Unraveling Surface Chemistry in Plasma Catalysis by Microscopic Modeling

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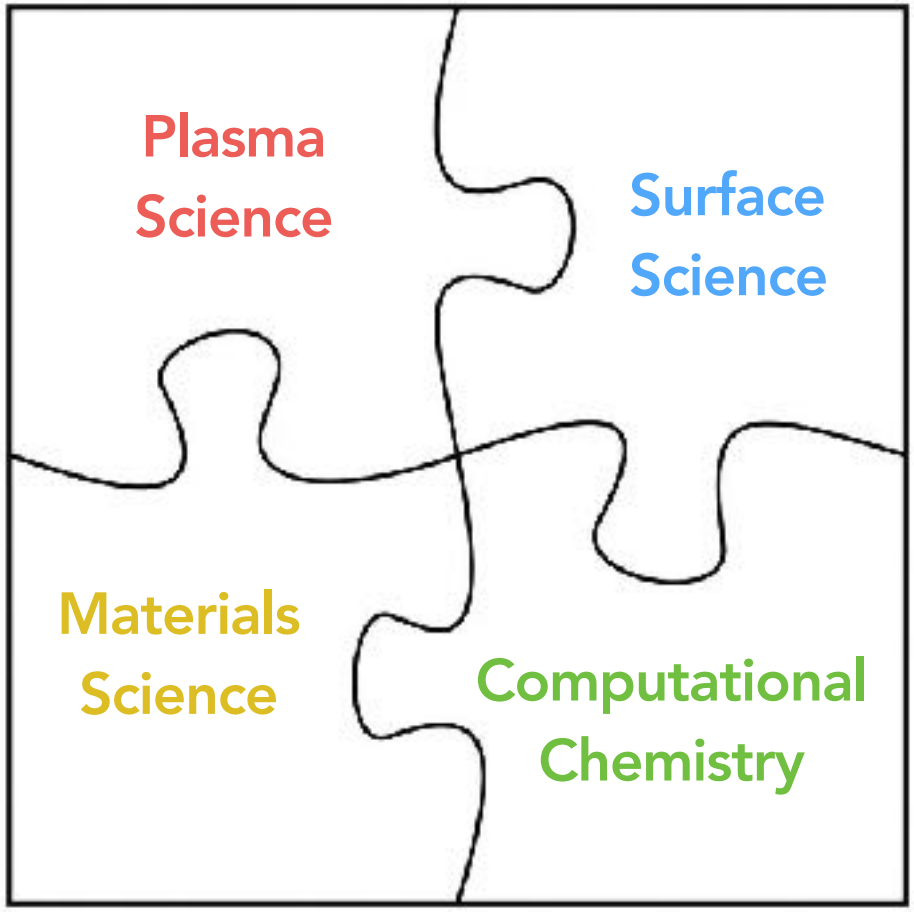
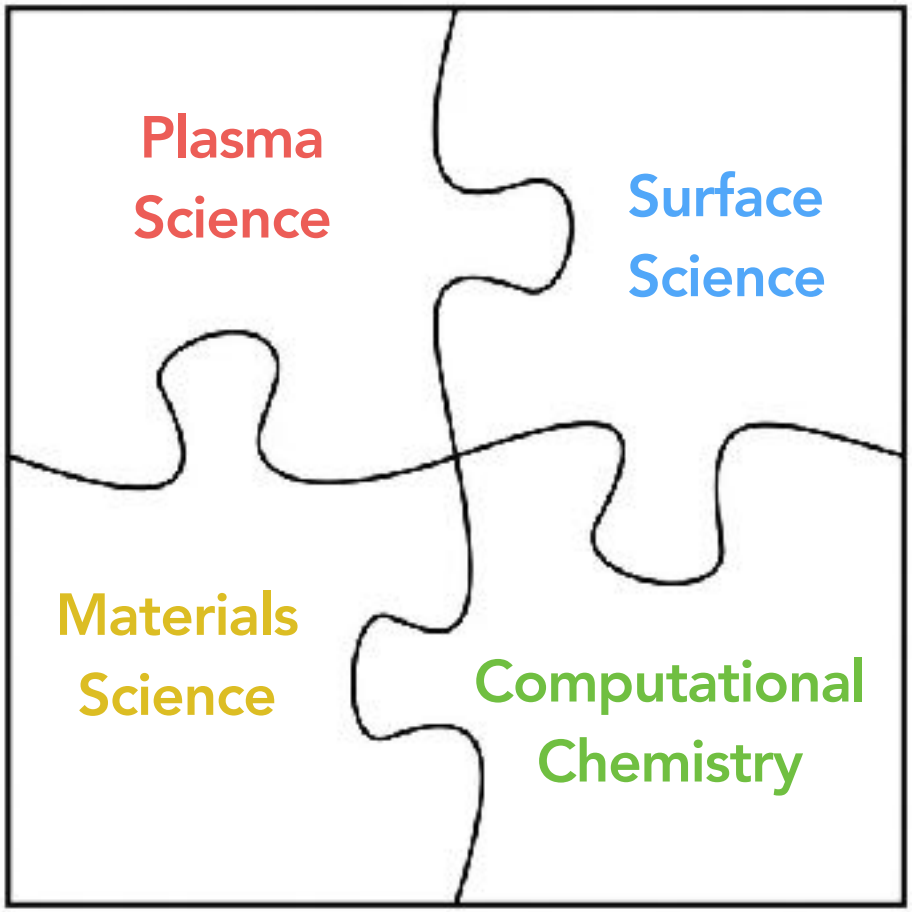
Computational plasma-surface studies



High degree of complexity is to be expected

Computational plasma-surface studies

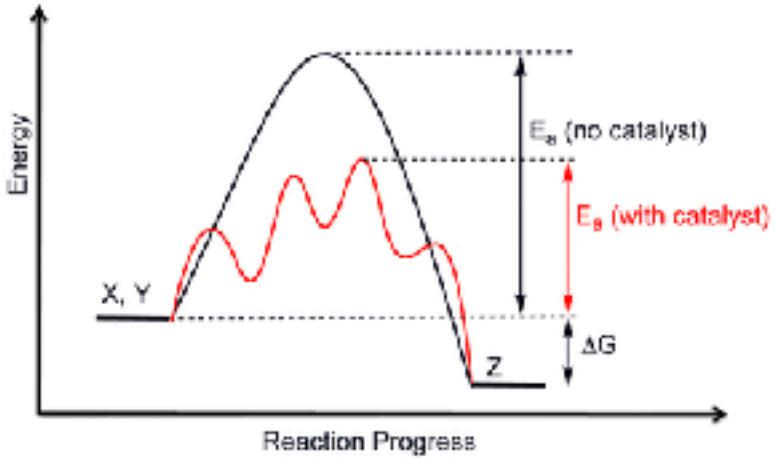


Can models & simulations disentangle this complexity?

High degree of complexity is to be expected

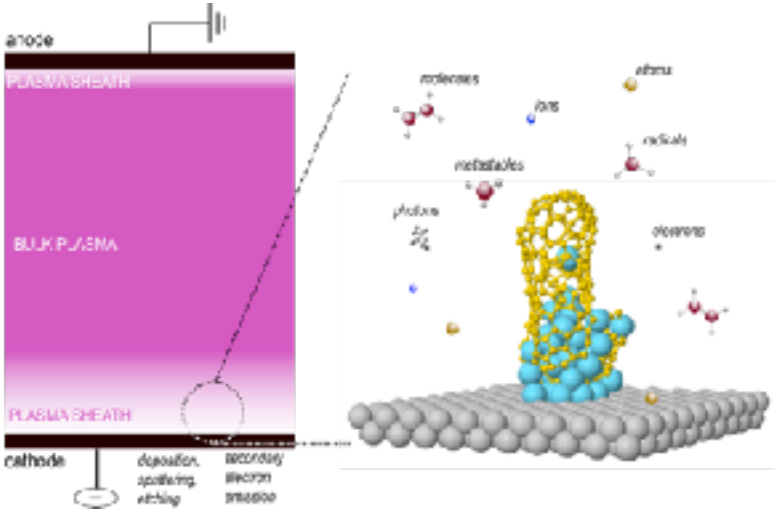
Motivation for modeling plasma catalysis

Catalysis



+

Plasma



Possible synergy! → **Origins??**

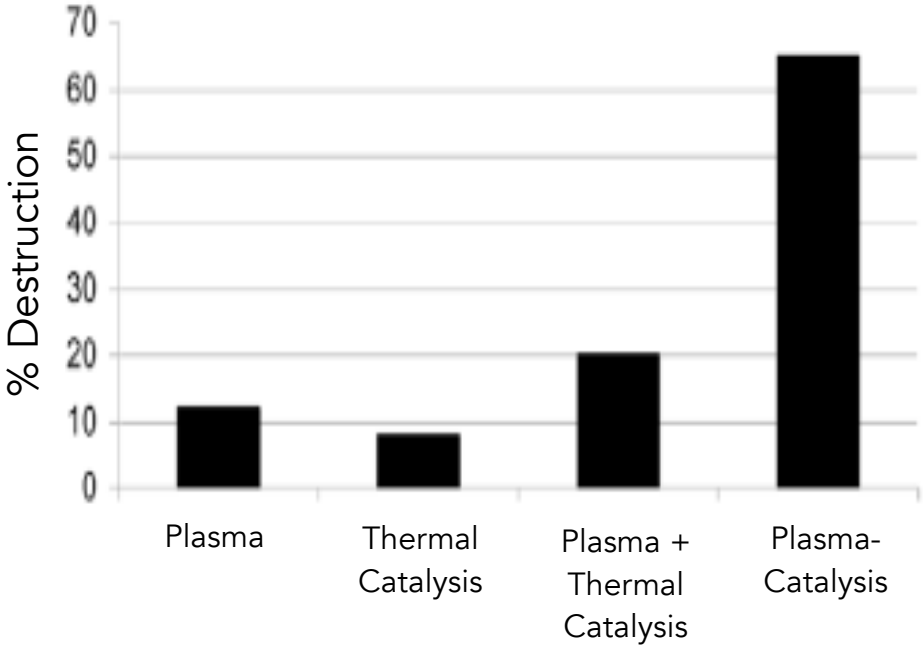
Neyts et al., ***Chem. Rev.*** 115 (2015) 13408

Plasma catalysis accepted as field on its own by larger chemical community

Motivation for modeling plasma catalysis

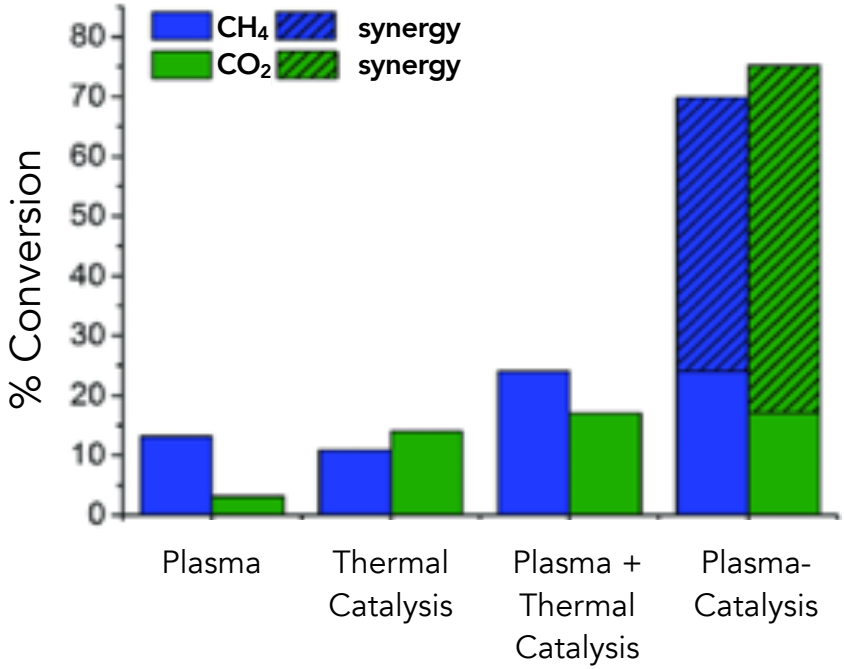
Gas cleaning:

Toluene decomposition



Gas conversion:

CH_4 / CO_2 reforming



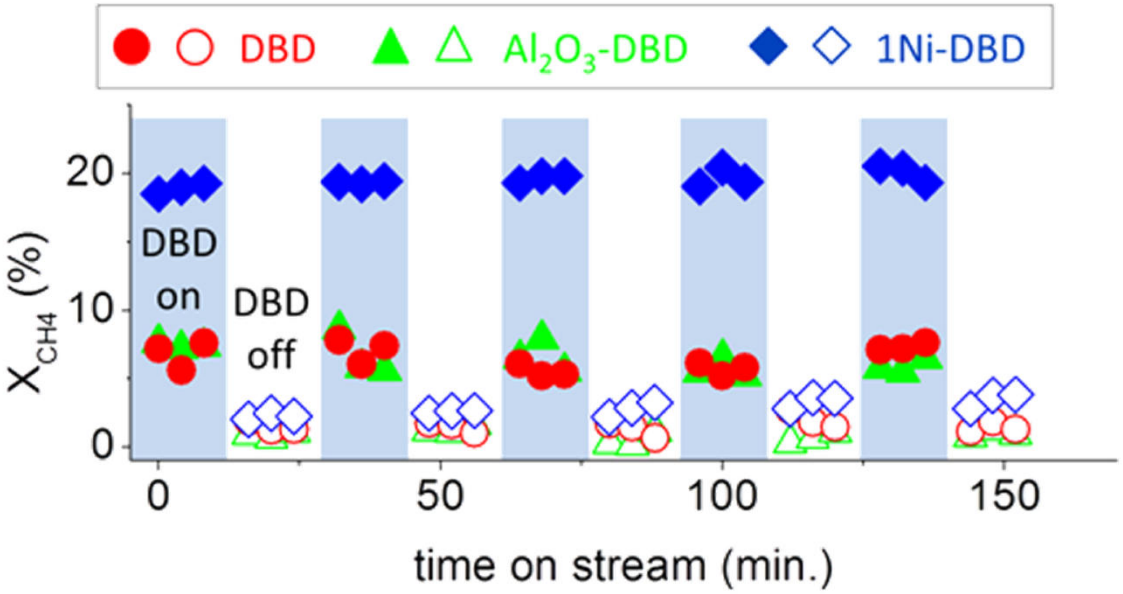
Clear interplay of catalyst and plasma

Mechanism?

