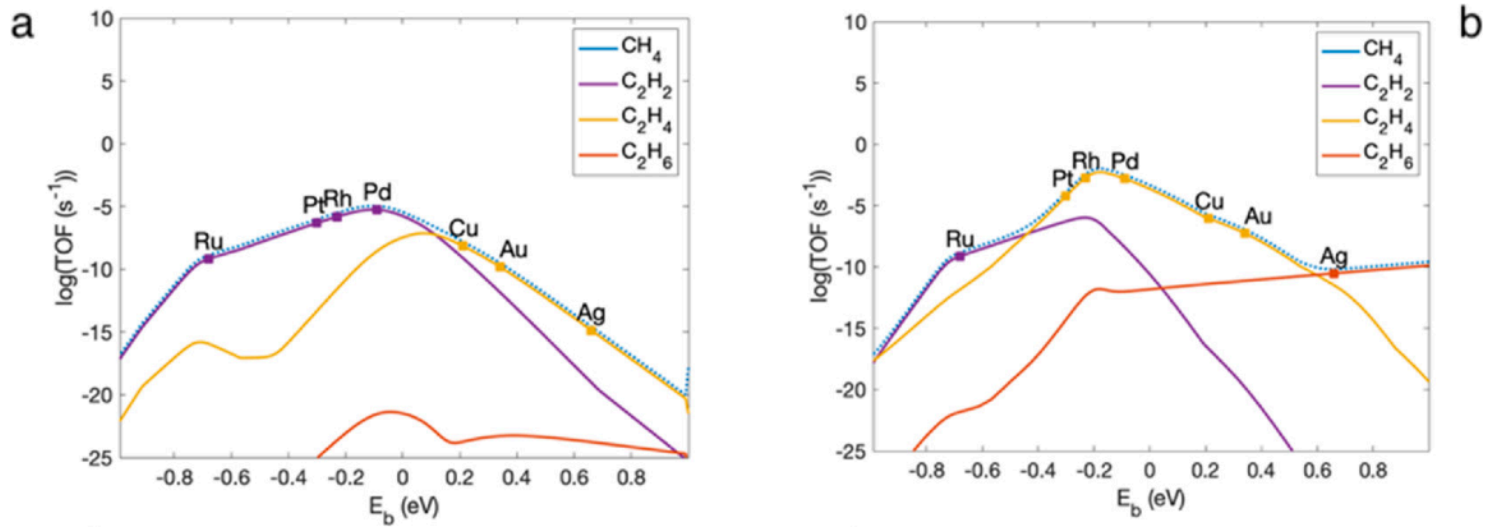

**Plasma models** use microscale knowns (rates, processes) to predict macroscopic unknowns

**But**: microscopic processes at the catalyst are not known!

Zhang, Bogaerts, Neyts, Plasma Sources Sci. Technol. **27** (2018) 055008

# Microscale modeling

Non-oxidative coupling of methane




Thermal

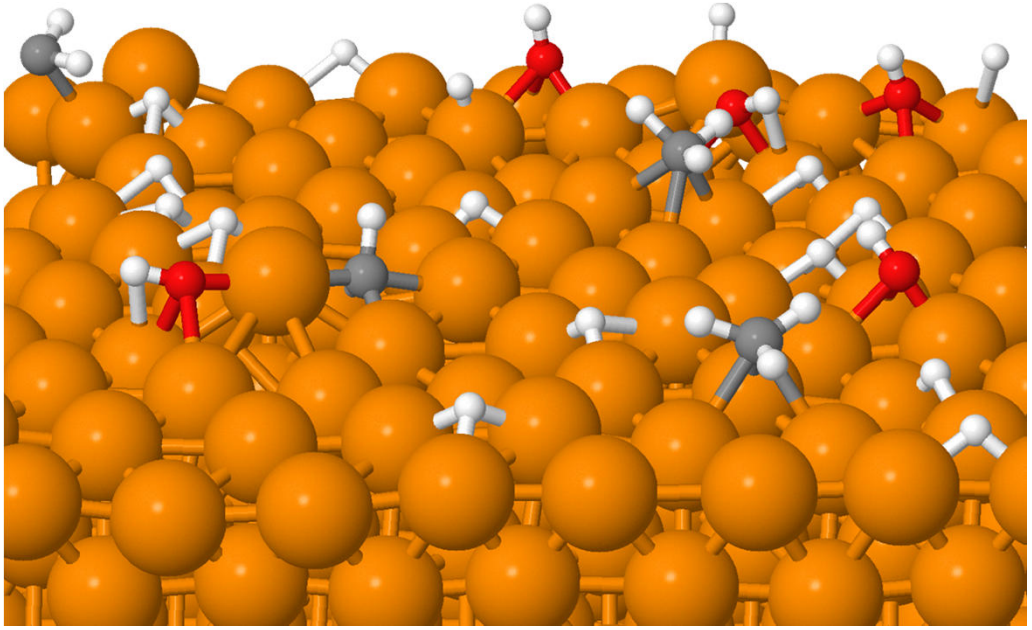
Vibrationally enhanced

Microscopic kinetic models use thermodynamics and kinetics of individual reactions to understand interplay of processes

**But**: Atomic scale processes at the catalyst are not known!

Engelmann, et al., ACS Sustainable Chem. Eng. 8 (2020) 6043

# Atomic scale modeling



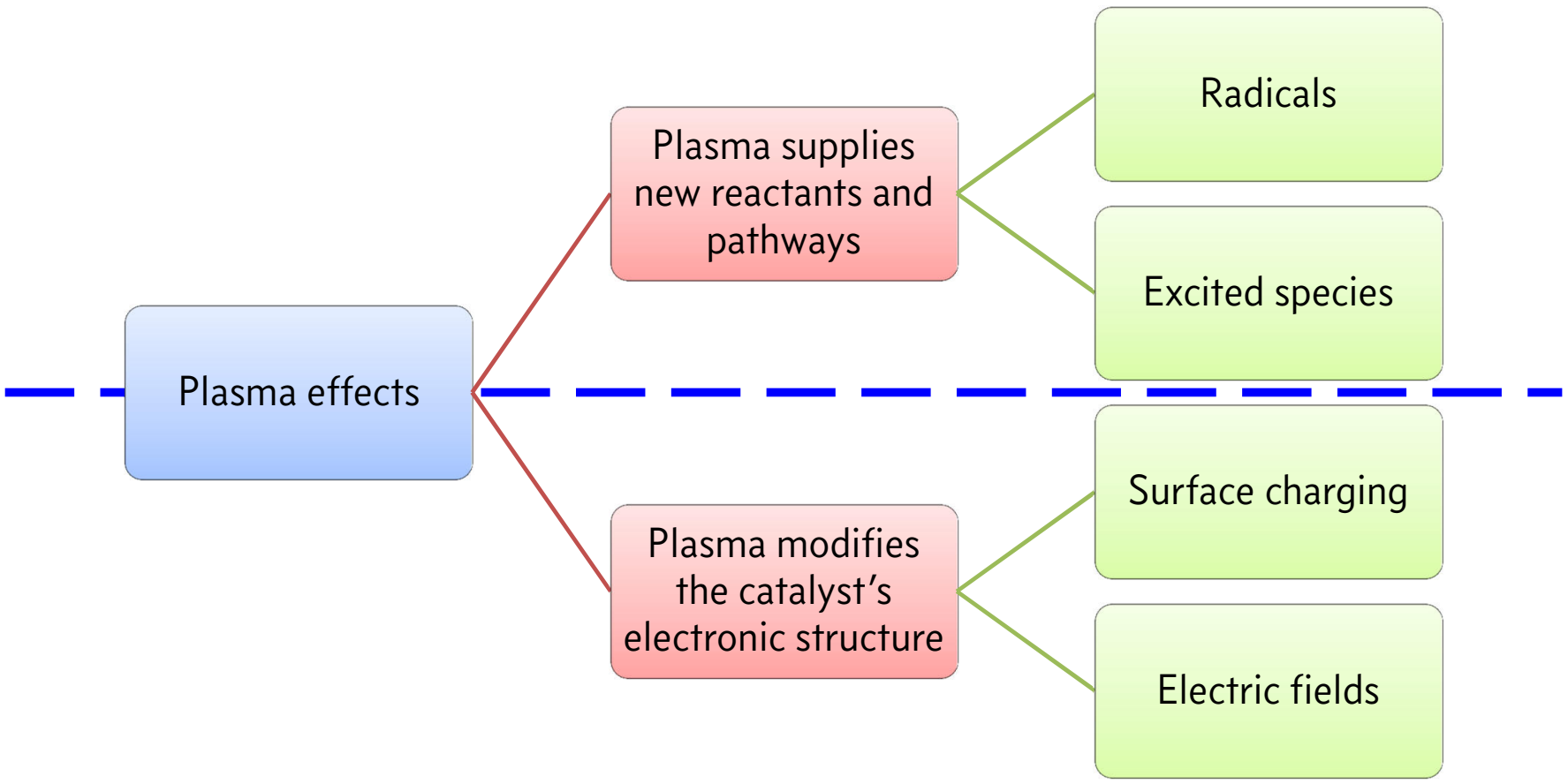
We need more fundamental information

→ Atomistic simulations: **classical MD** → requires appropriate force field

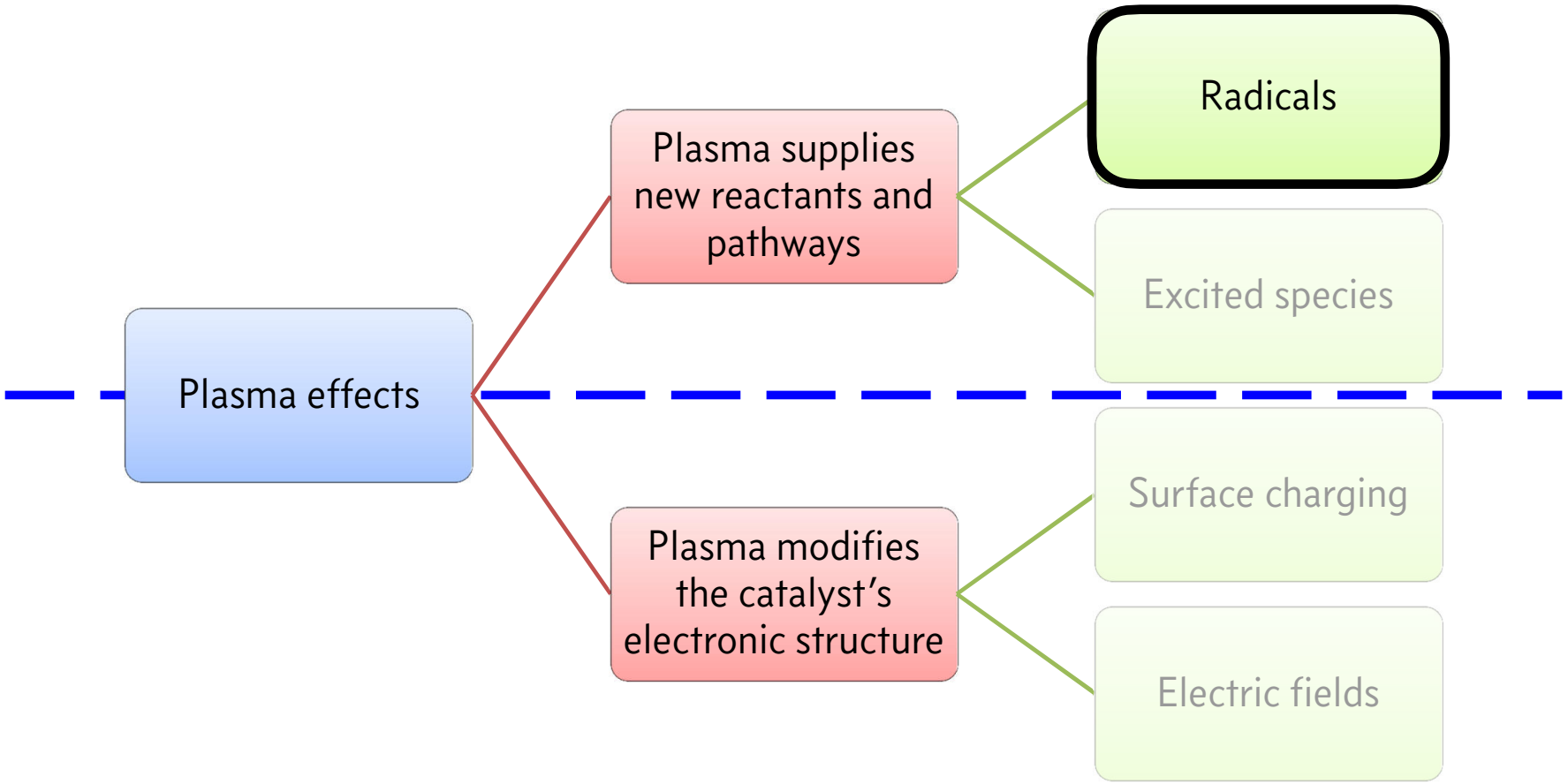
**DFT / ab initio** → limited in (time & length) scales

**Caveat:** all models & simulations come with their assumptions and limitations

# Approach


Plasma effects
Plasma supplies new reactants and pathways
Radicals
Excited species
Plasma modifies the catalyst's electronic structure
Surface charging
Electric fields

# Approach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# Radicals and excited species

The plasma supplies radicals and excited species. These are more reactive and react through new, faster pathways.

**THE PLASMA ACTS AS AN ADDITIONAL CATALYST**

**Radicals**

$$CH_4(g) \xrightarrow{\text{Catalyst}} CH_3(ads) + H(ads)$$

$$CH_4(g) \xrightarrow{\text{Plasma}} CH_3(g) + H(g)$$

$$CH_3(g) \xrightarrow{\text{Catalyst}} CH_3(ads)$$

$$H(g) \xrightarrow{\text{Catalyst}} H(ads)$$

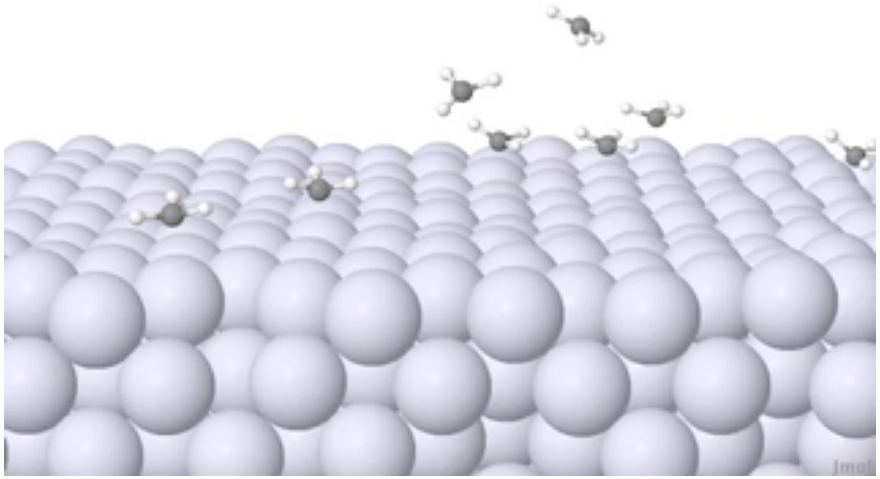
**Vibrational excitation**

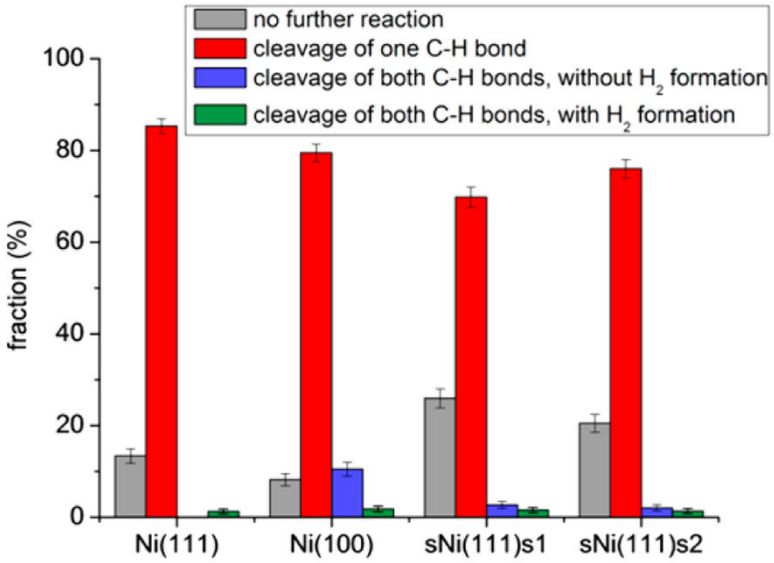
$$N_2(g) \xrightarrow{\text{Catalyst}} 2\,N(ads)$$

$$N_2(g) \xrightarrow{\text{Plasma}} N_2^*(g)$$

$$N_2^*(g) \xrightarrow{\text{Catalyst}} 2\,N(ads)$$

# Radicals






Radicals are fairly easy!

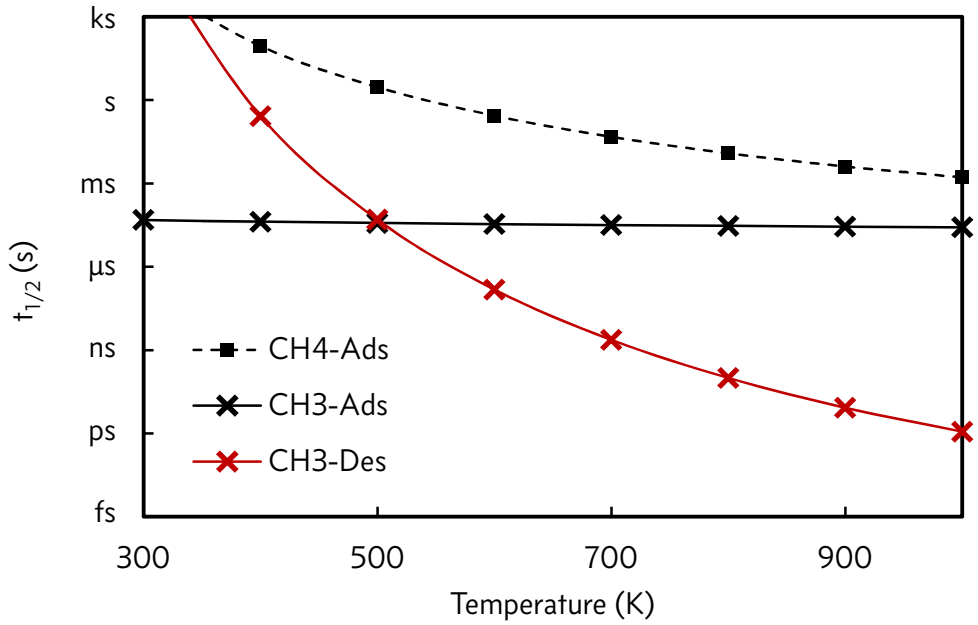
- Effects well-known for material growth, surface modification, …
- Usually included in standard atomistic models

MD simulations of $CH_x$ impact on Ni

- Radical sticking is basically spontaneous, even at 400 K
- Exothermic adsorption induces further reaction

W. Somers *et al.* J. Phys. Chem. C **116**, 20958 (2012).

# Radicals

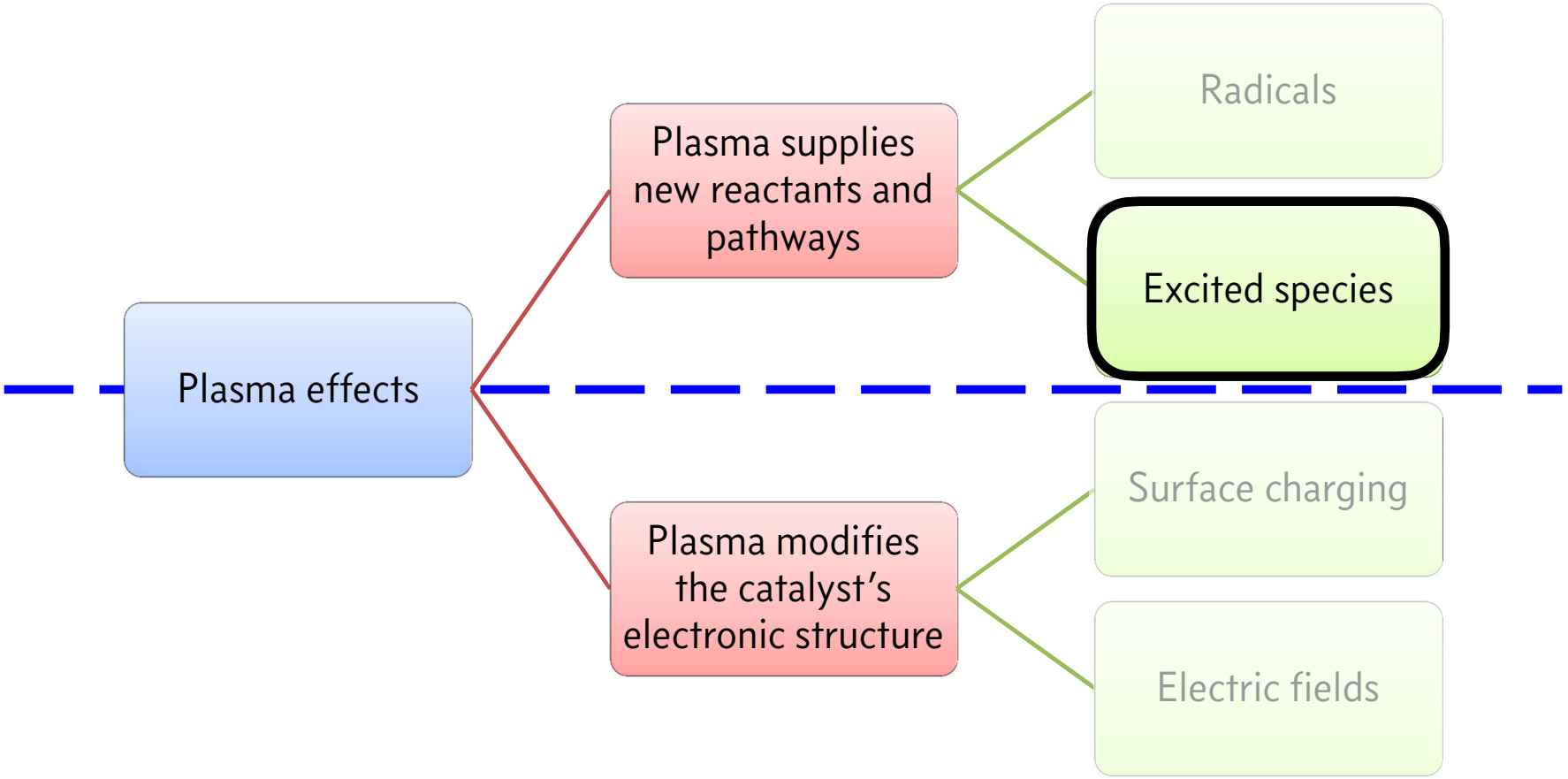



DFT calculation on $TiO_2$ anatase

- Lifetimes of species can be computed (using realistic densities)
- Treshold temperature for dry reforming is lowered
- Pathways to methanol formation are opened

S. Huygh *et al.* J. Phys. Chem. C **122**, 9389 (2018).

# Approach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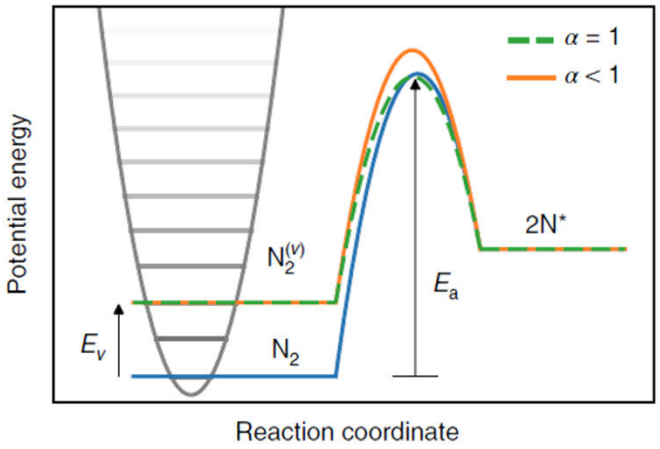
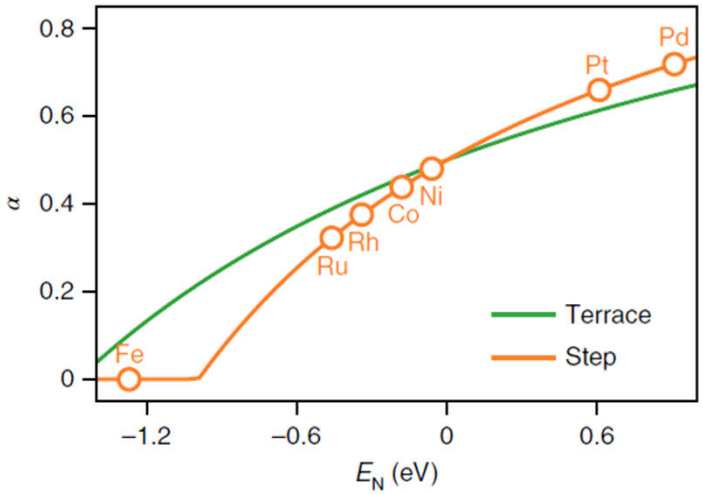
# Vibrationally excited species