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

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

Motivation for modeling plasma catalysis

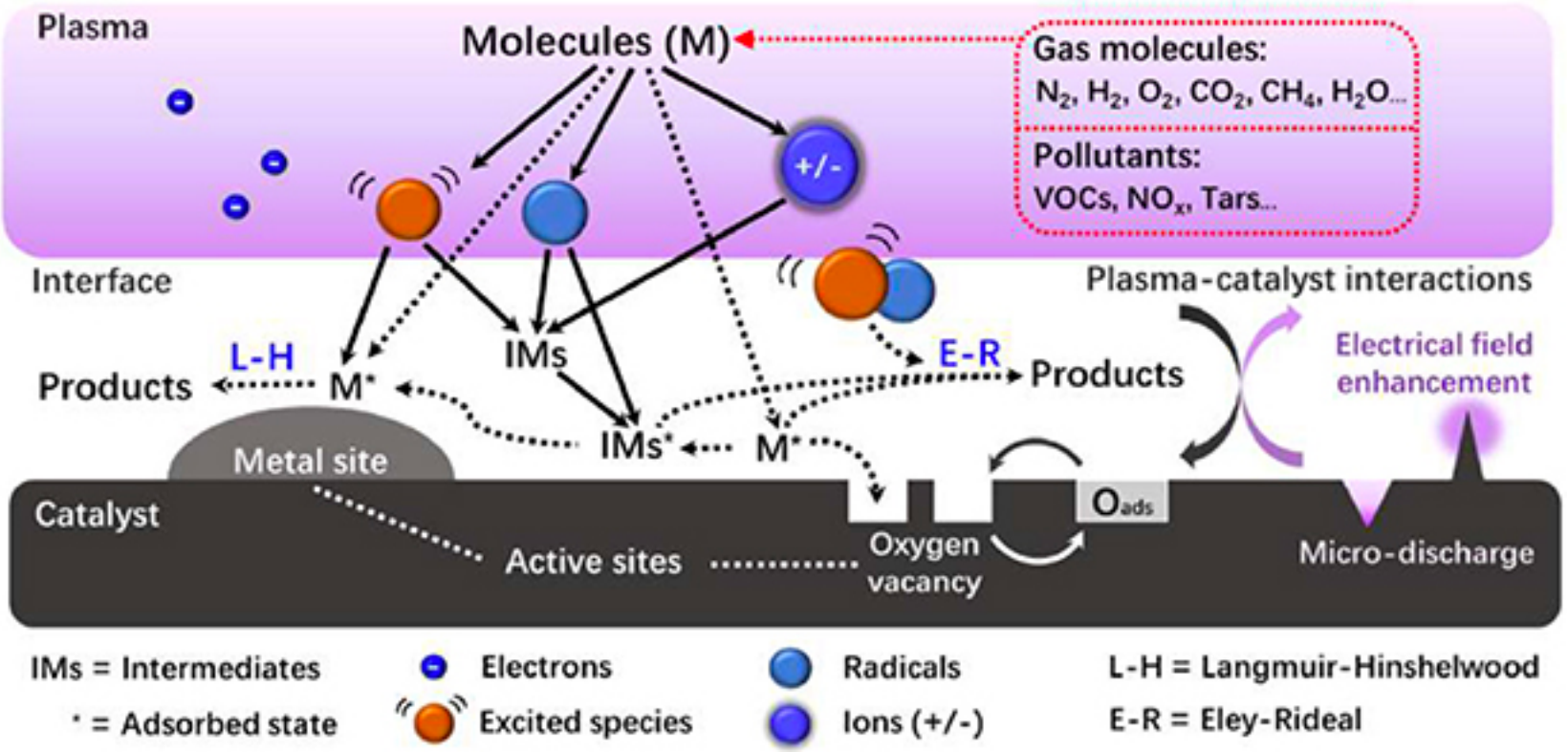


Clear *reversible* interplay of catalyst and plasma

Mechanism?

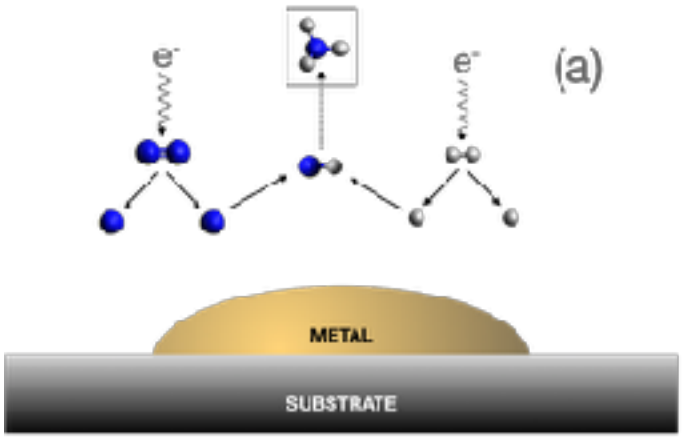
J. Kim, ACS Energy Lett. **1** (2016) 96