Vibrationally excited states are overpopulated

Mehta *et al.* proposed a simple microkinetic model to test their effect

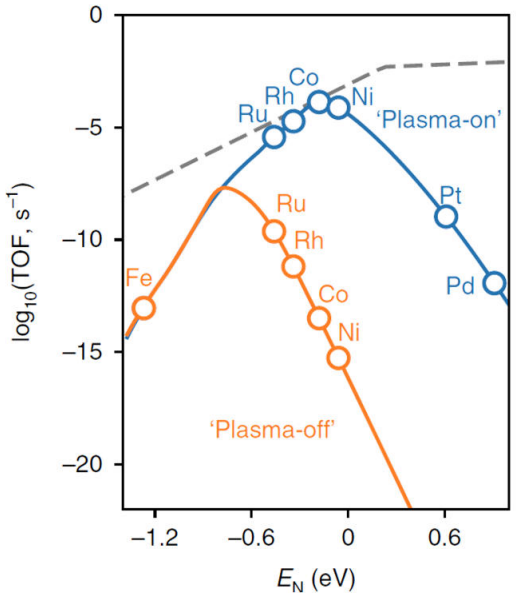
- Ground state $NH_3$ synthesis rates from literature
- Excited state rates through simple additive rules

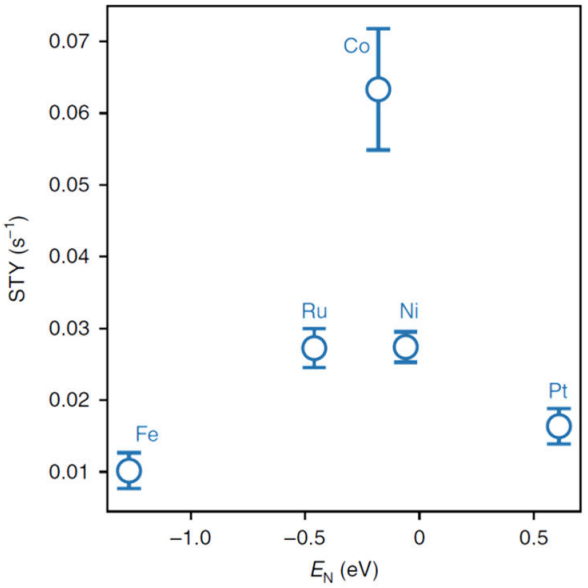
Fridman-Macheret (FM model)

$$k_{vib} \sim \exp\left(-\frac{E_a - \alpha E_{vib}}{k_B T}\right) \text{ with } \alpha = \frac{E_a^{forward}}{E_a^{forward} + E_a^{reverse}}$$

P. Mehta *et al.* Nat. Catal. **1**, 269 (2018)

# Vibrationally excited species



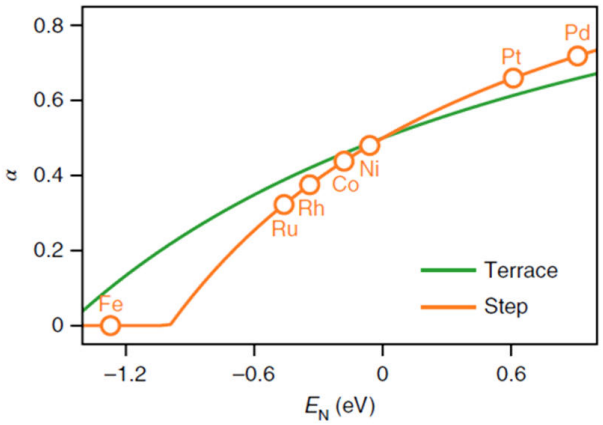



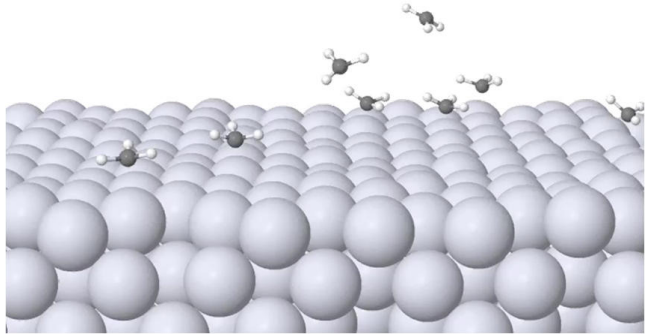

Preference shifts towards weaker-binding catalysts and rate increases

Experiments sort of agree

P. Mehta *et al.* Nat. Catal. **1**, 269 (2018)

# Vibrationally excited species



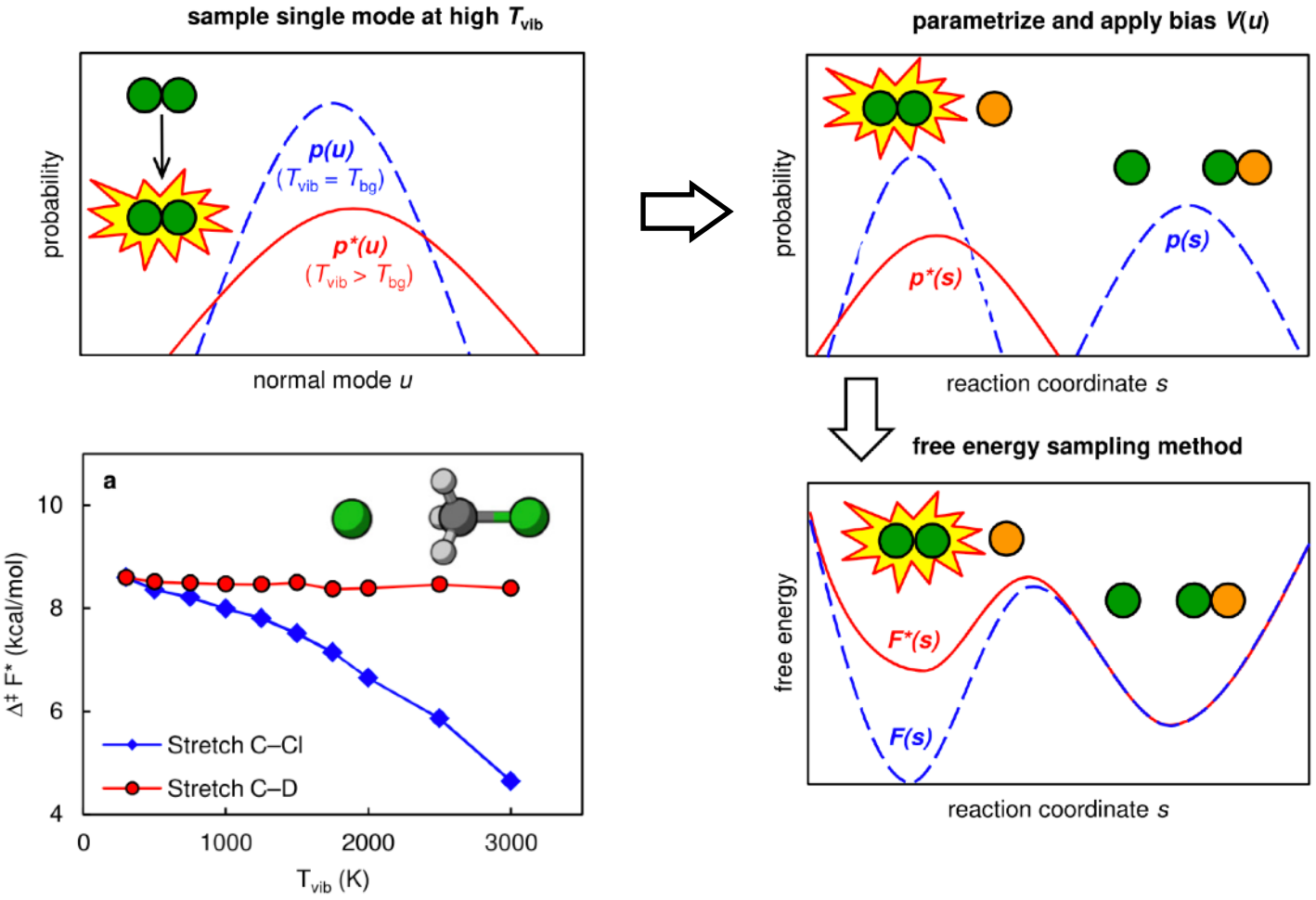
This model is not atomistic and relies on rather crude approximations

Perform explicitly atomistic simulations to verify the microkinetic model:

Background thermostat keeping all modes at temperature T…

… except around a frequency **ω** which is at a higher $T_{vib}$

# Vibrationally excited species

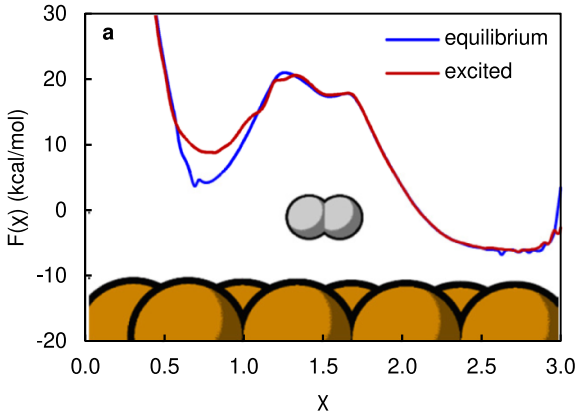


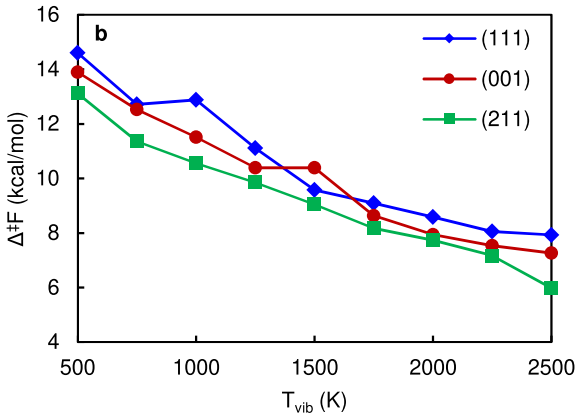

Approach works well for gas-phase reactions

=> Attempt to apply to surface reactions as well

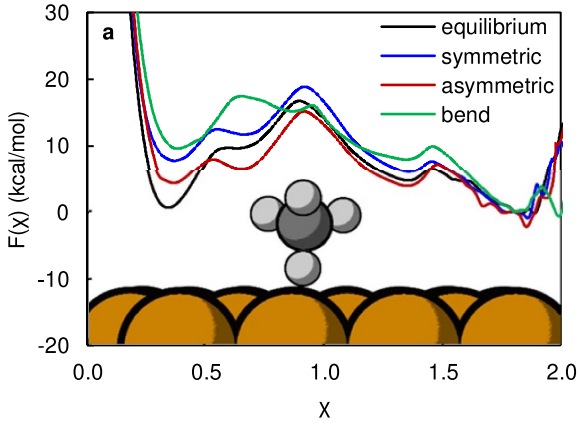
K. M. Bal, et al., *JCPL* **11** (2020) 401