Manyfold of individual processes

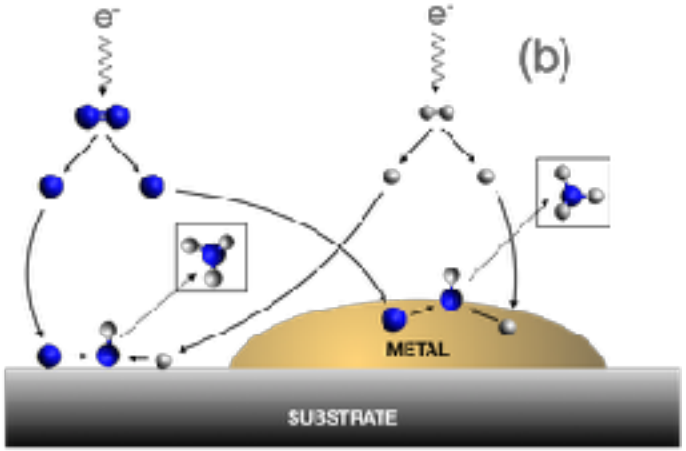


A. Bogaerts et al., J. Phys. D: Appl. Phys. **53** (2020) 443001

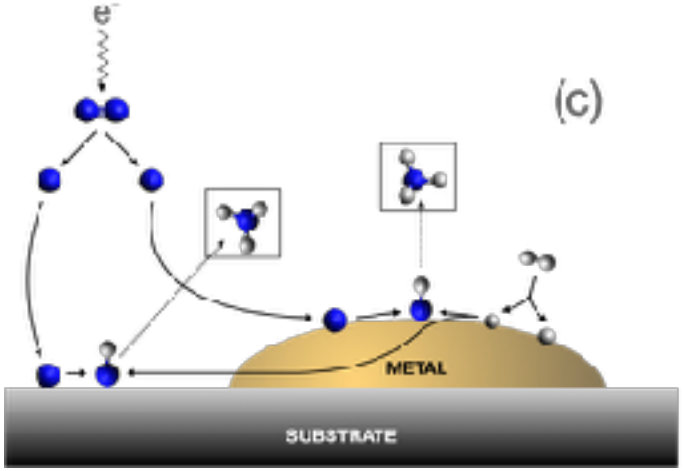
Plasma catalysis ≠ plasma + catalysis



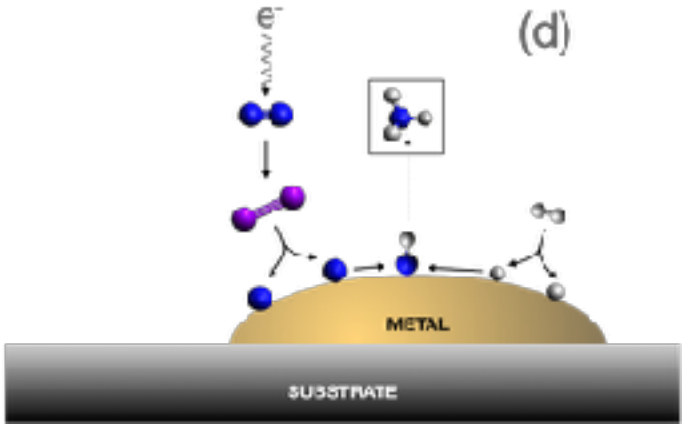
gas-phase



surface-enhanced plasma-driven



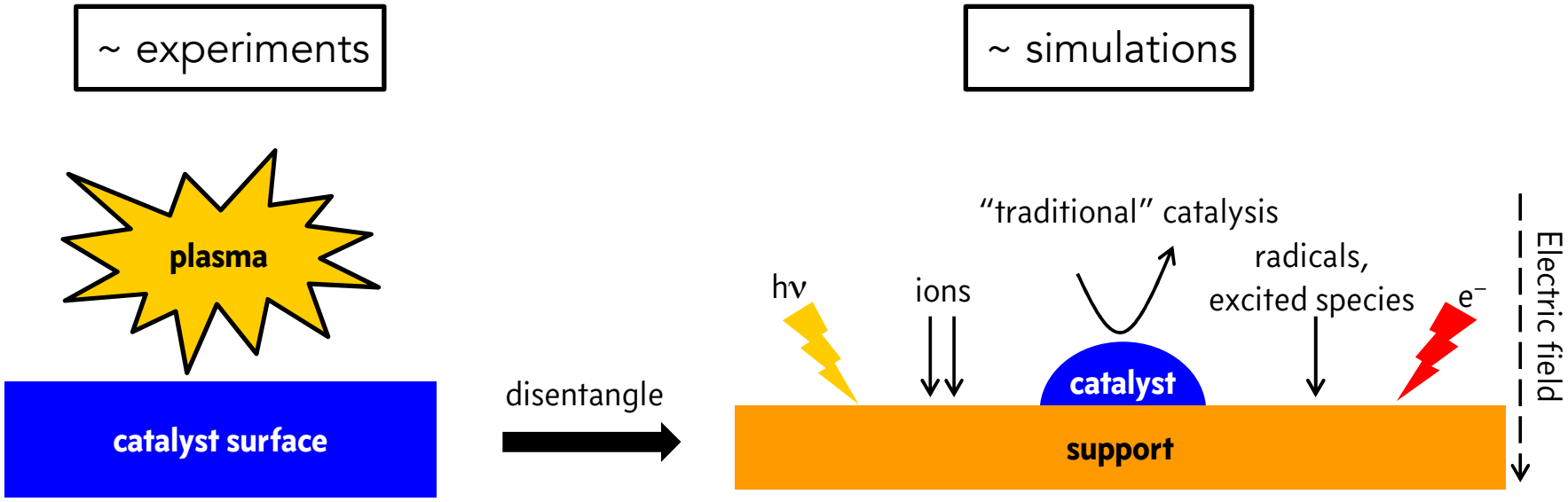
plasma-enhanced, semi-catalytic



plasma-catalytic

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

From experiment to modeling

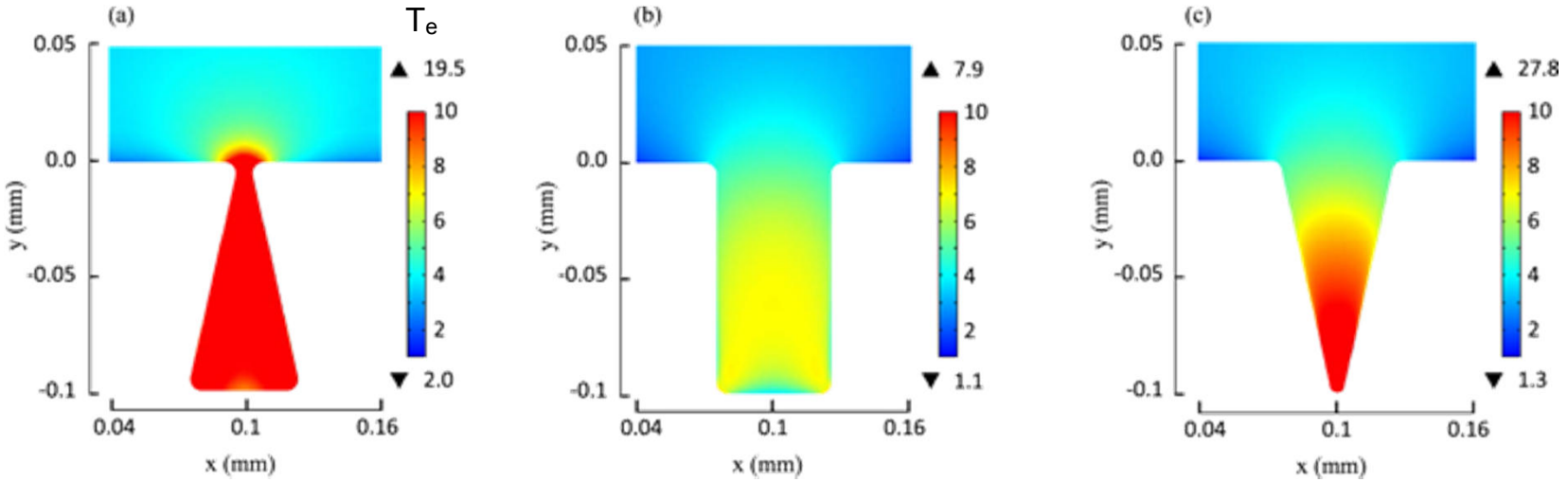


Modeling allows a bottom-up approach
to disentangle the process

Typical: Start off with plasma, then add catalyst

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

Macroscale modeling



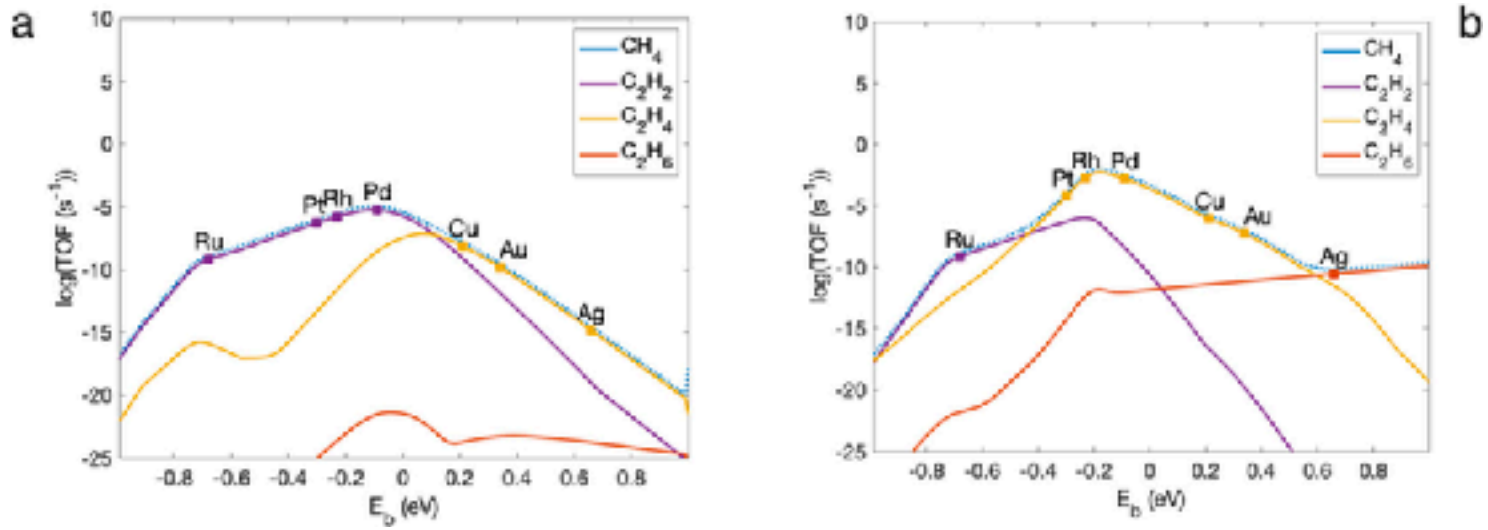
Plasma models use microscale knowns (rates, processes) to predict macroscopic unknowns

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

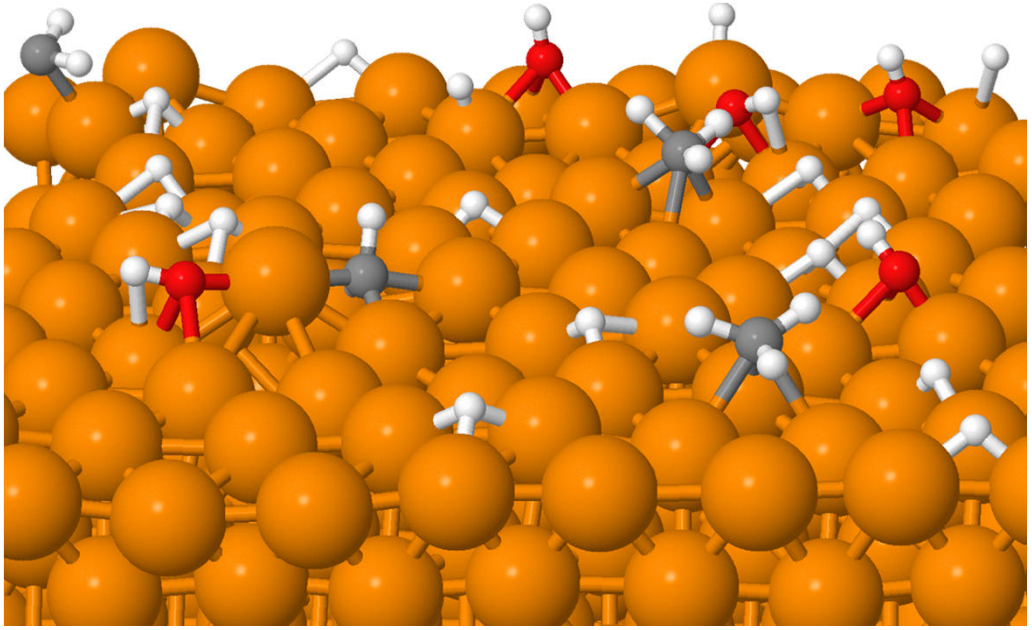
Vibrationally enhanced

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

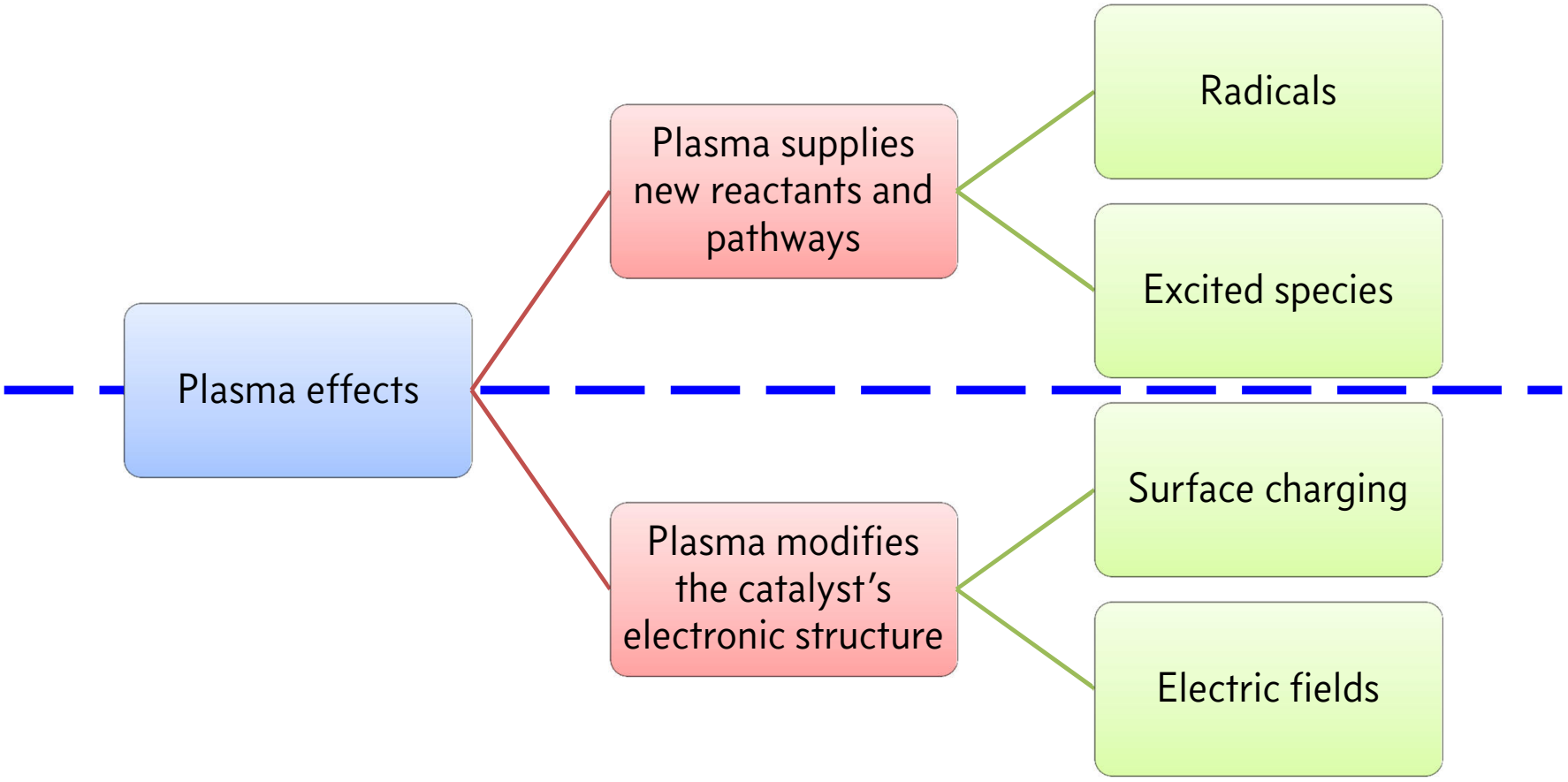


We need more fundamental information

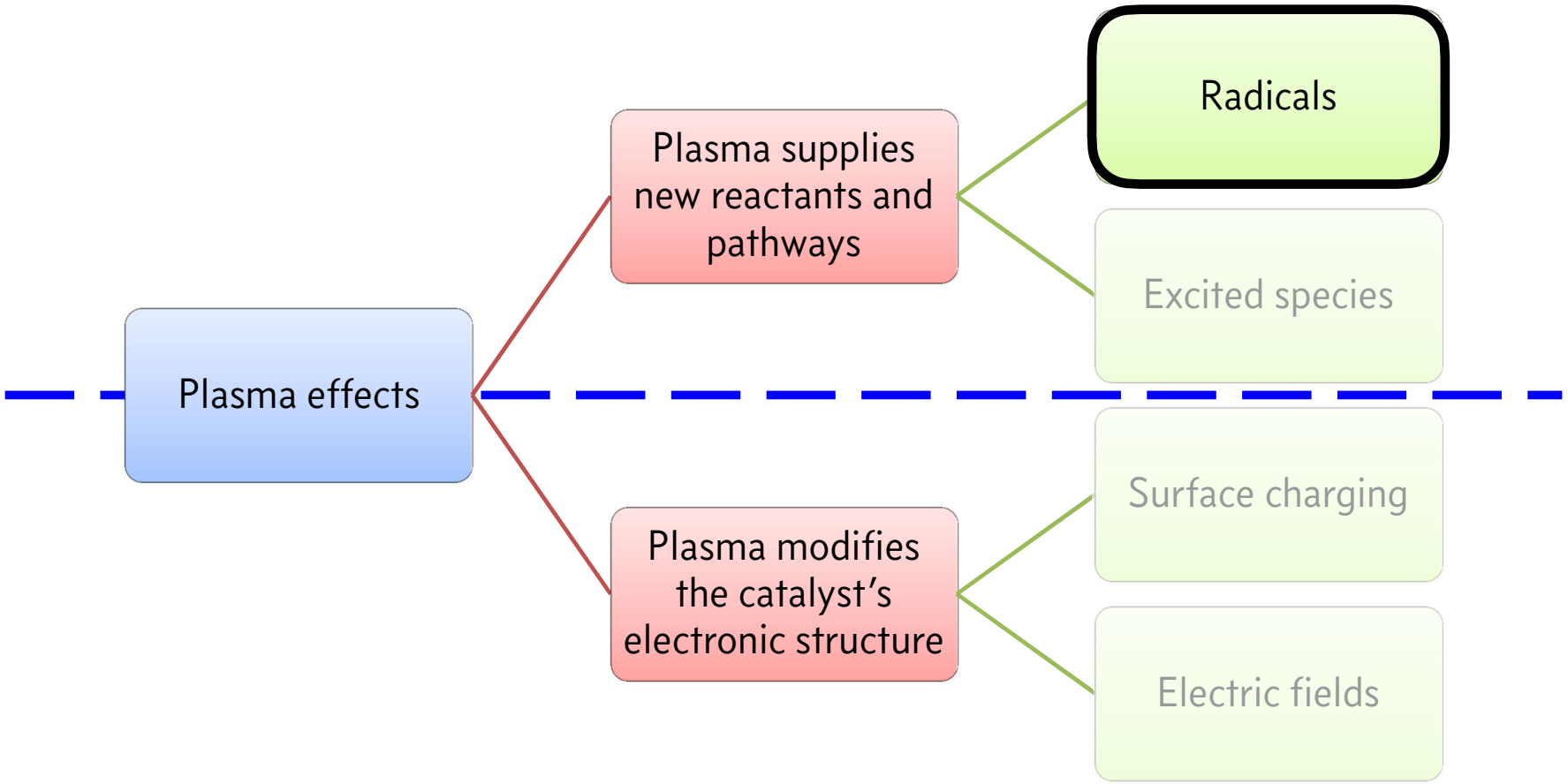
→ Atomistic simulations: **classical MD** → requires appropriate force field

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

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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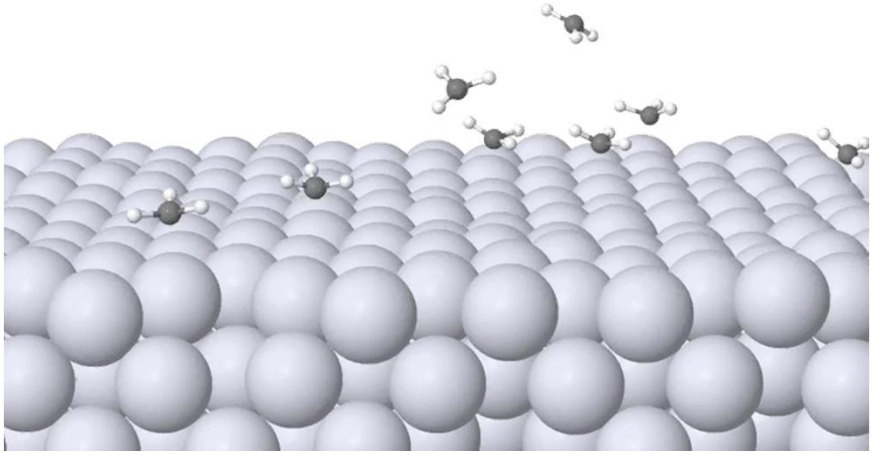
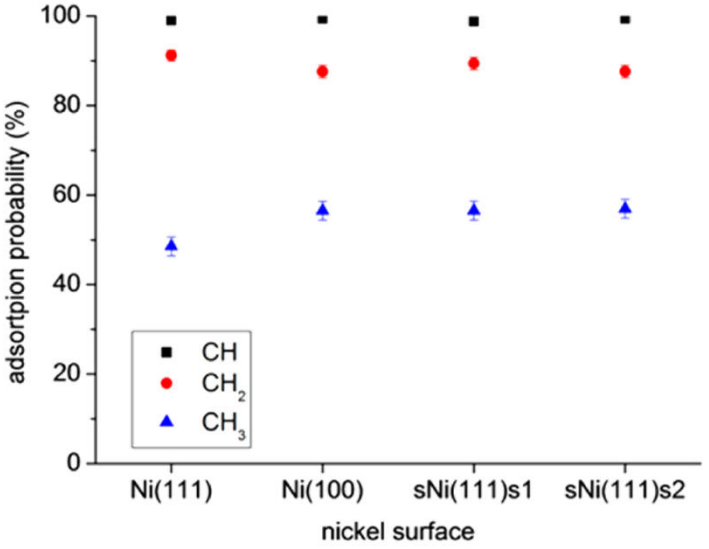
Radicals and excited species

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





Radicals are fairly easy!

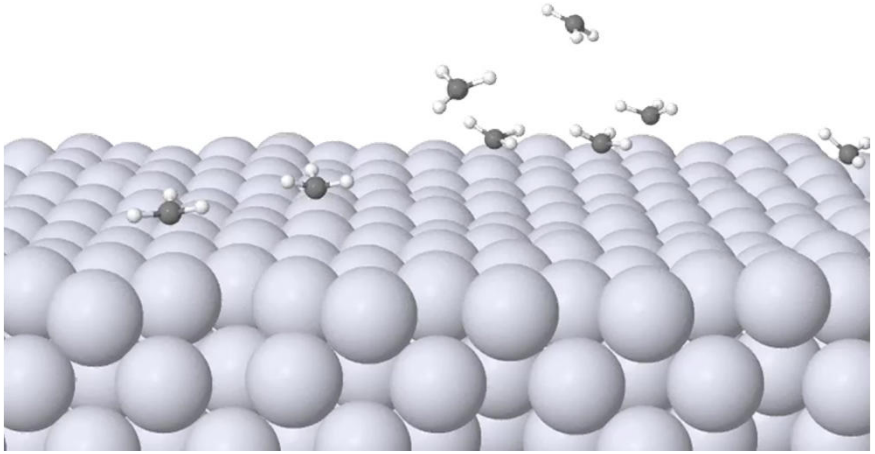
- Effects well-known for material growth, surface modification, …
- Usually included in standard atomistic models

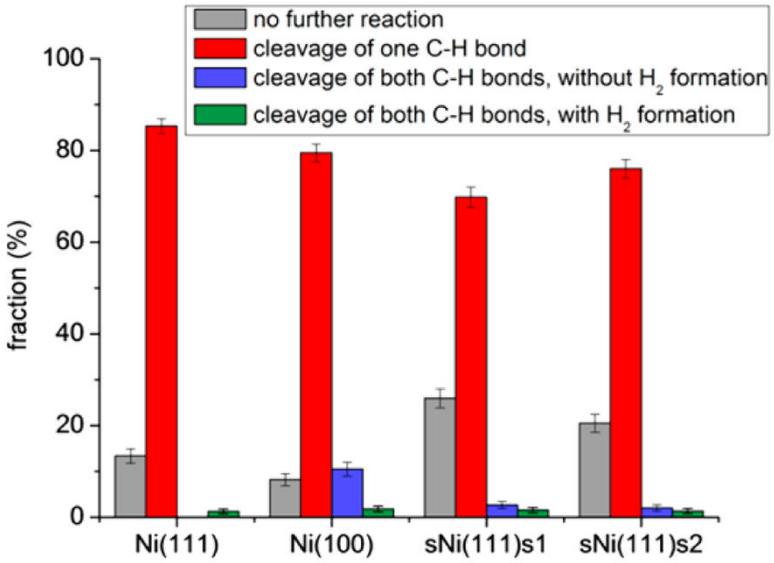
MD simulations of CH_x impact on Ni

- 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





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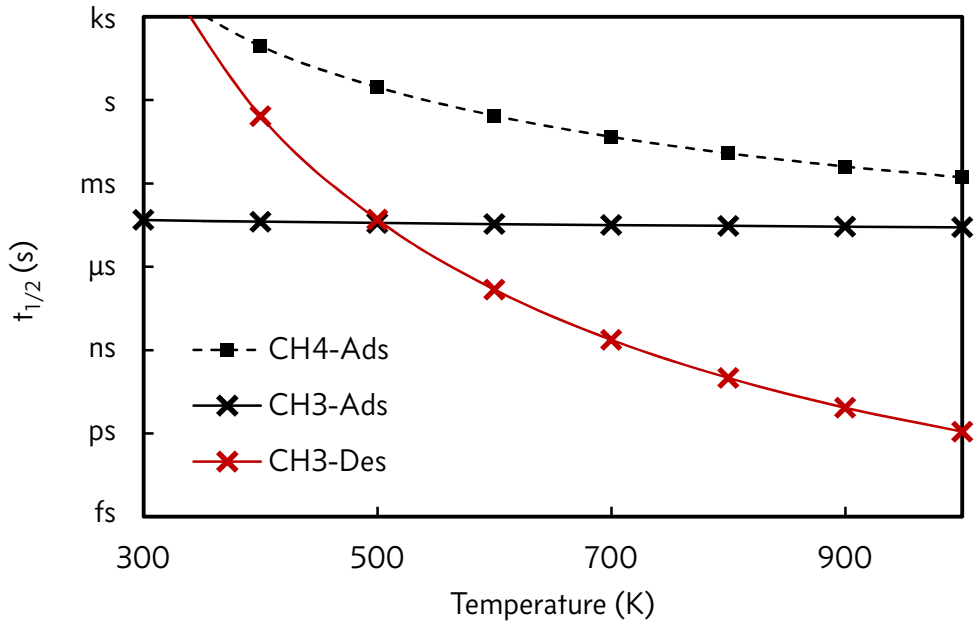
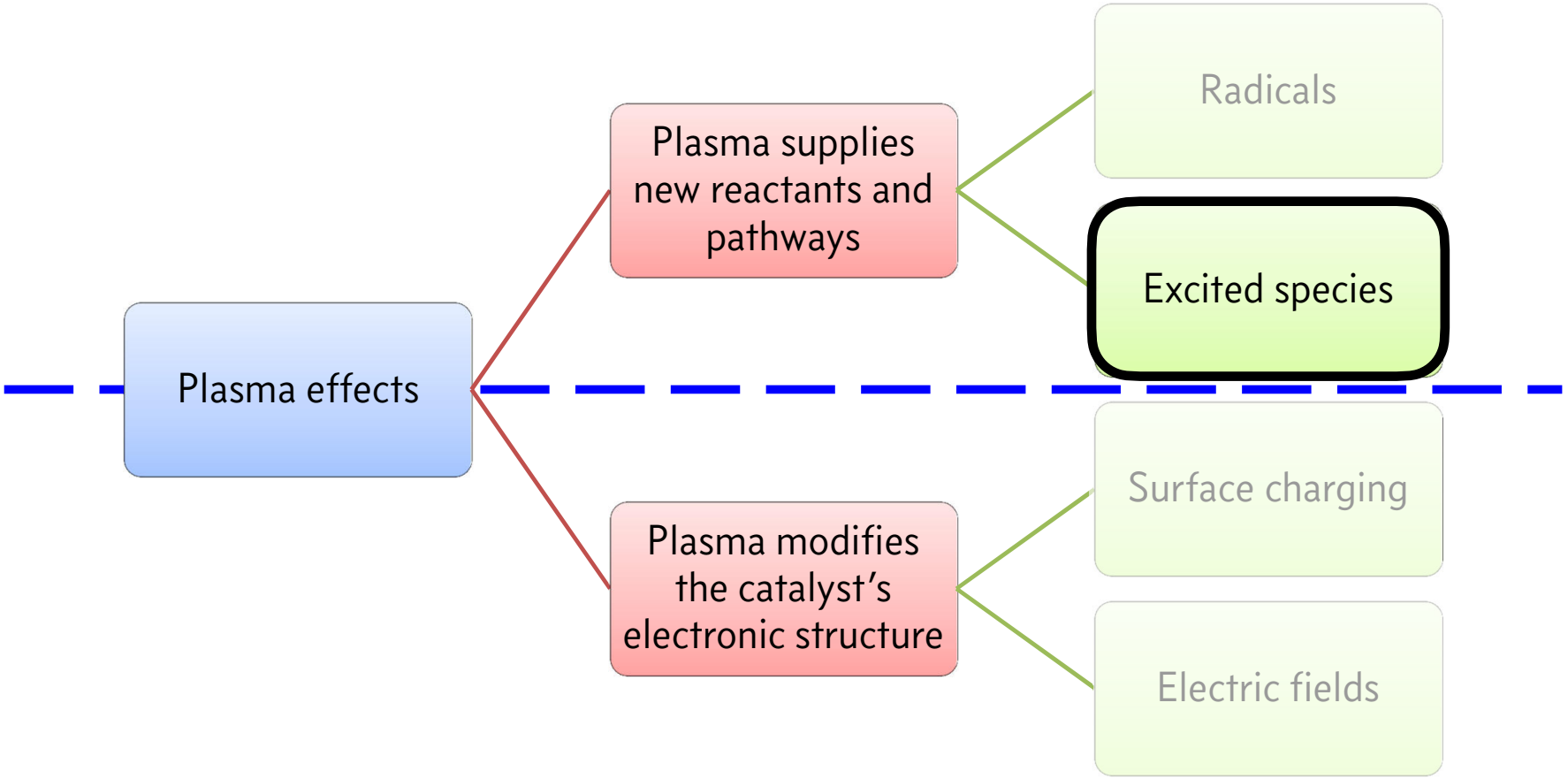