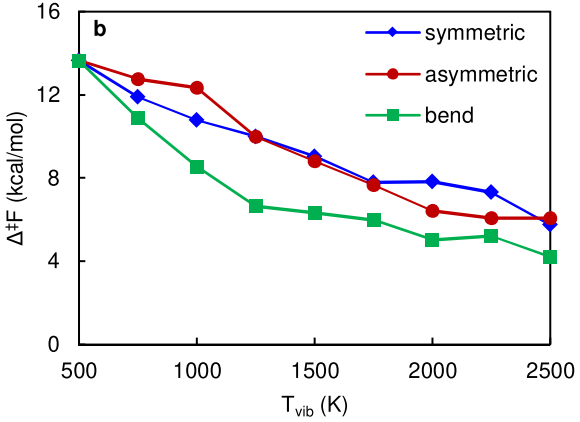
# Vibrationally excited species

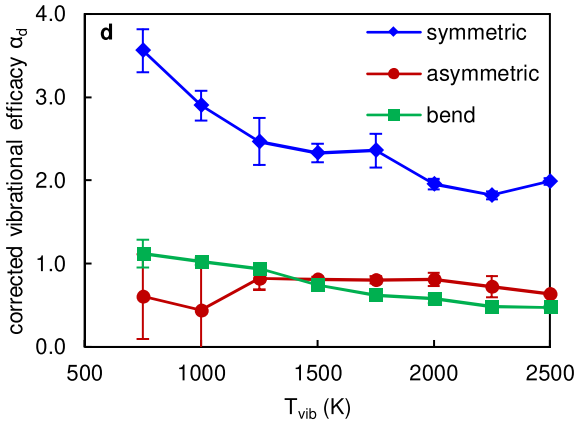



invalidates FM model

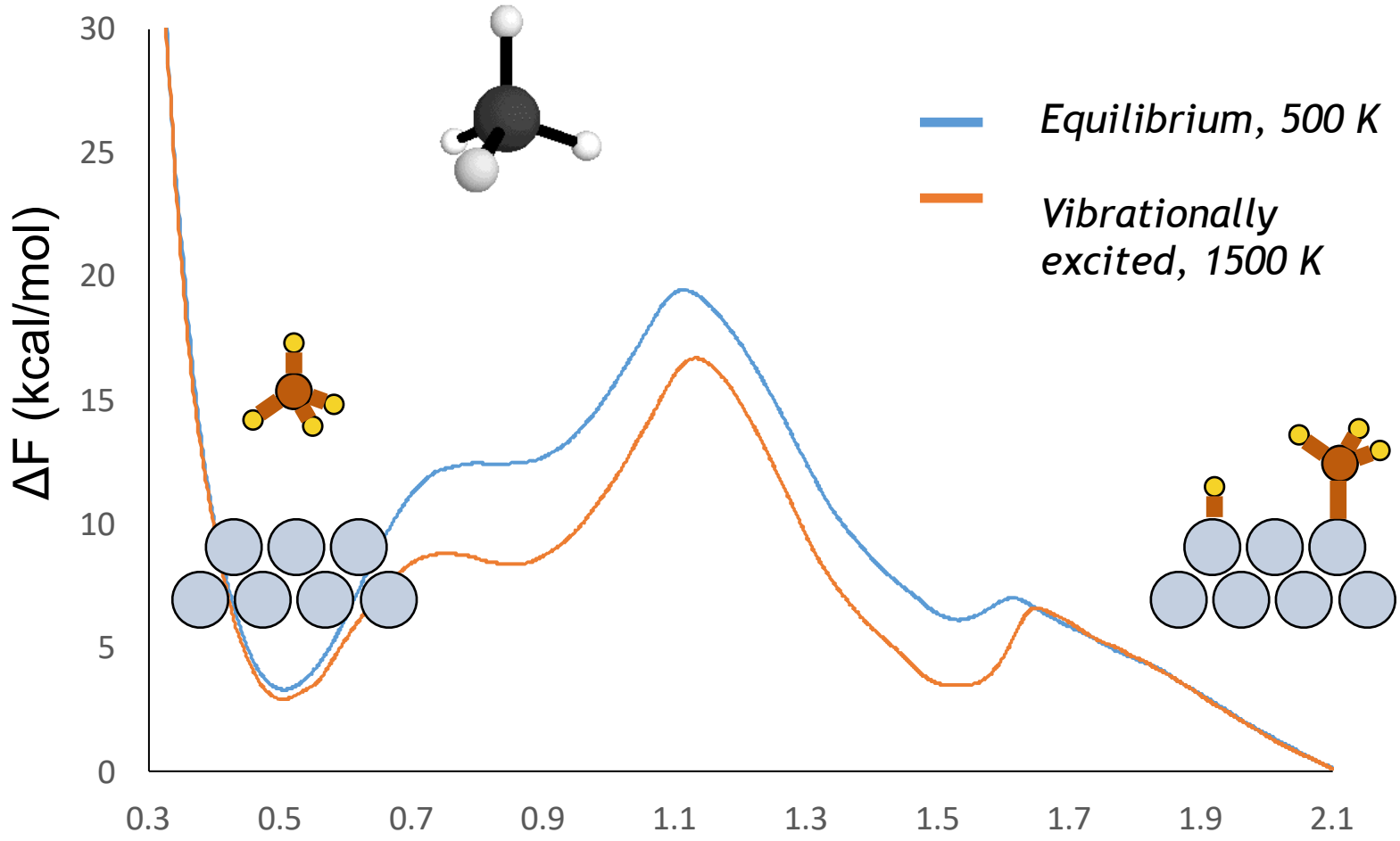


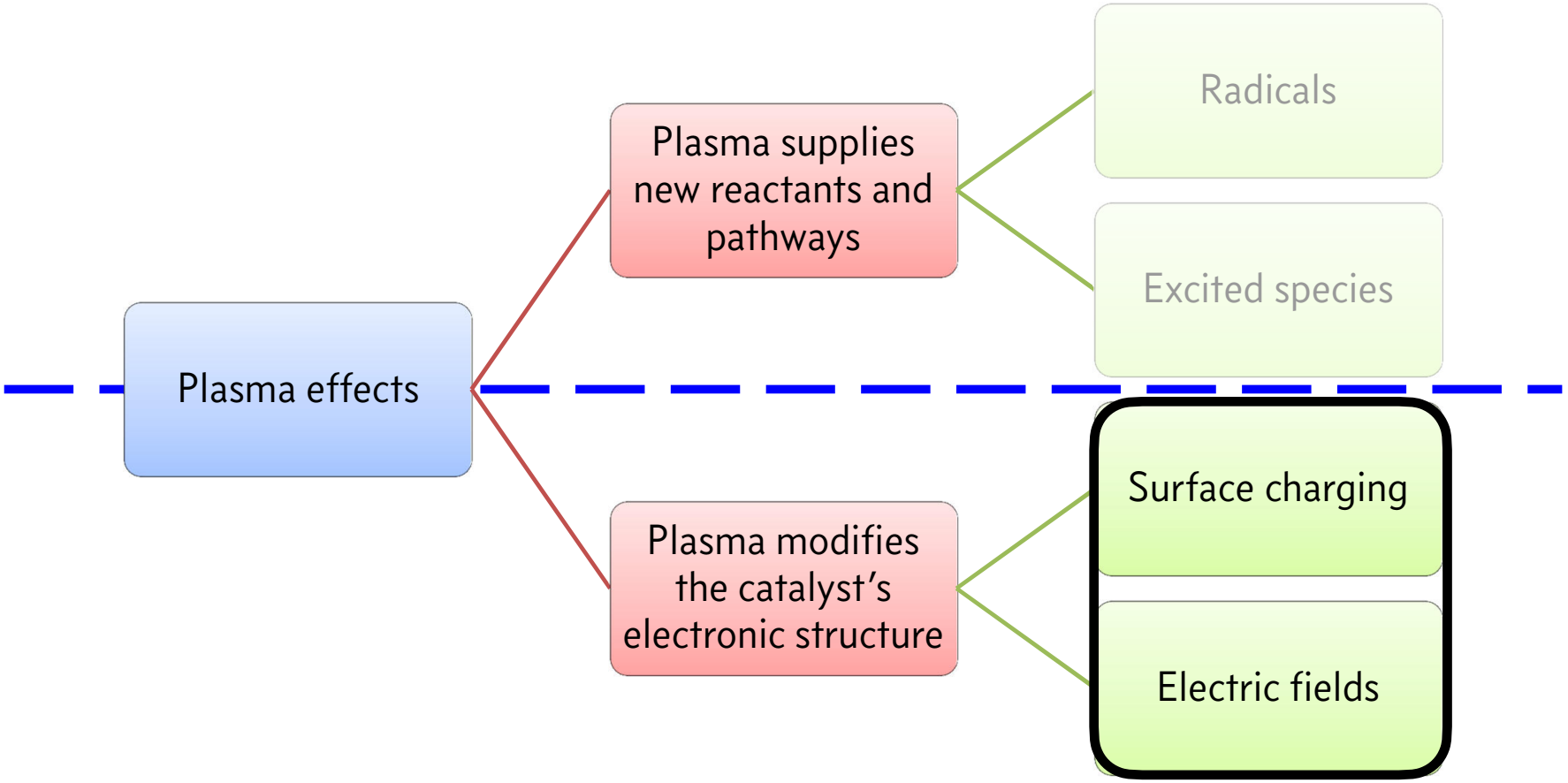

K. M. Bal, et al., *J. Phys. D: Appl. Phys.* ***54*** (2021) 394004

# Vibrationally excited species




POC: K. M. Bal, A. Bogaerts, E. C. Neyts, J. *Phys. Chem. Lett.* **11** (2020) 401

# Approach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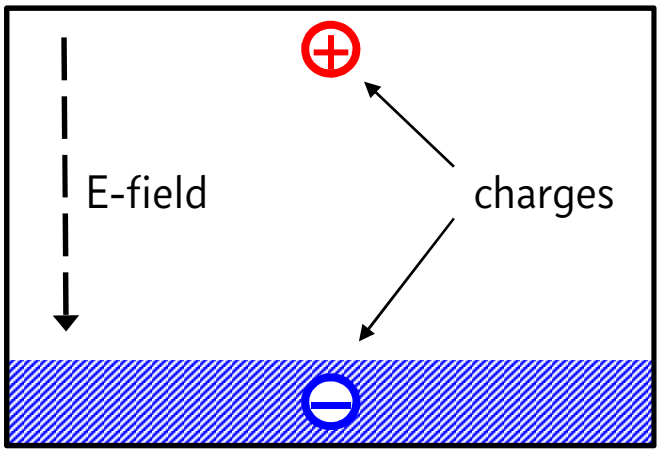
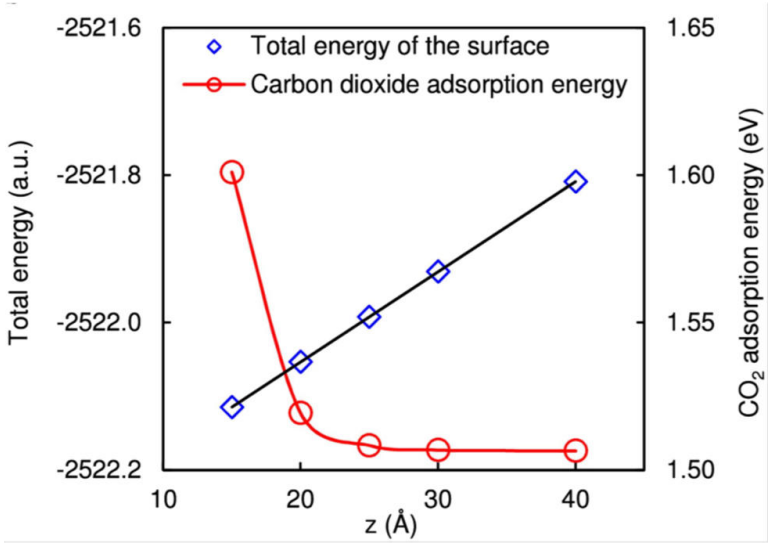
# Modeling charges

Electron mobility » ion mobility

⇒ **natural negative surface charging**




**Computationally:**

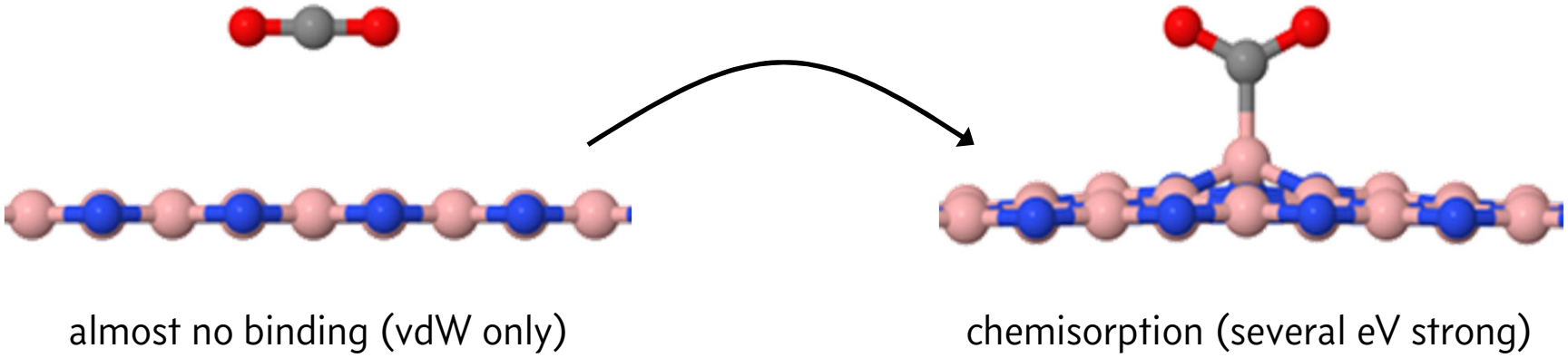
Define a H-atom in gas phase, but don't associate wavefunction with it
=> electron localises in surface, with $H^+$ as gas phase counter ion
=> avoids divergence of energy, and corresponds to reality

# Modeling charges in plasma-catalysis

**Electronic structure is key**

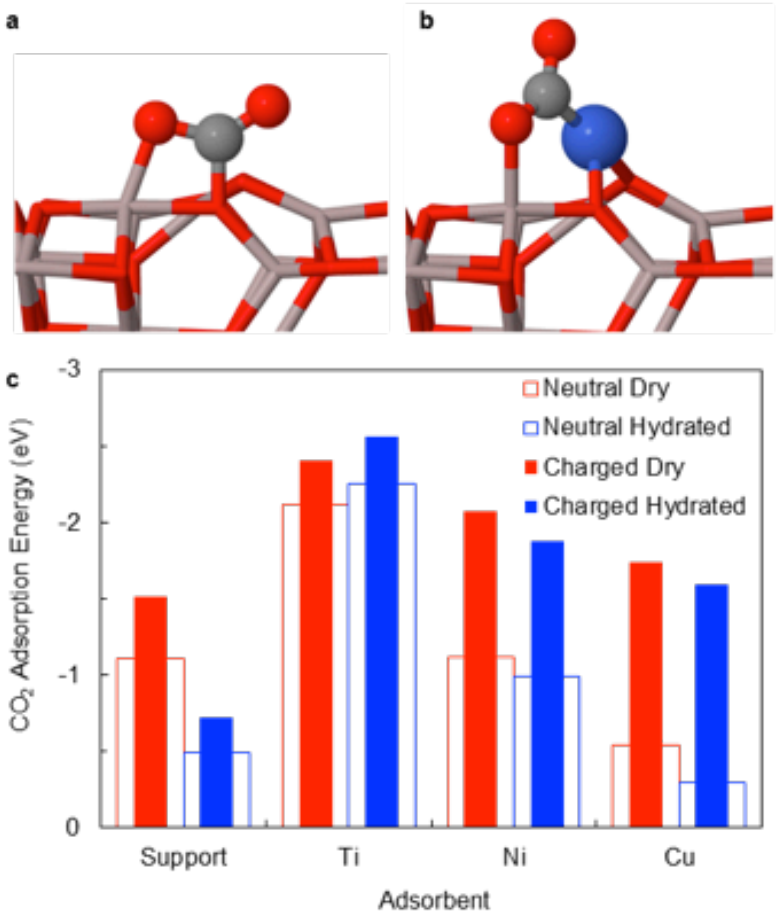
What happens when charge is added?