DFT calculation on TiO_2 anatase

- 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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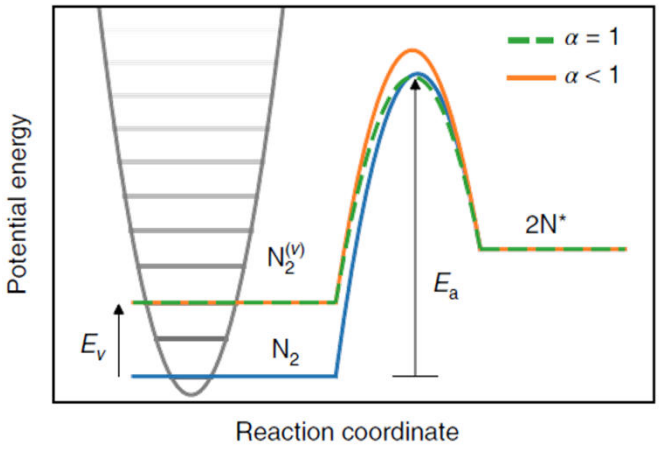
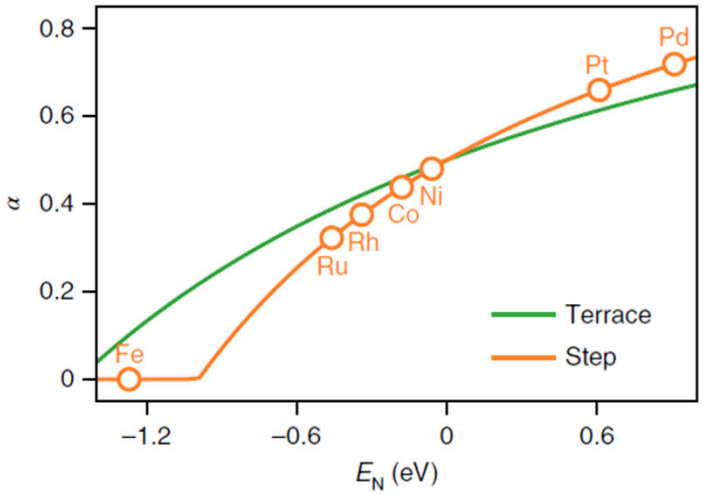
Vibrationally excited species





Vibrationally excited states are overpopulated

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

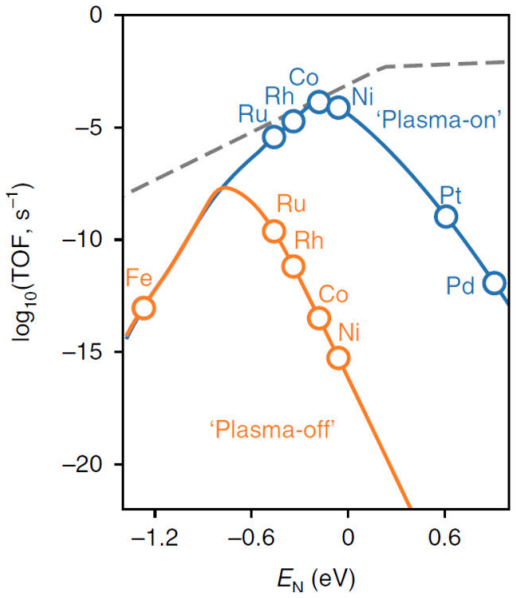
- Ground state NH_3 synthesis rates from literature
- Excited state rates through simple additive rules

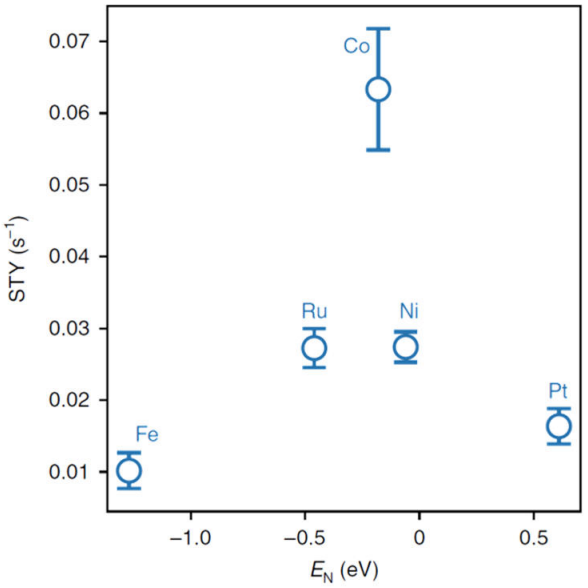
Fridman-Macheret (FM model)

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

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

Vibrationally excited species



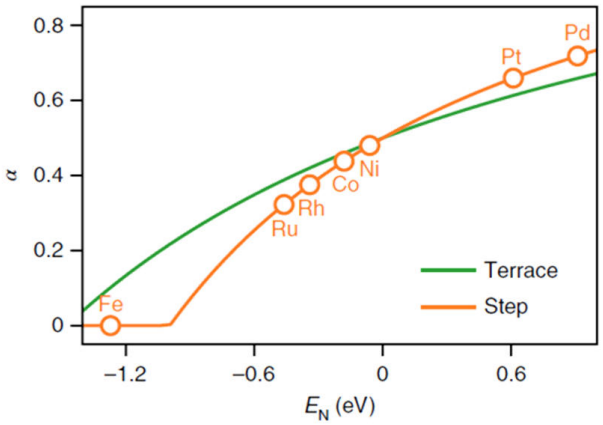


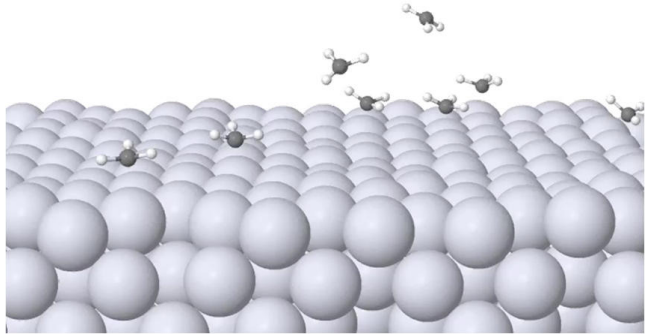
Preference shifts towards weaker-binding catalysts and rate increases

Experiments sort of agree

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

Vibrationally excited species





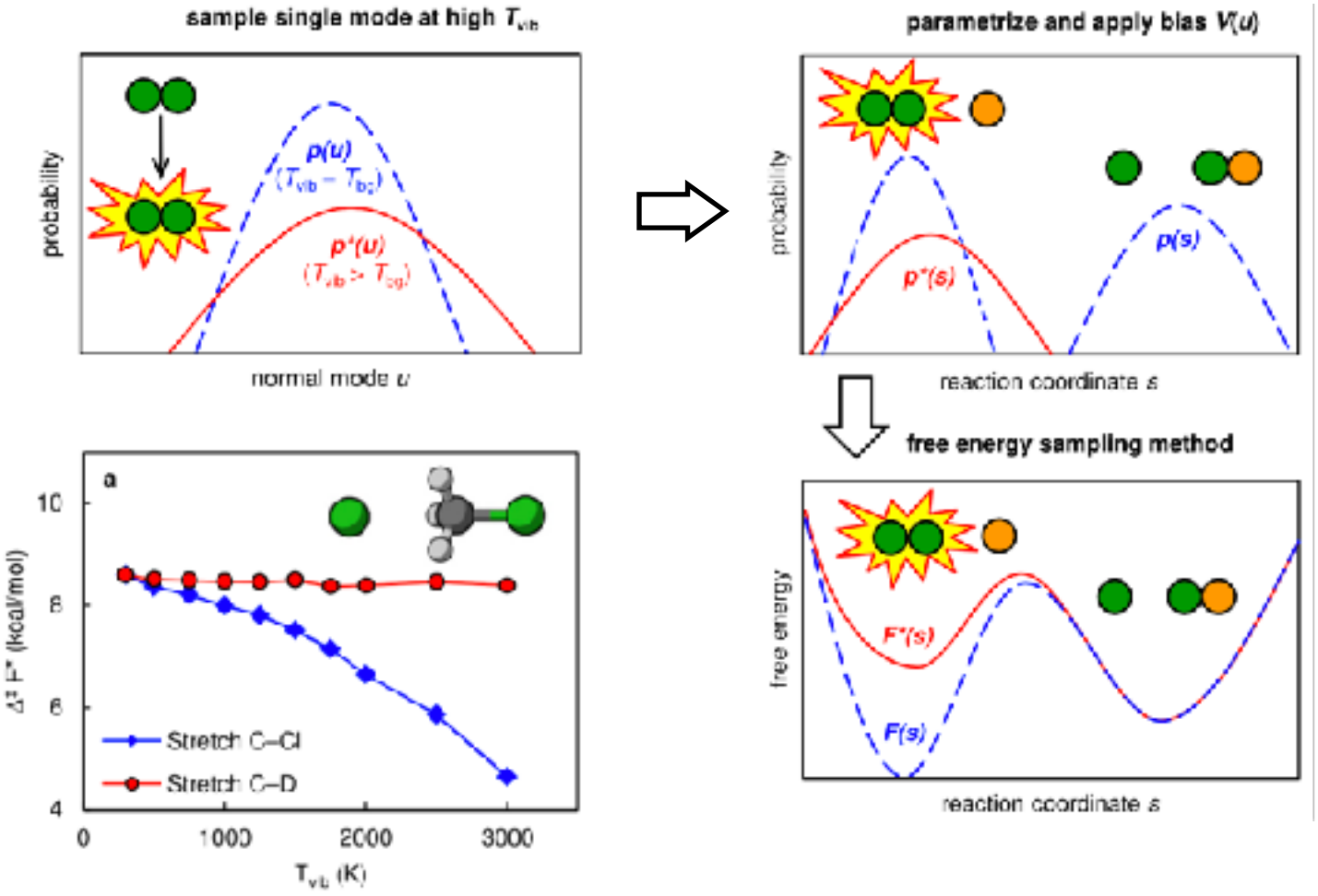
This model is not atomistic and relies on rather crude approximations

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

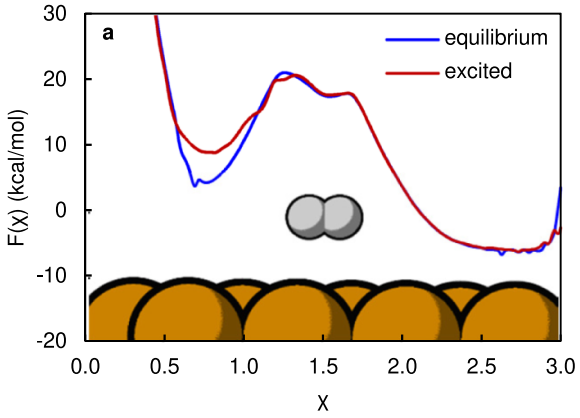


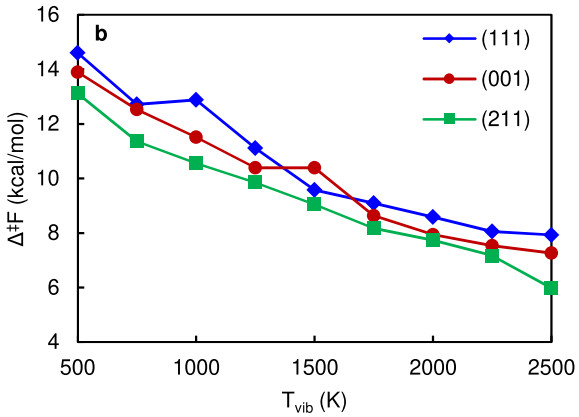
Approach works well for gas-phase reactions

=> Attempt to apply to surface reactions as well

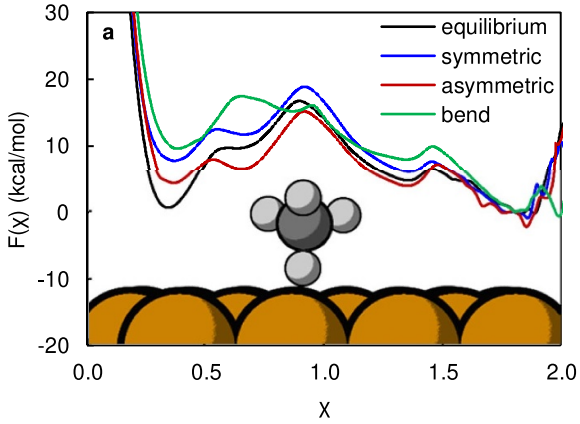
K. M. Bal, et al., *JCPL* **11** (2020) 401

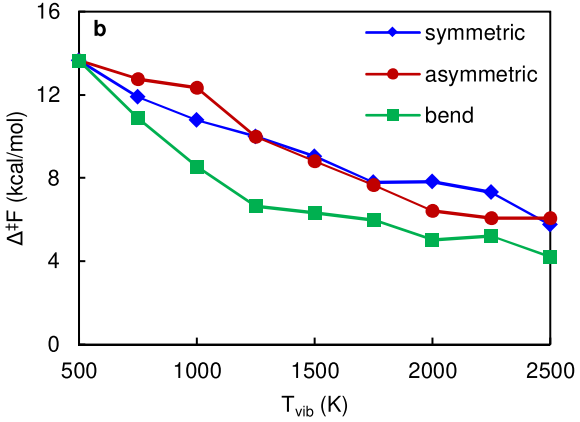
Vibrationally excited species

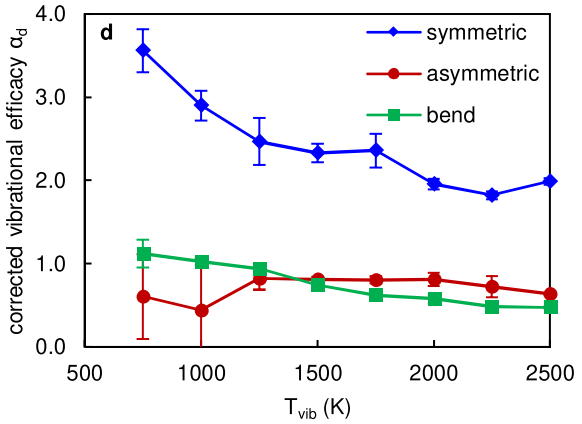




invalidates FM model

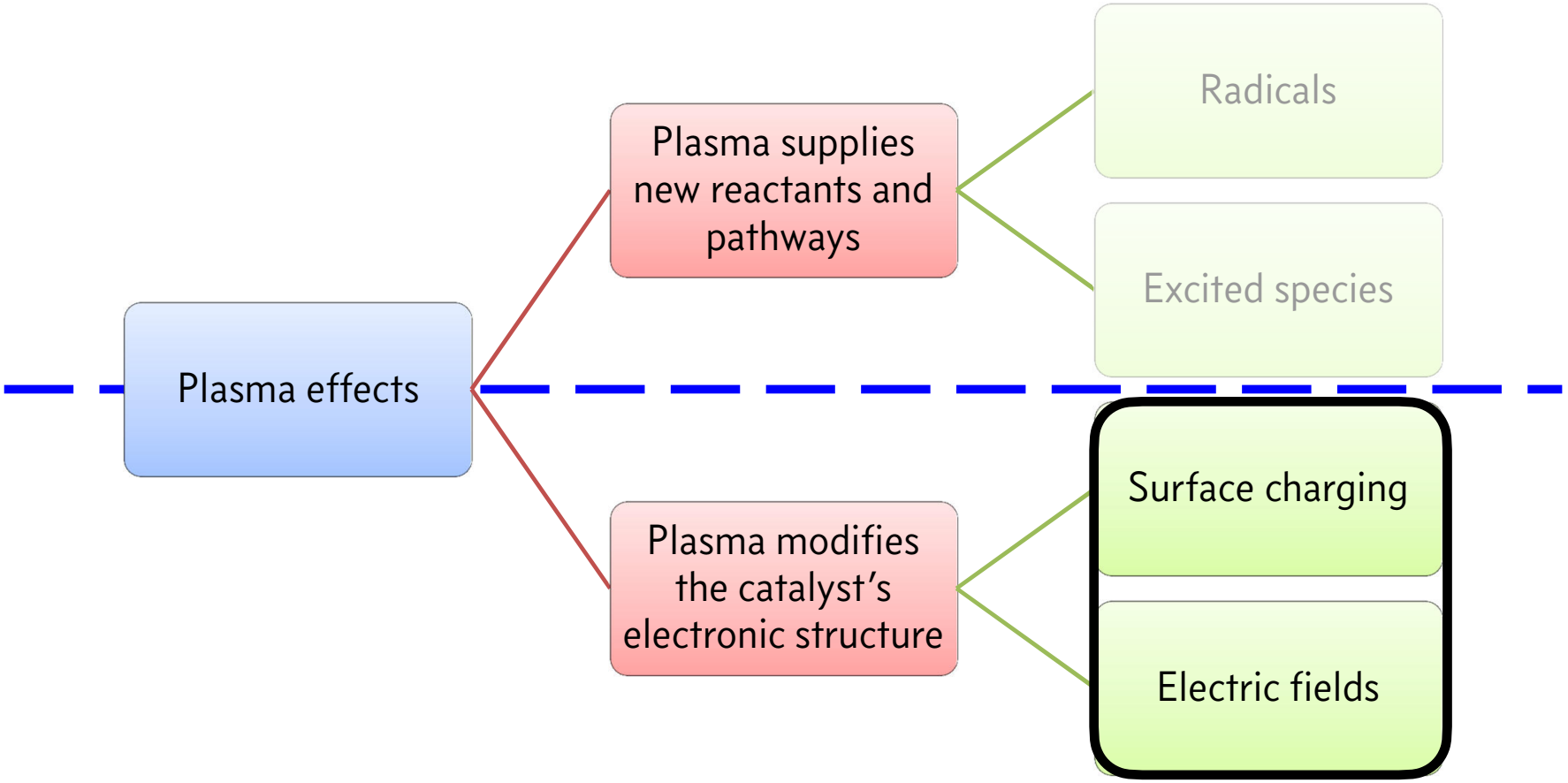






K. M. Bal, et al., *J. Phys. D: Appl. Phys.* ***54*** (2021) 394004

Approach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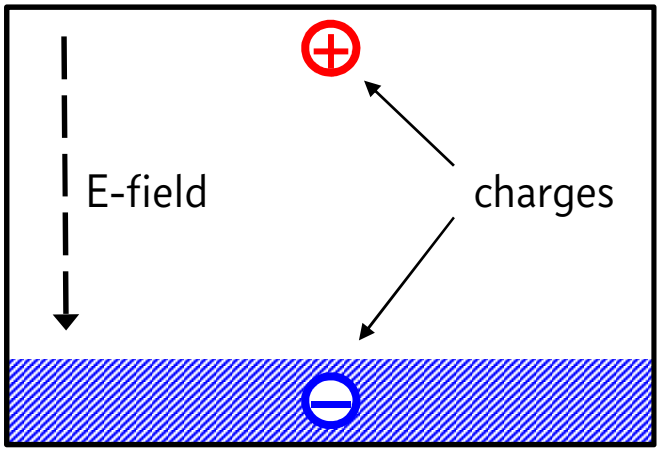
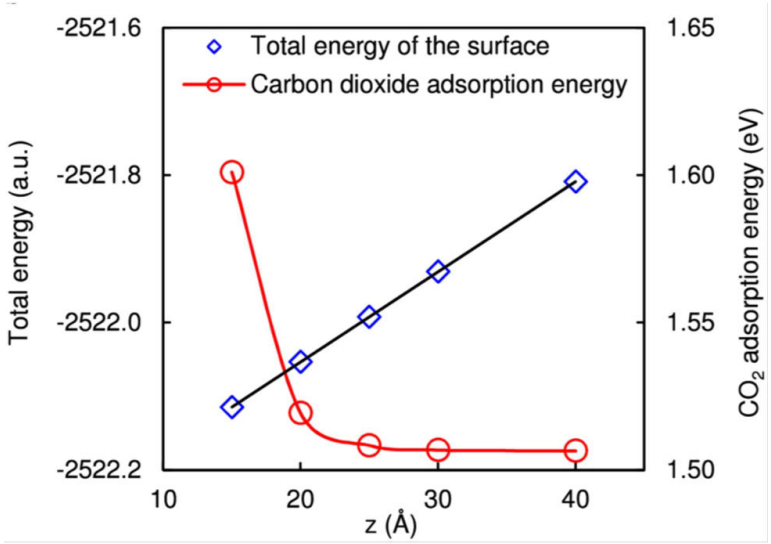
Modeling charges

Electron mobility » ion mobility

⇒ **natural negative surface charging**





Computationally:

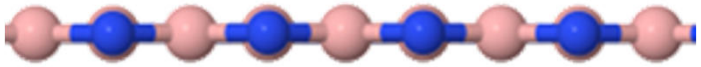
Define a H-atom in gas phase, but don't associate wavefunction with it
=> electron localises in surface, with H^+ as gas phase counter ion
=> avoids divergence of energy, and corresponds to reality

Modeling charges in plasma-catalysis

Electronic structure is key

What happens when charge is added?

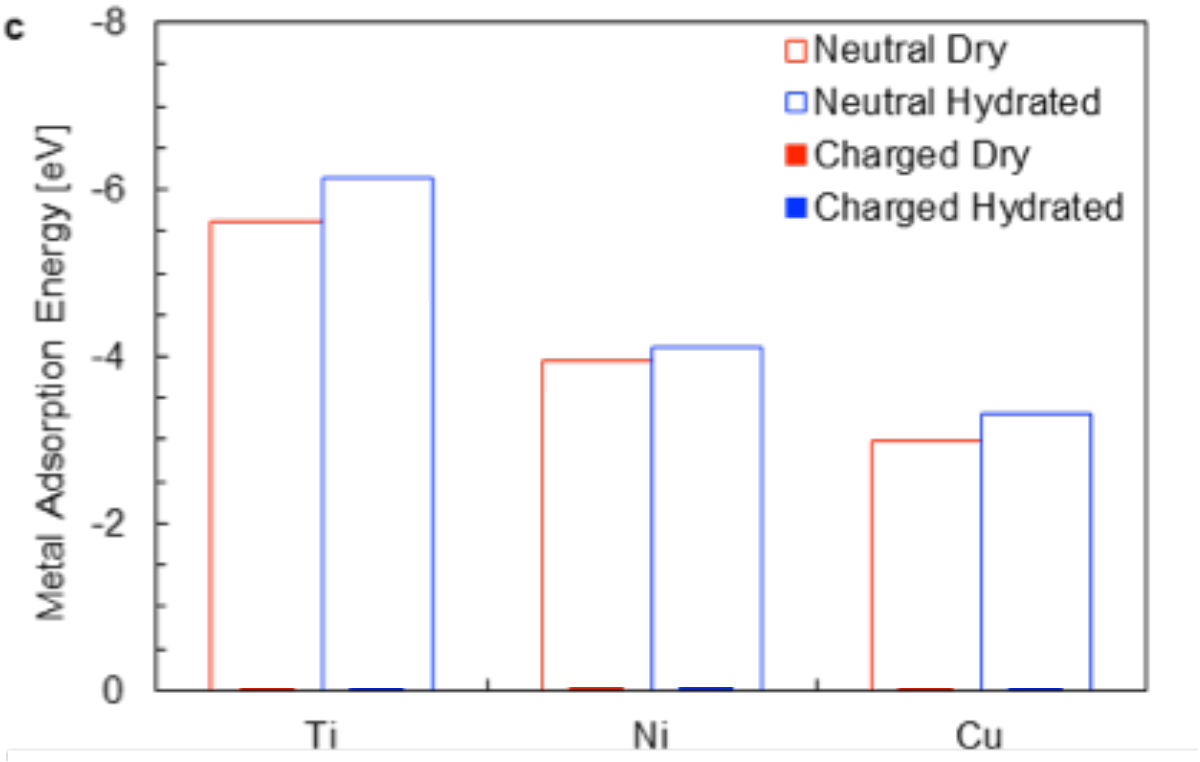
Might the plasma modify the catalyst electronic structure and thereby enhance chemical processes?



almost no binding (vdW only)