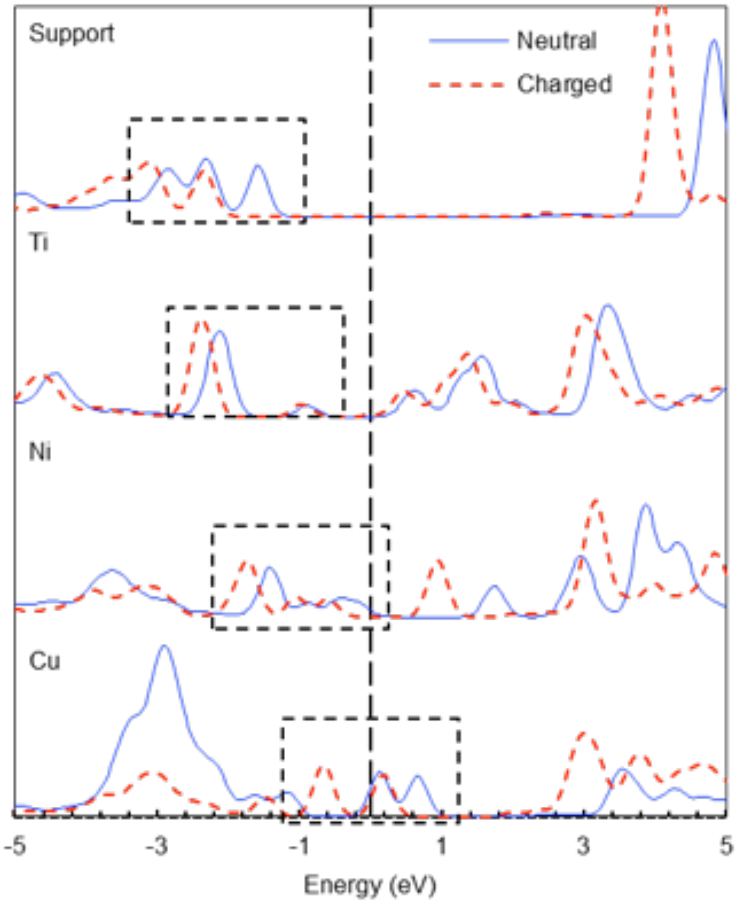
Might the plasma modify the catalyst electronic structure and thereby enhance chemical processes?




K. M. Bal, E. C. Neyts, *PCCP* **20** (2018) 8456

# Surface charging - $CO_2$ chemisorption




Significant increase in $CO_2$ adsorption energy…

… due to lowering of bonding states

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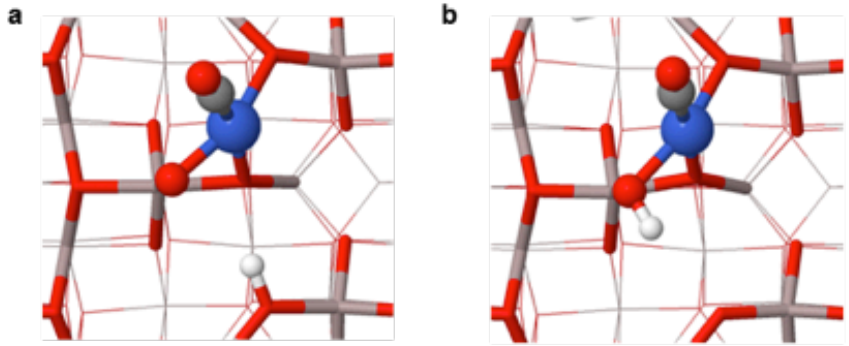
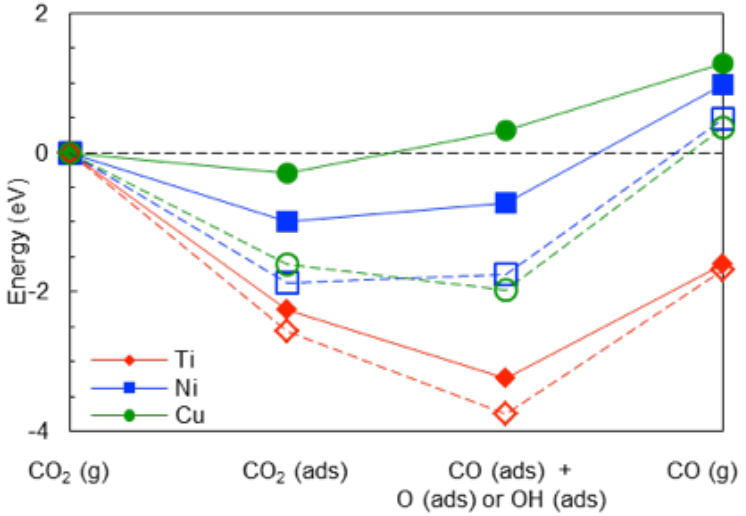
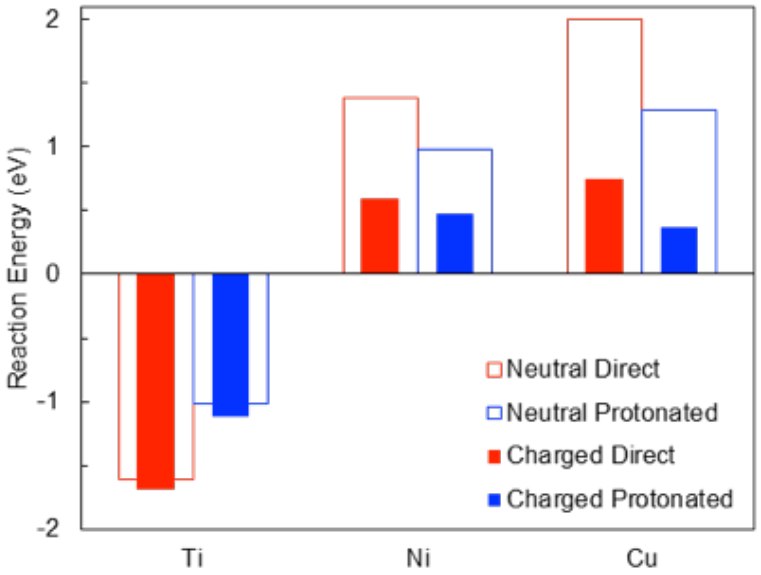
# Surface charging - $CO_2$ dissociation



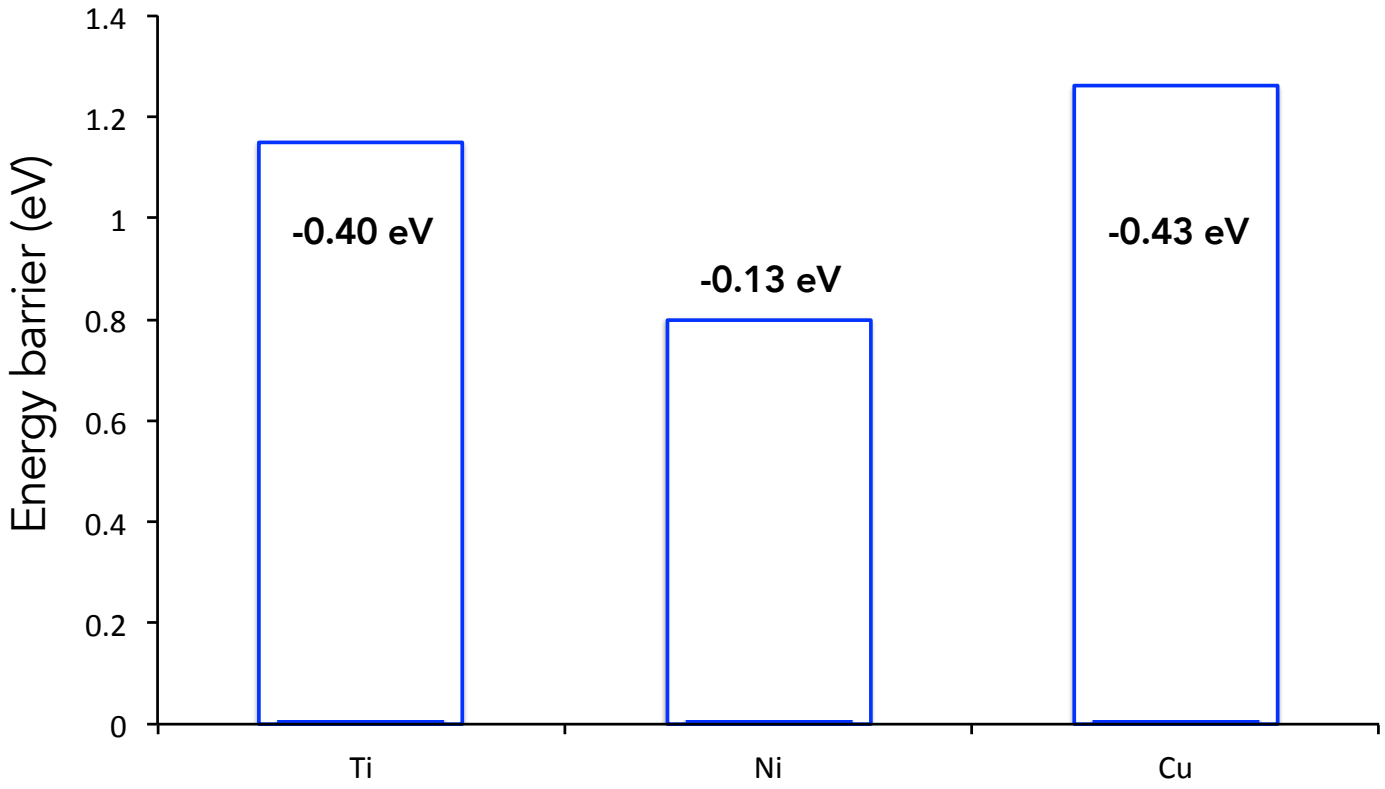




Upon surface charging, $CO_2$ dissocation becomes (much) less endothermic!

K. M. Bal, E. C. Neyts, *PCCP* **20** (2018) 8456

# Surface charging - $CO_2$ dissociation

So far: thermodynamics. Are kinetics affected as well?