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

Surface charging - metal chemisorption



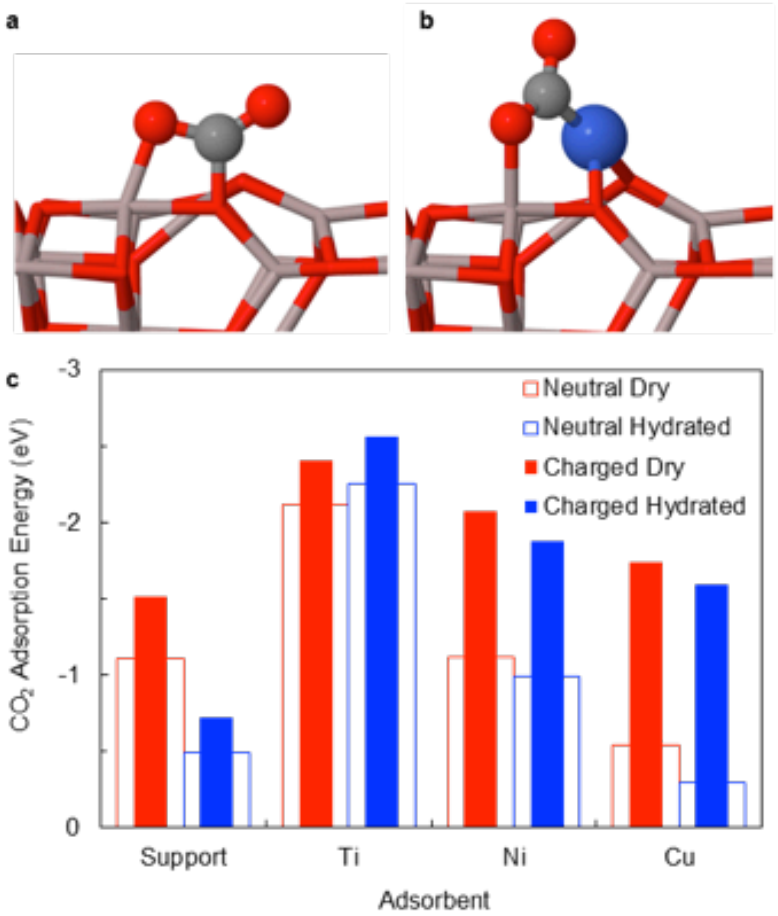
Surface charge of -0.06 C.m^{-2} destabilizes metal atom

Decrease in adsorption energy, due to

decrease in substrate electron affinity

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

Surface charging - CO_2 chemisorption



Significant increase in CO_2 adsorption energy

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

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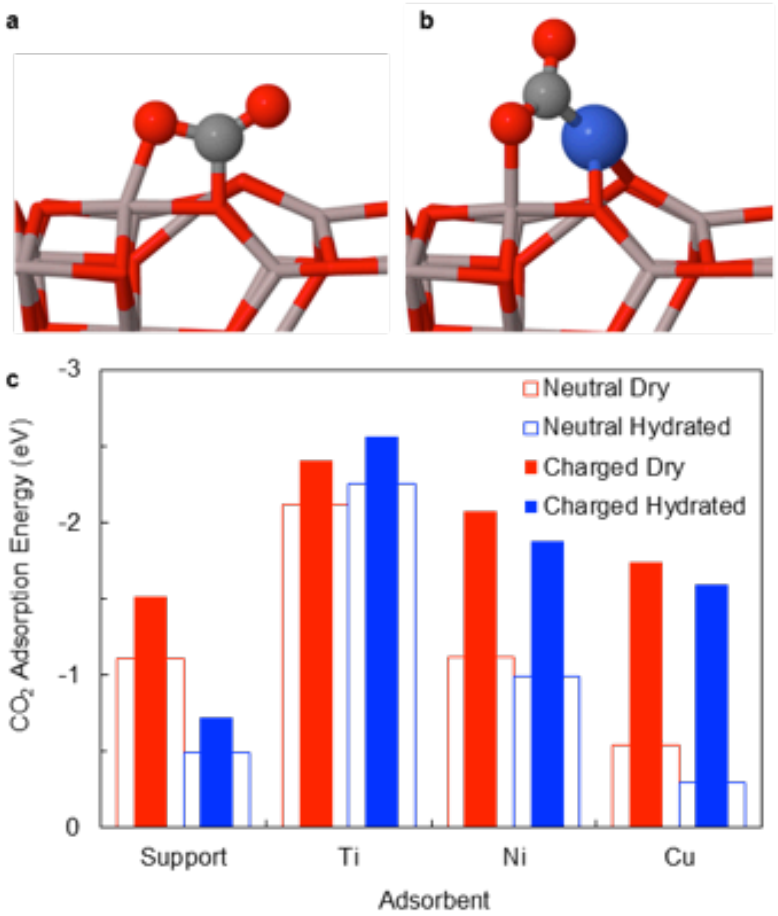
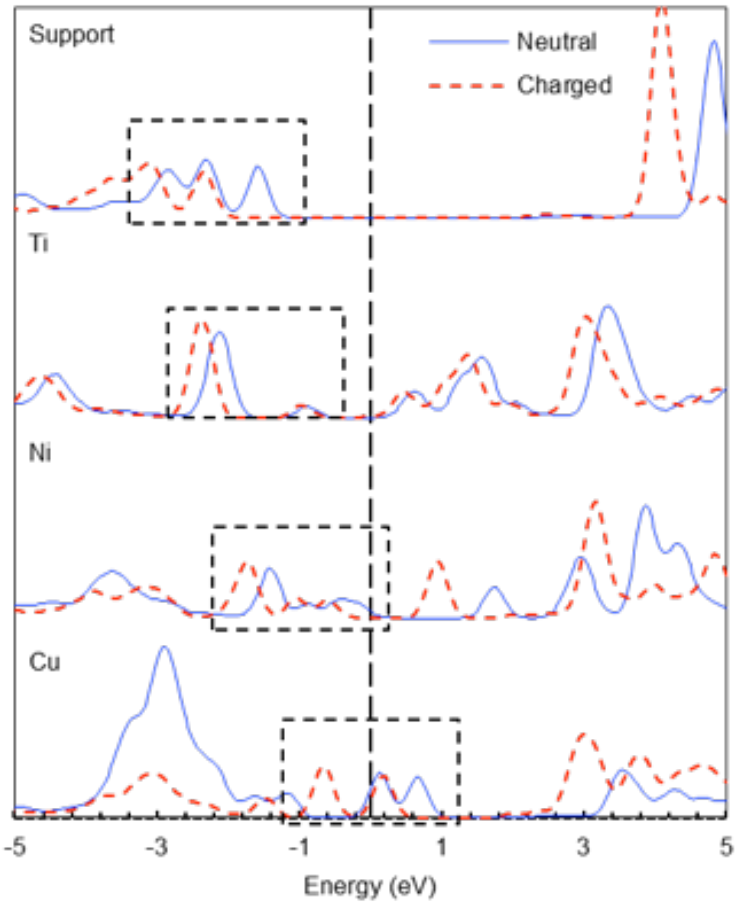


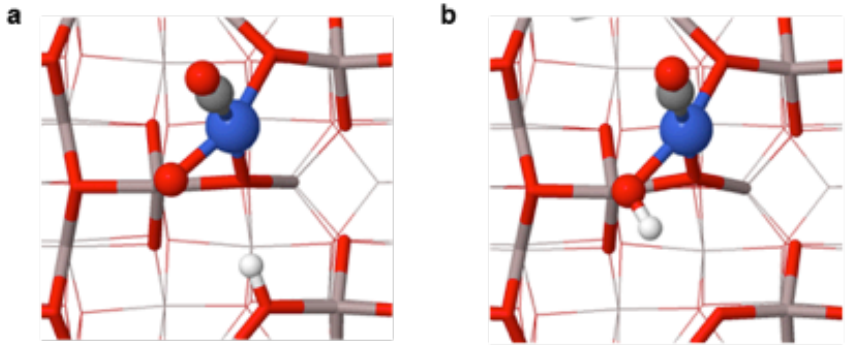


Significant increase in CO_2 adsorption energy…

… due to lowering of bonding states

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

Surface charging - CO_2 dissociation

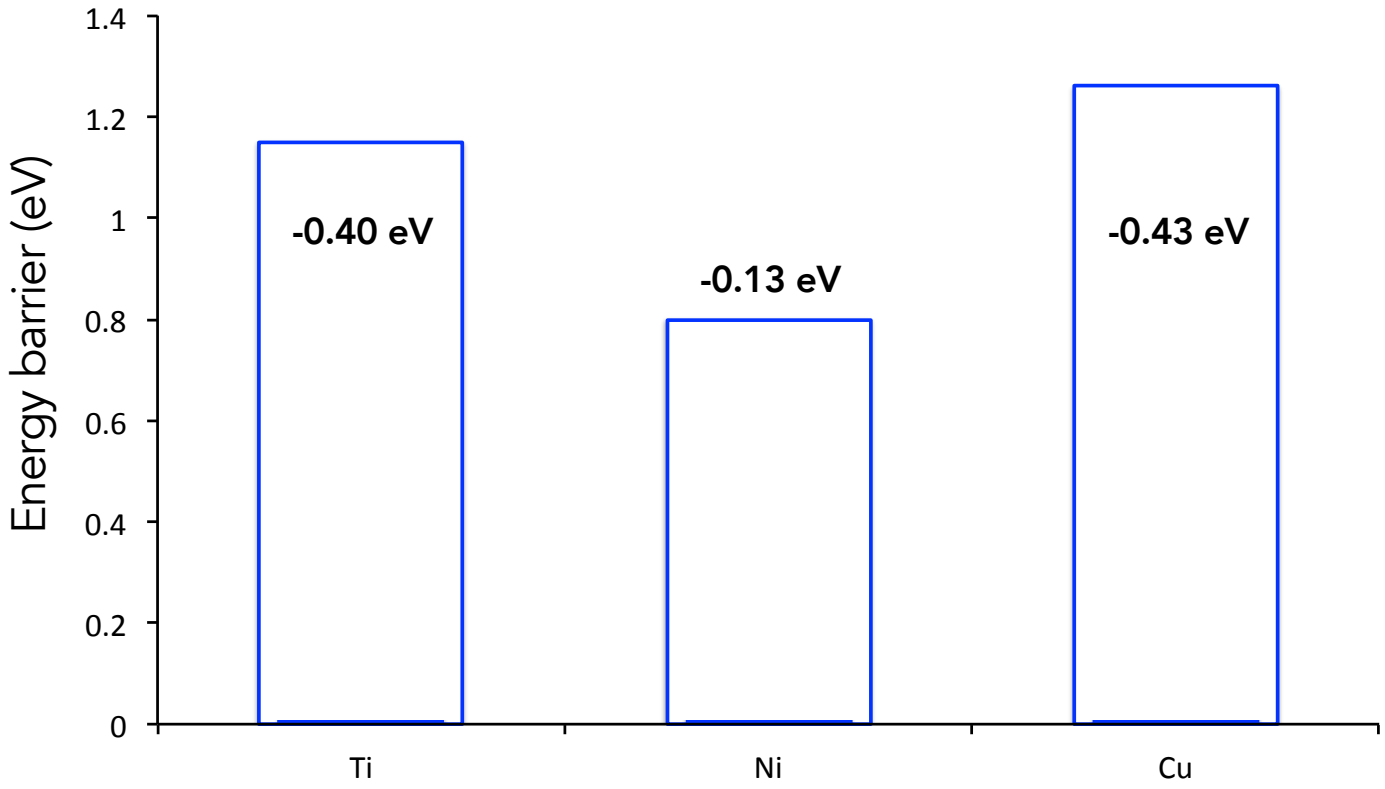


Upon surface charging, CO_2 dissocation becomes (much) less endothermic!

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

Surface charging - CO_2 dissociation

So far: thermodynamics. Are kinetics affected as well?



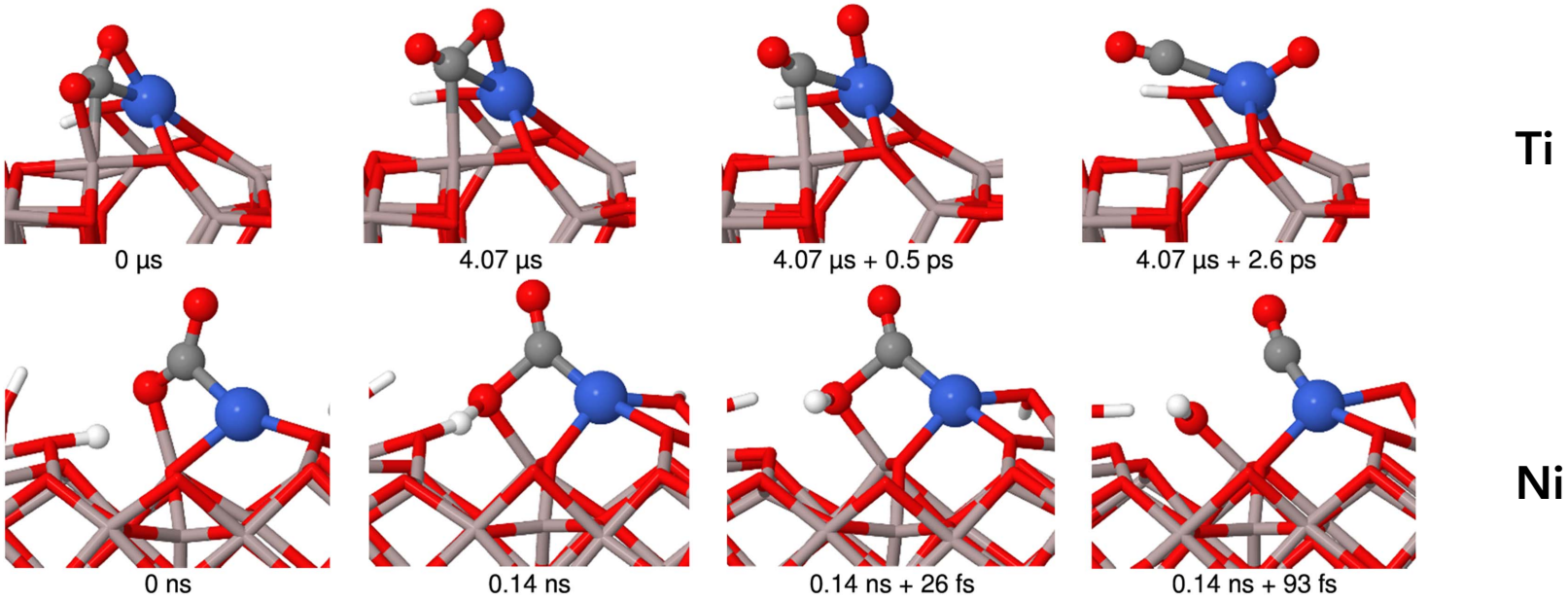
CO_2 splitting barrier is lowered by up to ~0.4 eV