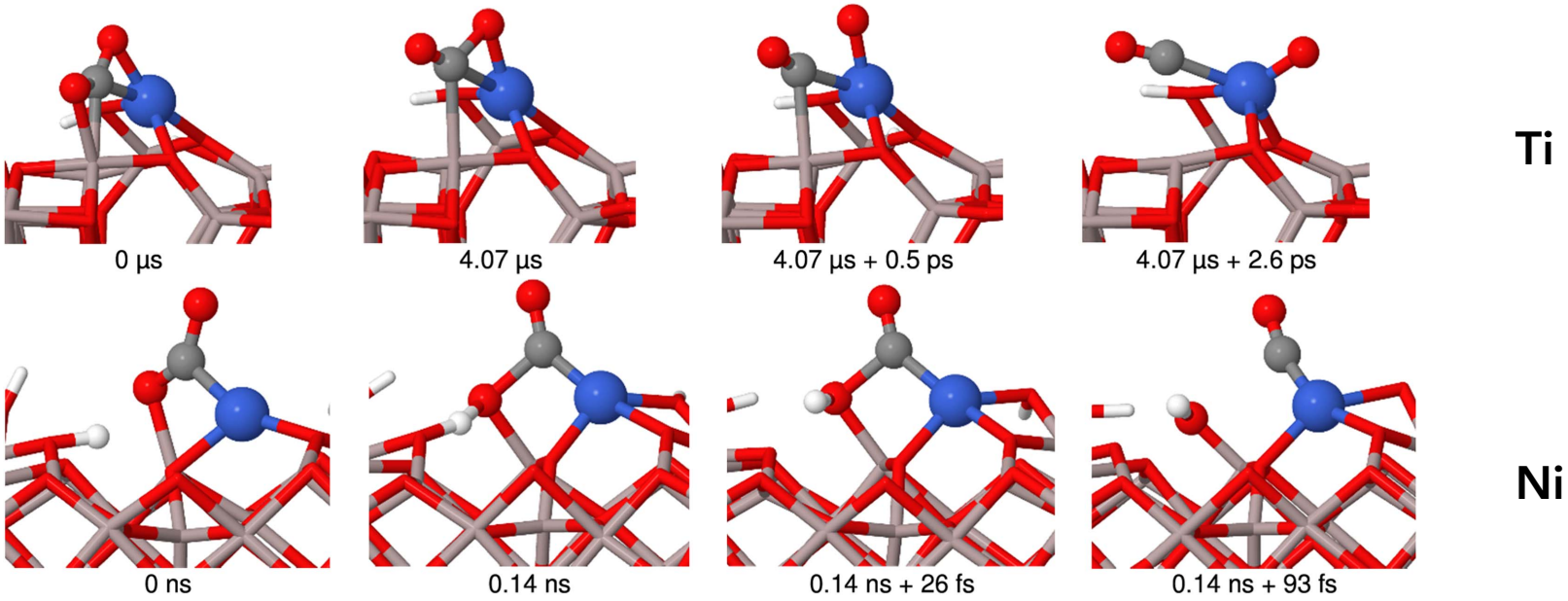

$CO_2$ splitting barrier is lowered by up to ~0.4 eV

(@500K: increase in rate by 4 orders of magnitude…)

K. M. Bal, E. C. Neyts, *PCCP* **20** (2018) 8456

# Dynamics

Can hyperdynamics* simulations add additional insight?




On Ti: *direct* splitting (at 400 K) - elementary process

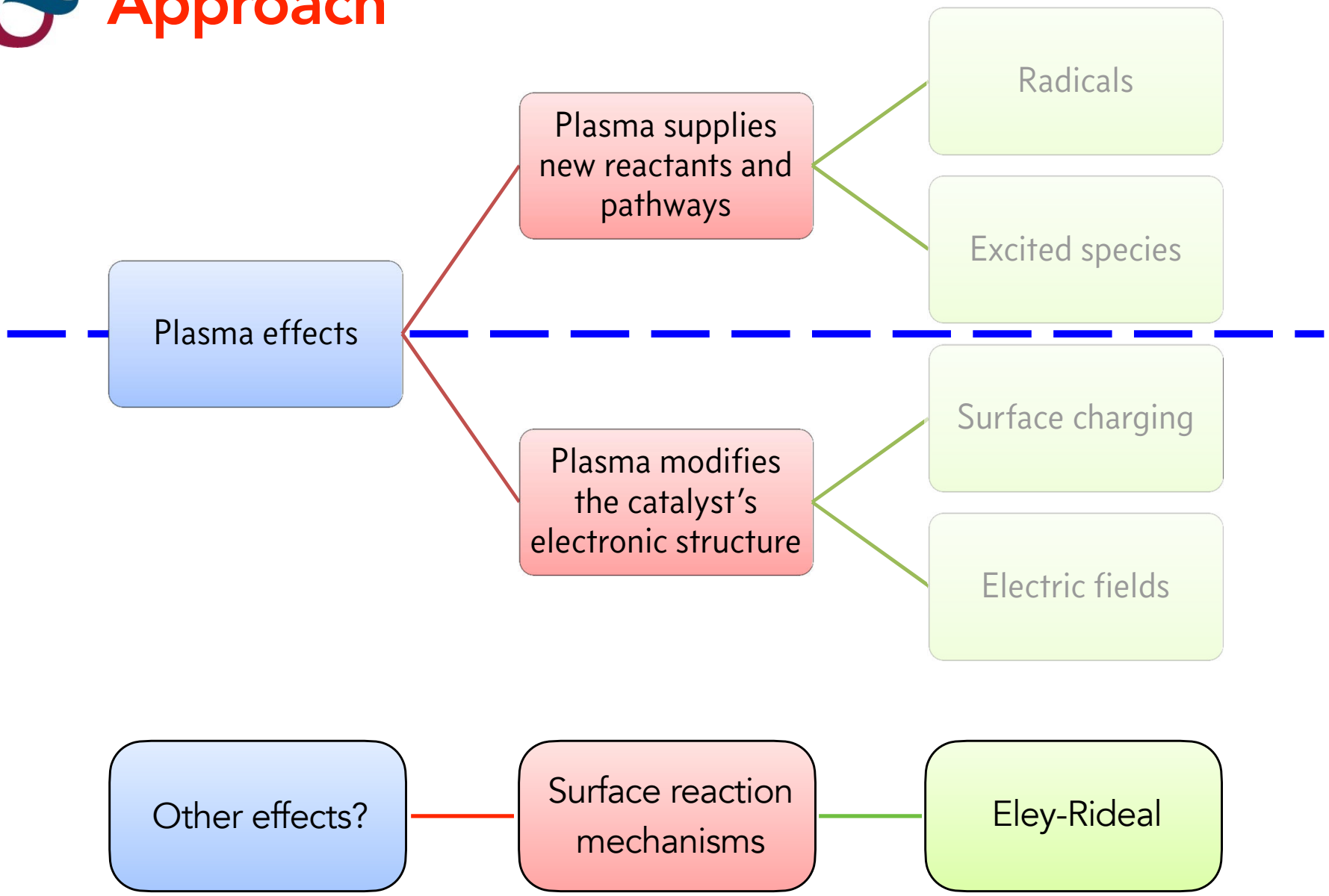
On Ni: *proton-mediated* splitting - concerted mechanism

**Dynamic atomistic simulations allow to *directly* observe the mechanism**

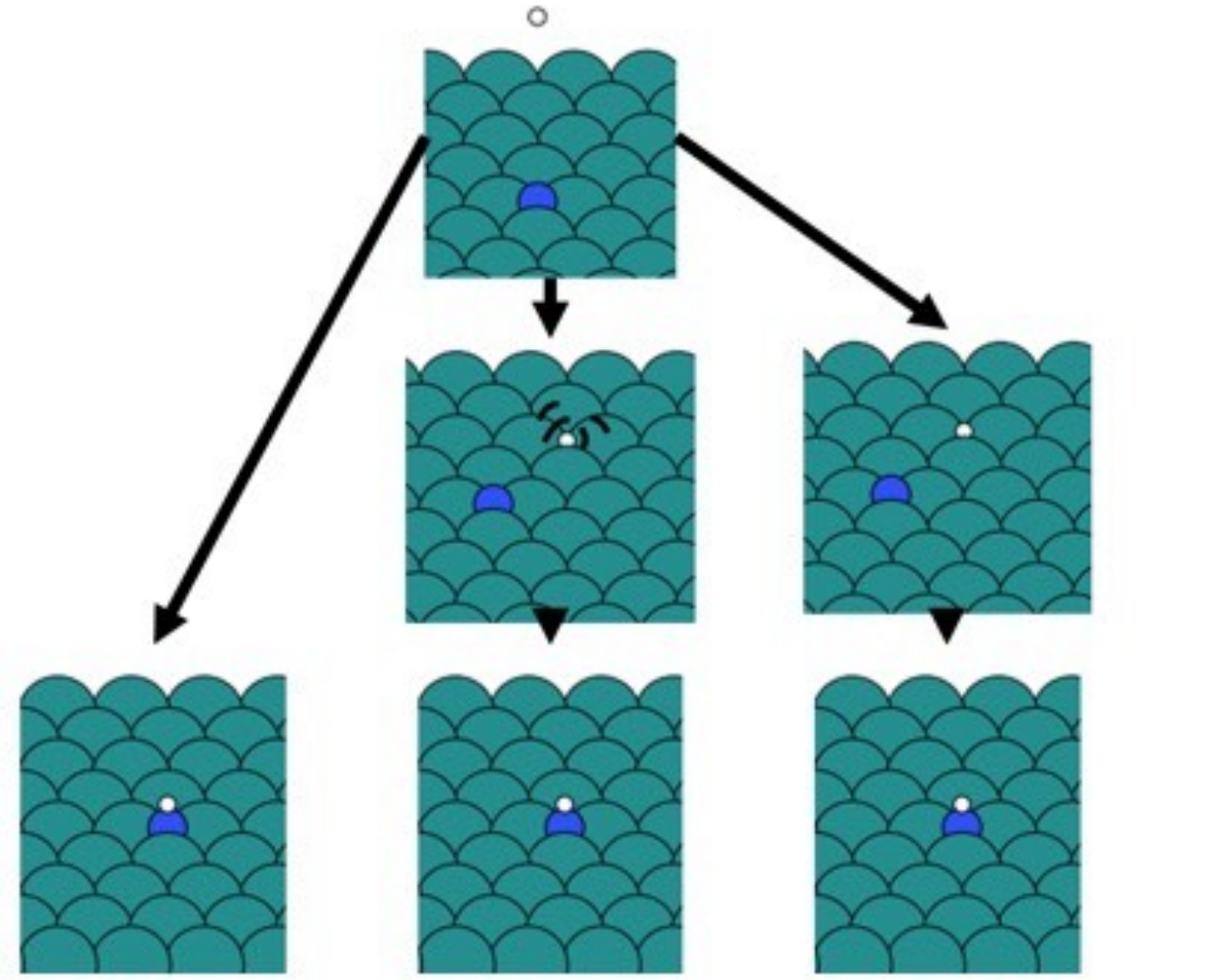

K. M. Bal, E. C. Neyts, *PCCP* **20** (2018) 8456

* K. M. Bal, E. C. Neyts, *J. Chem. Theory Comput.* **11** (2015) 4545

# Approach


Plasma effects
Plasma supplies new reactants and pathways
Radicals
Excited species
Plasma modifies the catalyst's electronic structure
Surface charging
Electric fields
Other effects?
Surface reaction mechanisms
Eley-Rideal

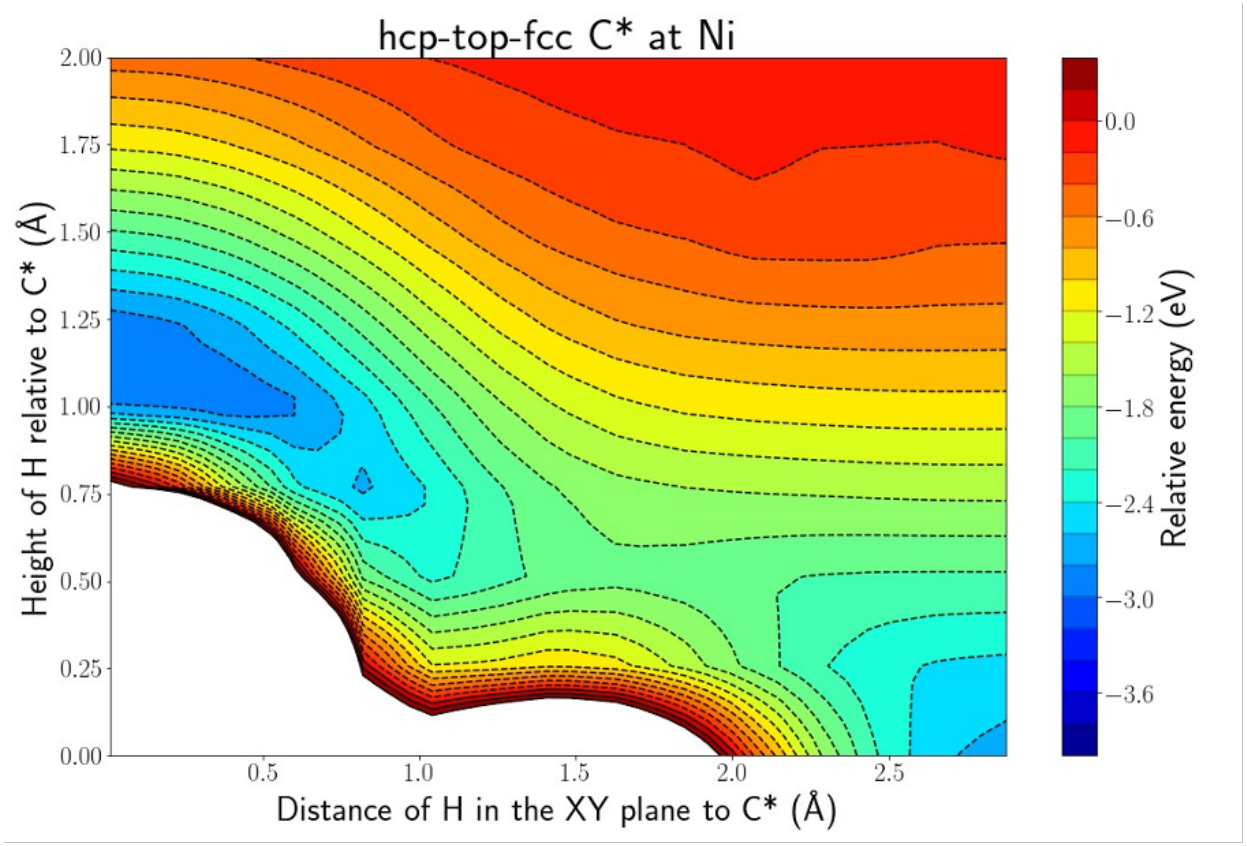
# Introducing Eley-Rideal



Eley-Rideal "hot atom" Langmuir-Hinshelwood

# How important is Eley-Rideal?

**Where does an incoming H-atom end up?**

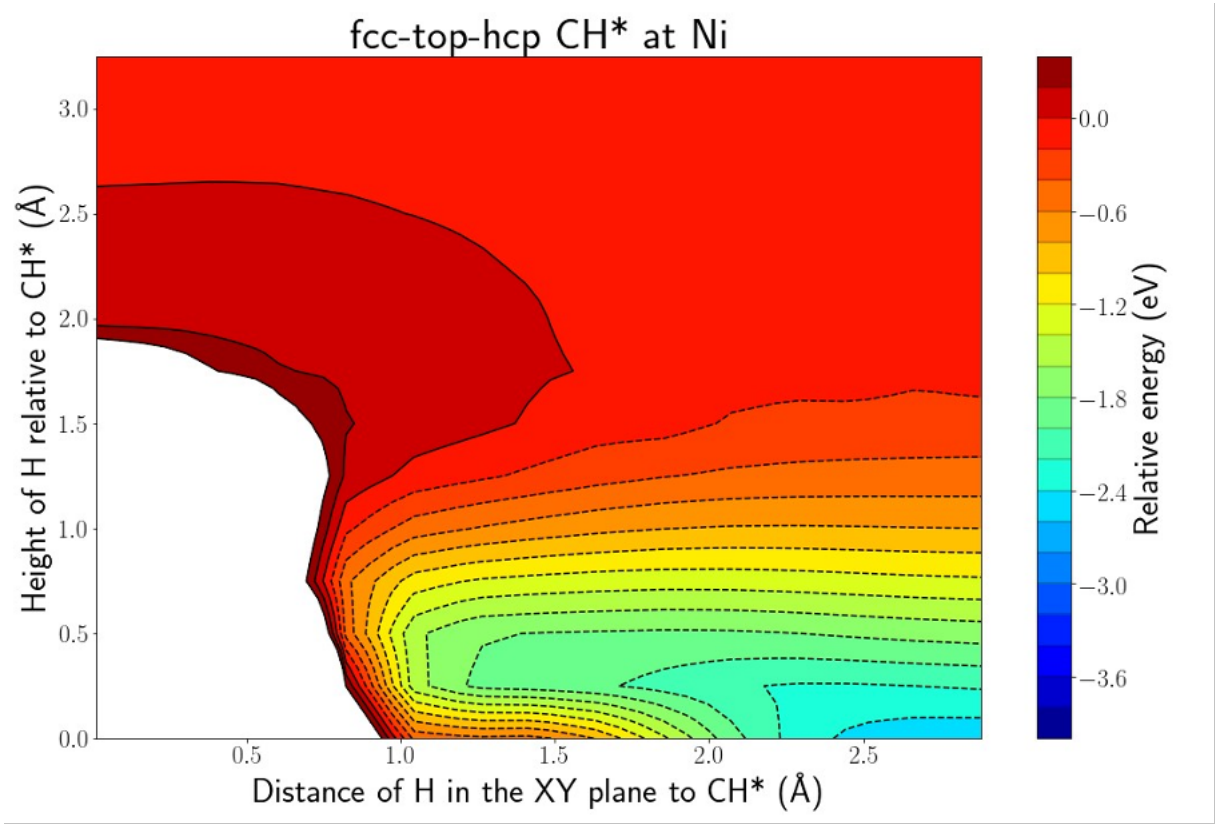



**On C*: H (unsurprisingly) adds to the C-atom => ER is possible**

R. Michiels *et al.*, JPCC 2024, 28, p. 11196

# How important is Eley-Rideal?

**Where does an incoming H-atom end up?**



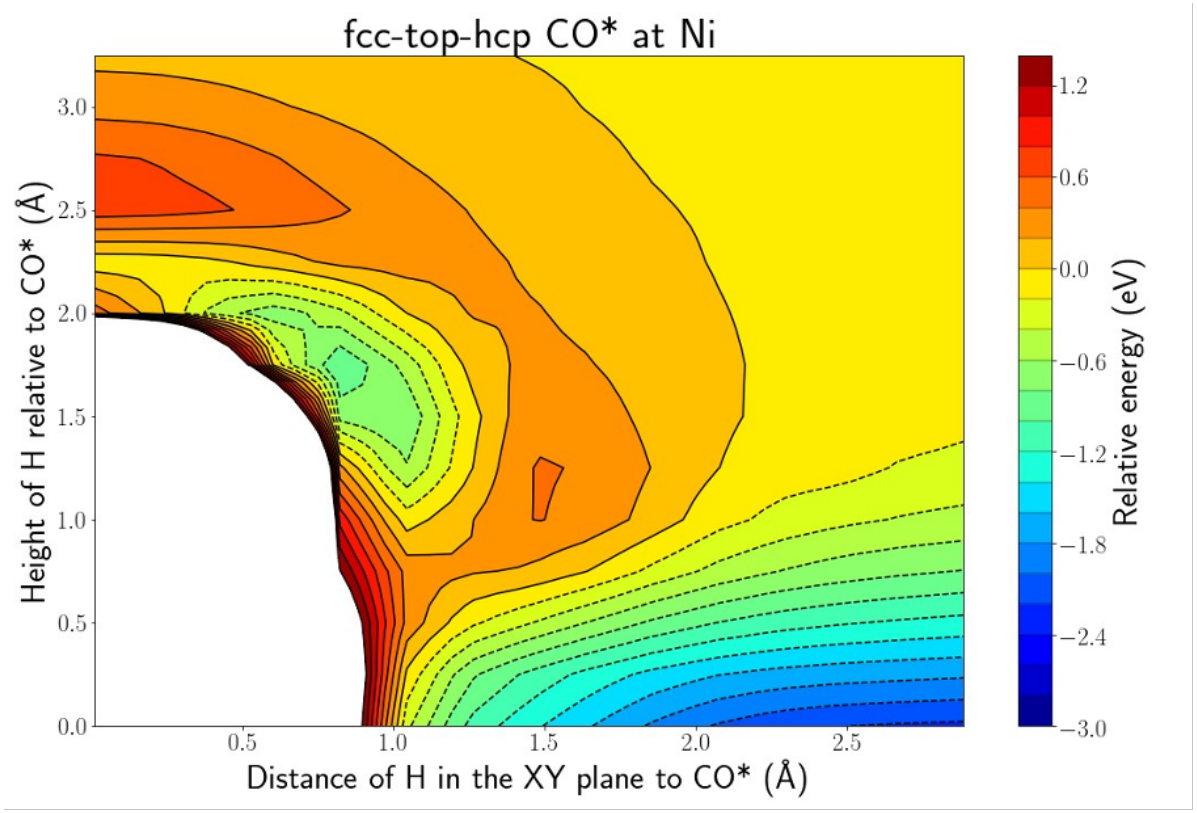

**On CH*: H (surprisingly) DOES NOT add to the CH-fragment**

**=> ER is not possible (Similar results on $CH_2$ and $CH_3$)**

R. Michiels *et al.*, JPCC 2024, 28, p. 11196

# How important is Eley-Rideal?

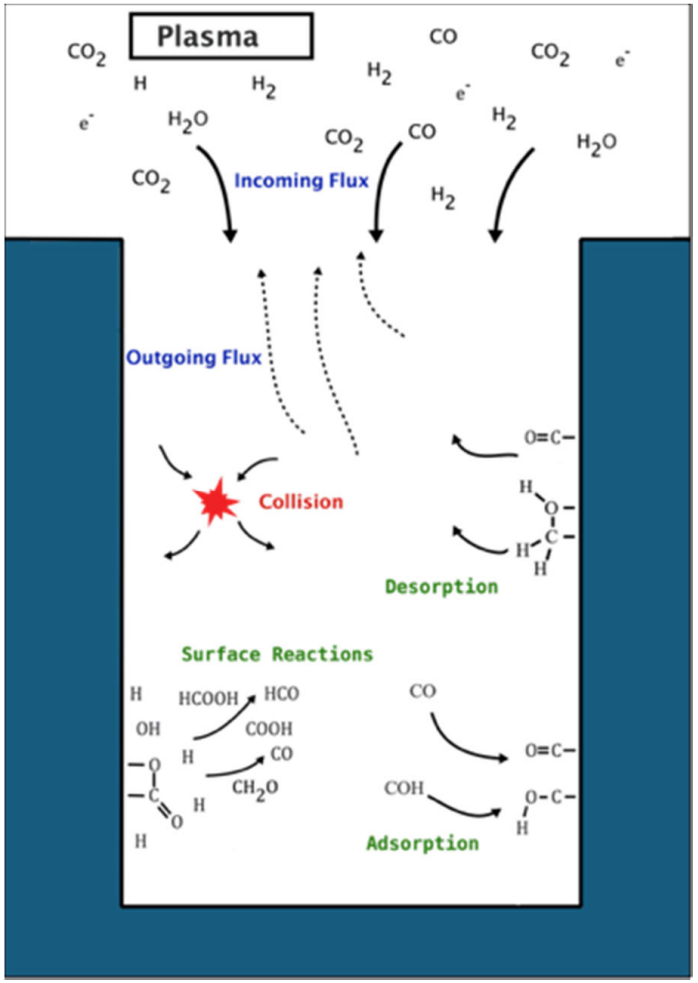
**Where does an incoming H-atom end up?**




**On CO*: Barrier to form ER-product COH => ER is rather unlikely**

R. Michiels *et al.*, JPCC 2024, 28, p. 11196

# How far should we re-entangle?



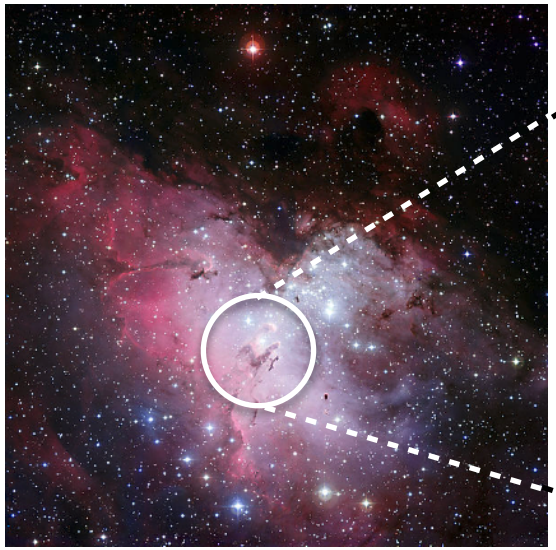

Reality is highly complex,
due to cross-interactions

Current models are very simple
cross-interactions are absent

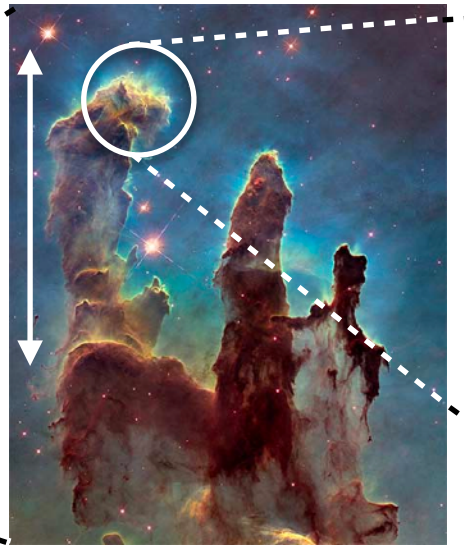
Bridge gap with experiments

# Annex: plasma-surface astrochemistry

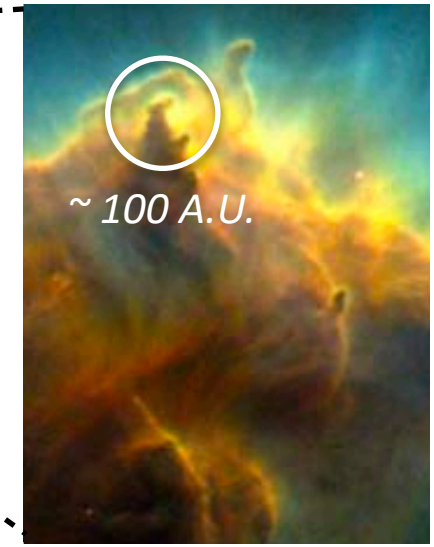
# Plasmas are not confined to earth…



Eagle Nebula




Pillars of Creation

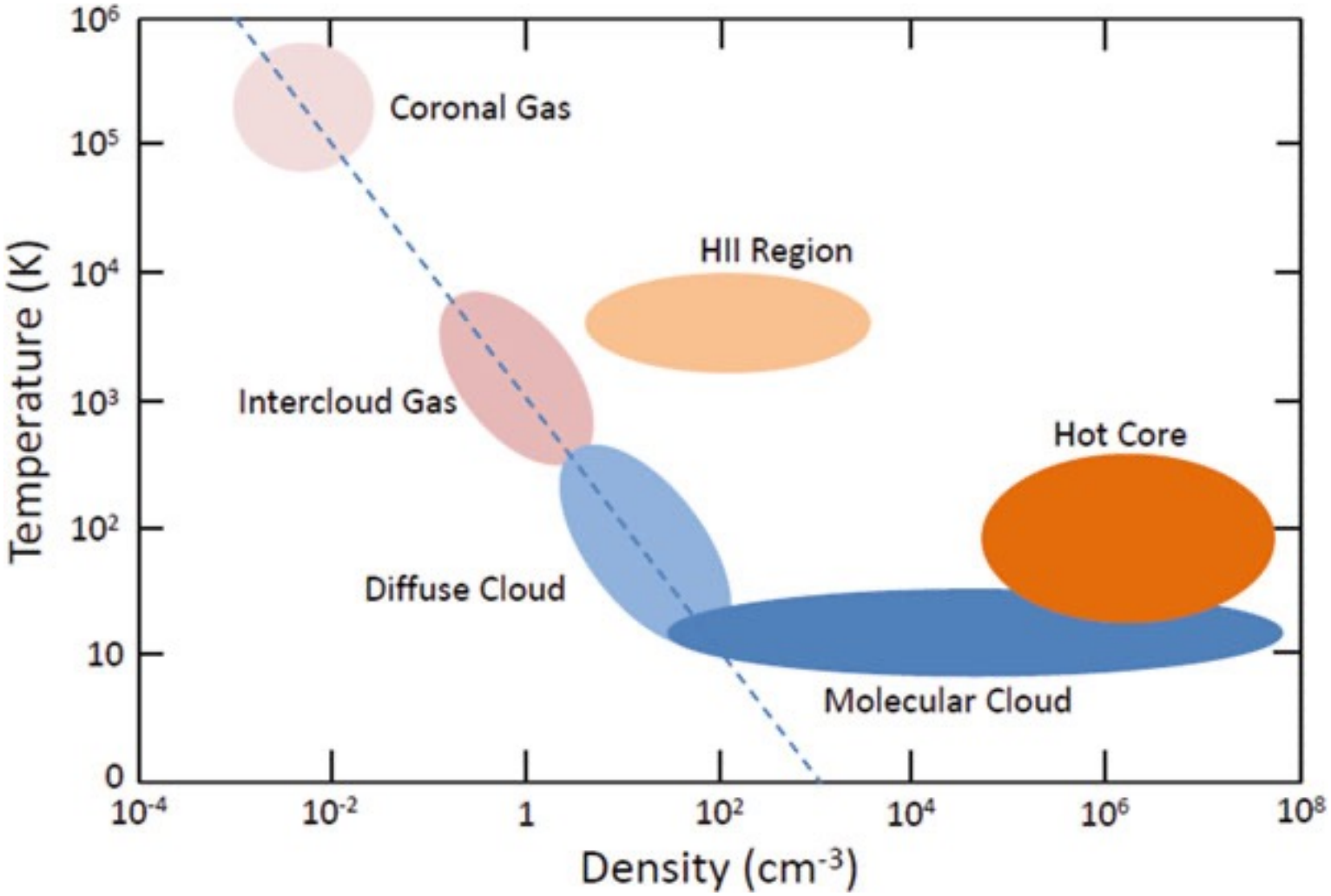



Evaporating Gaseous Globules

Partially ionized gases

Despite extreme conditions: bunch of interesting chemistry!

# Plasmas are not confined to earth…




S. Yamamoto, "Introduction to astrochemistry", Springer (2017)

# Chemistry in the interstellar medium (ISM)

**Gas phase reactions**

barrierless exothermic

not efficient

**Gas-surface reactions**

"catalyse" the reaction

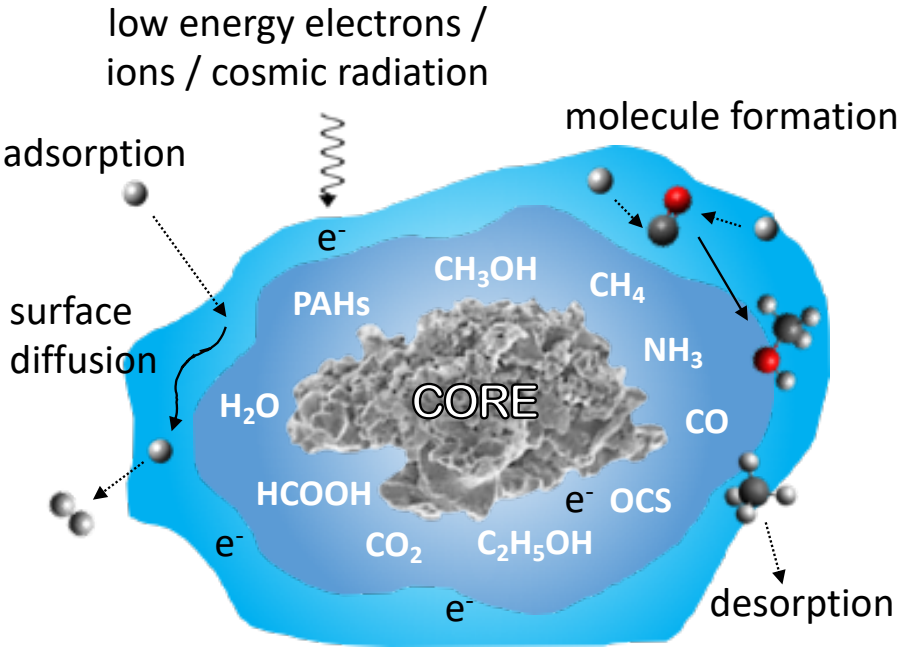
critically depend on binding energies

**Dust particles** Size range: nm ~ μm

silicates & amorphous carbon core

in molecular clouds: ice mantle (ASW)

may be charged




How does charge affect binding energies?
How does the plasma affect how and which molecules are formed?

# Neutral ASW

**CO: dipole moment**

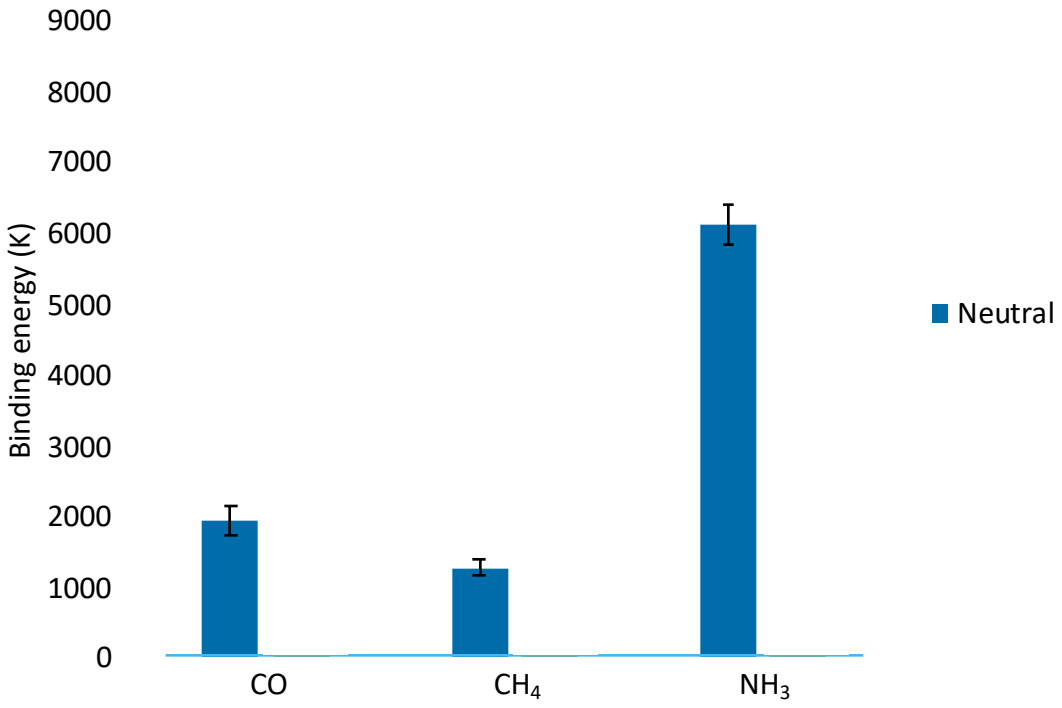
neutral: 1975 ± 195 K

**$CH_4$: no dipole, no H-bonds**

neutral: 1306 ± 123 K

**$NH_3$: dipole, H-bonds**

neutral: 6150 ± 278 K




DFT calculations; hybrid PBE0 functional + D3 dispersion

6-311++G(d,p) basis set

42 data points per molecule

# Neutral vs Charged ASW

**CO: dipole moment**

neutral: 1975 ± 195 K

charged: 7749 ± 472 K

**$CH_4$: no dipole, no H-bonds**

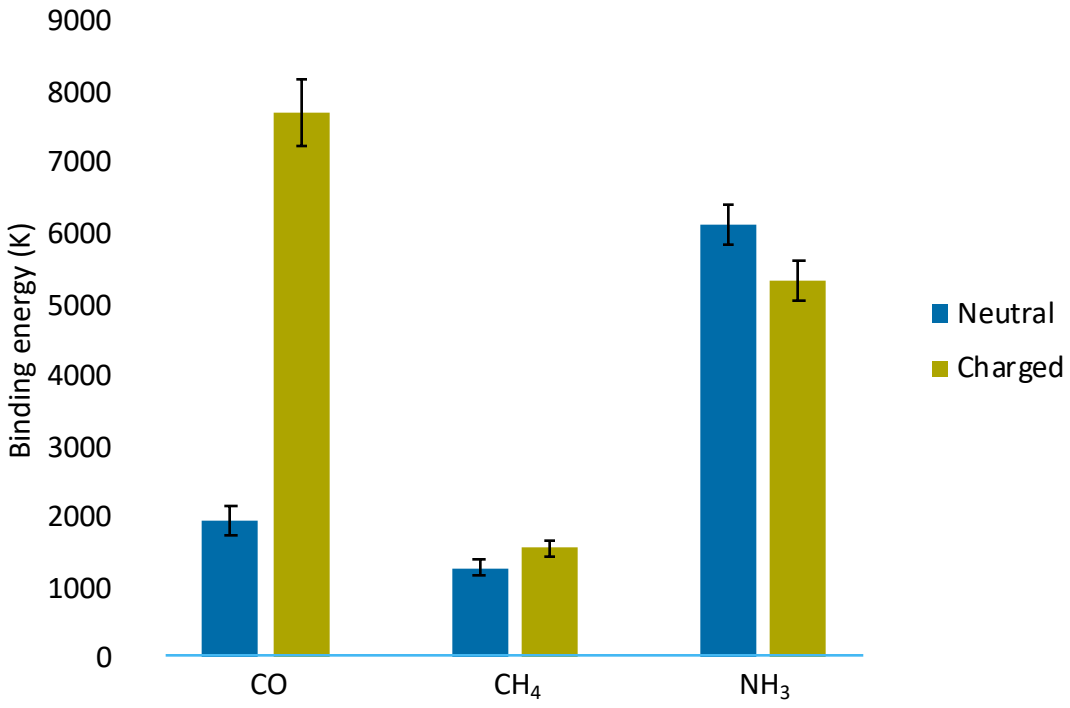
neutral: 1306 ± 123 K

charged: 1586 ± 104 K

**$NH_3$: dipole, H-bonds**

neutral: 6150 ± 278 K

charged: 5360 ± 276 K




Charge <u>does</u> have a significant effect on at least some molecules

=> affect surface reaction rates

=> plasma determines which, why and how molecules are formed in space

# Conclusions & final remarks

- Models/simulations are complementary to experiments, they do not replace them
- We - experimentalists and modellers - need to reach out to each other to strengthen this complementarity

- We - scientists - can and should reach out to other disciplines as well, focus on what binds us, and strengthen each other

# Acknowledgments

## People involved in this work

Prof. dr. Erik Neyts
head of MOSAIC group

dr. Kristof Bal

Prof. dr. Annemie Bogaerts
head of PLASMANT group

Roel Michiels

Tobe Vorsselmans

# Thank you