(@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

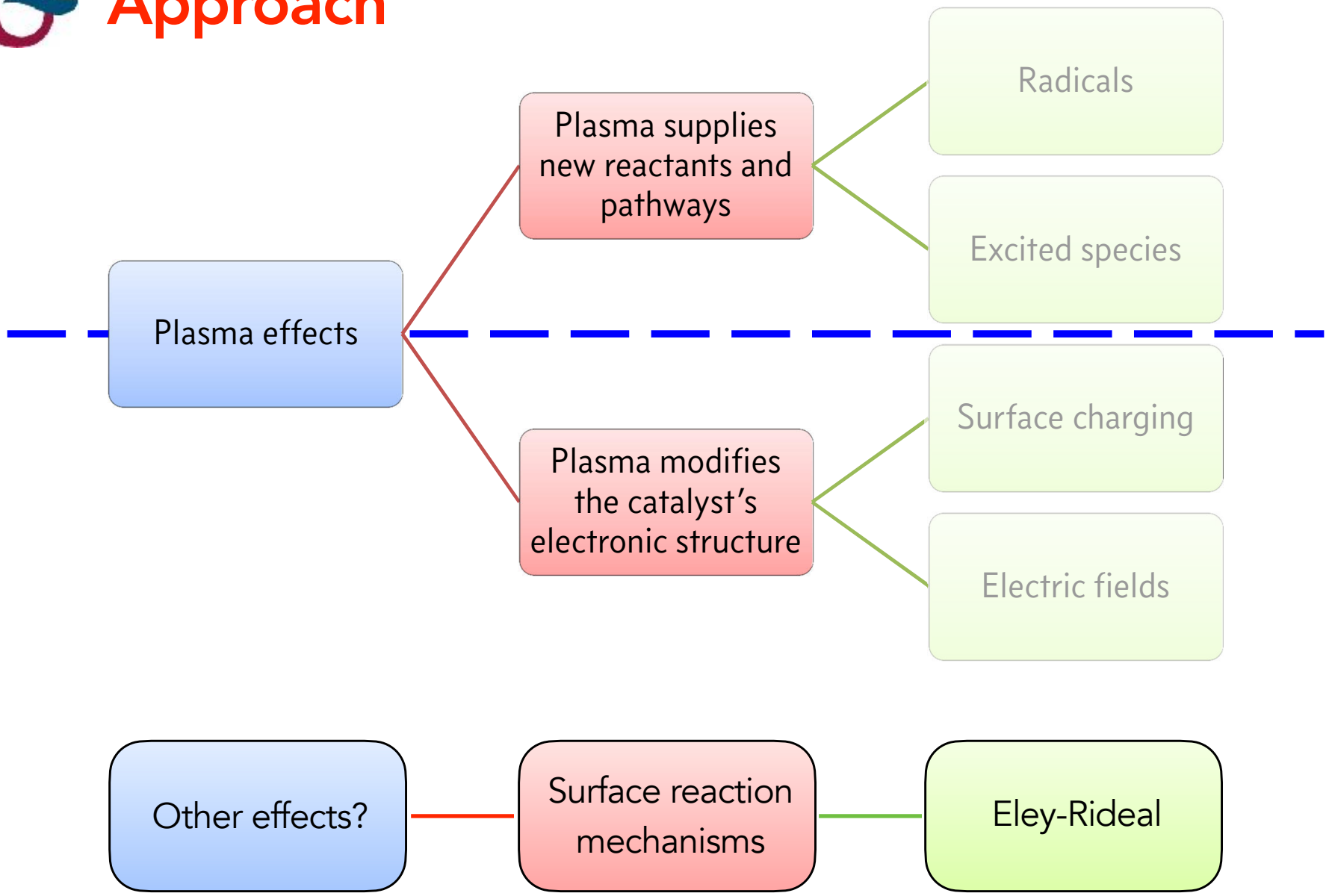
On Ni: *proton-mediated* splitting - concerted mechanism

Dynamic atomistic simulations allow to *directly* observe the mechanism

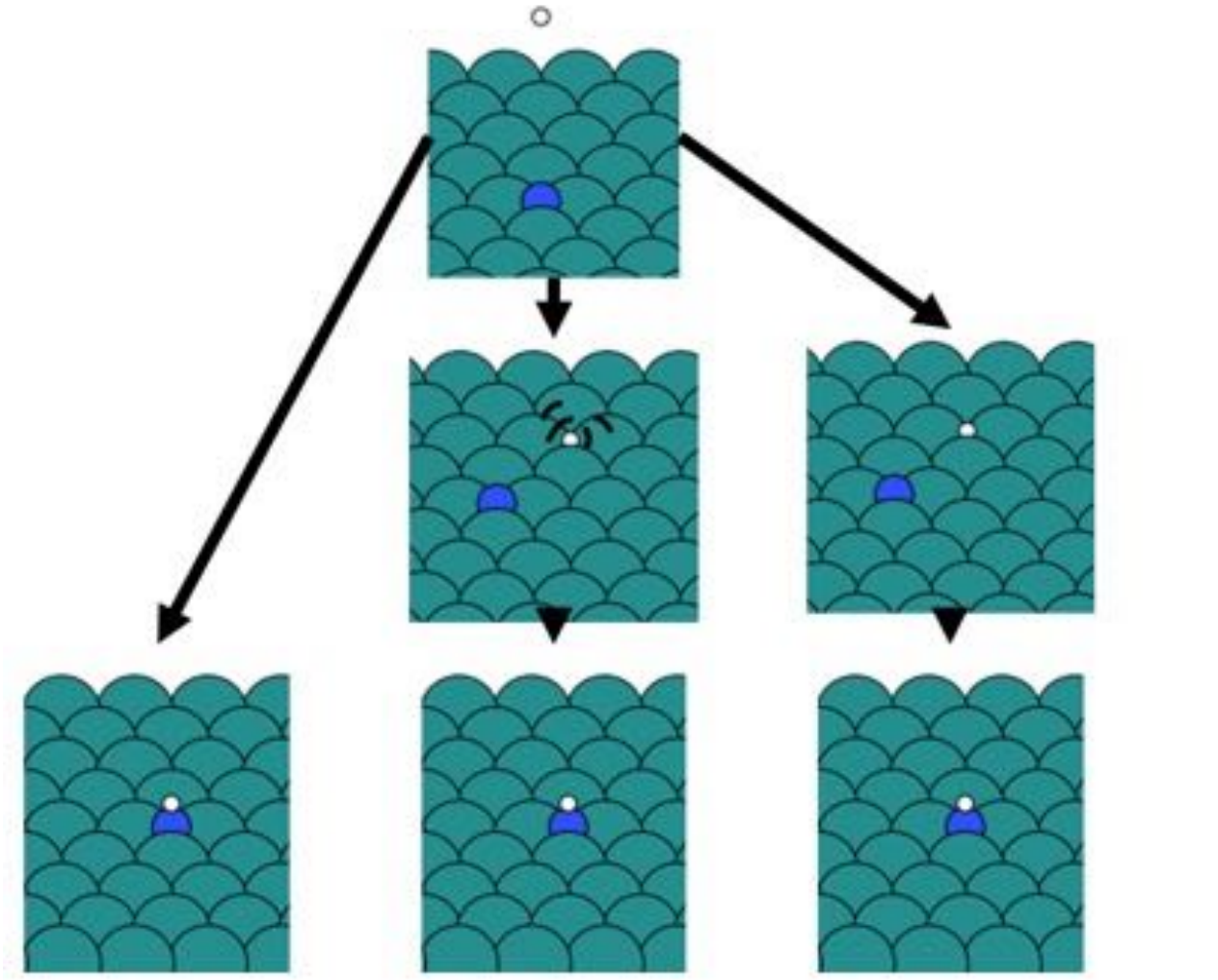
K. M. Bal, E. C. Neyts, *PCCP* **20** (2018) 8456

* 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

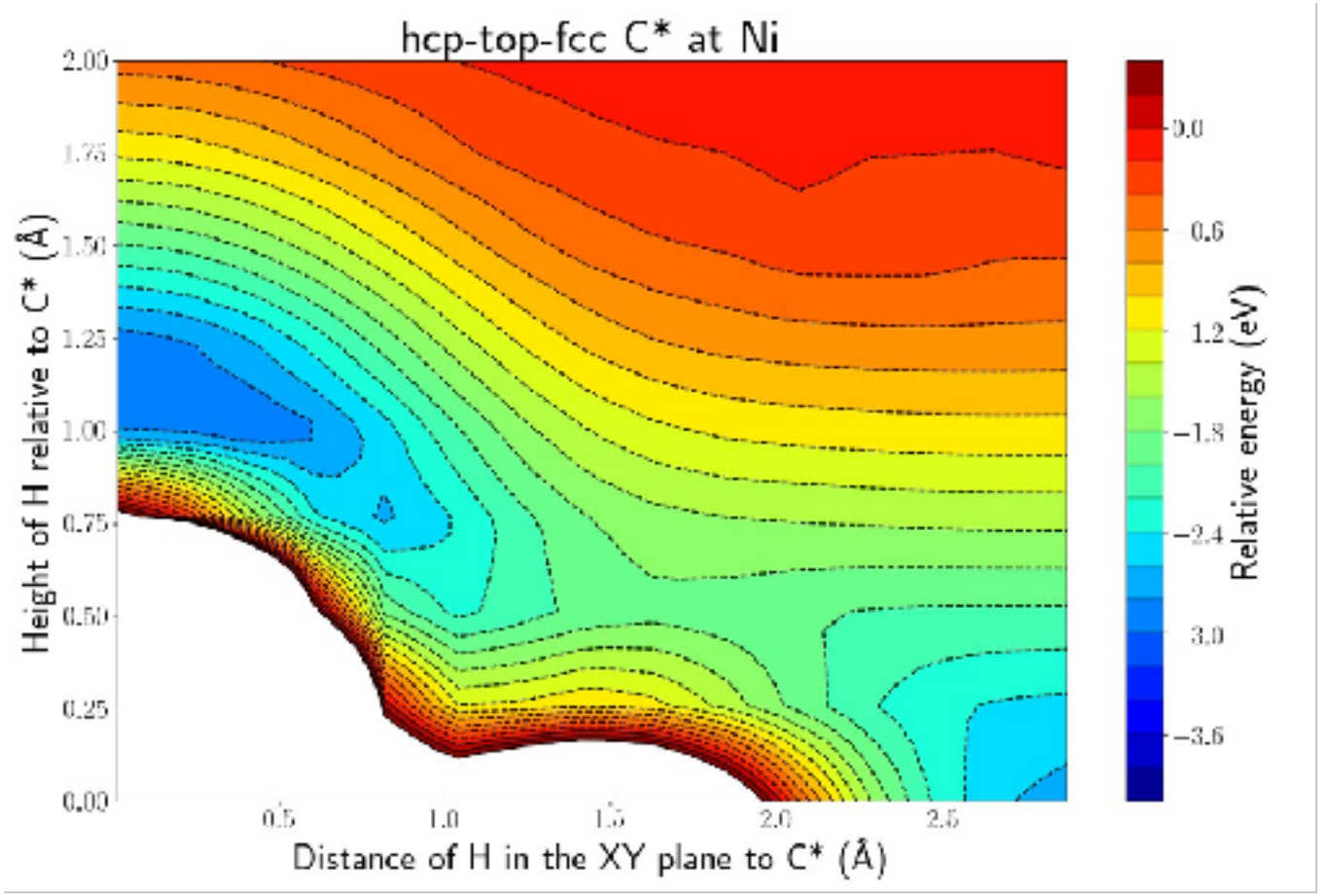
Introducing Eley-Rideal



Eley-Rideal "hot atom" Langmuir-Hinshelwood

How important is Eley-Rideal?

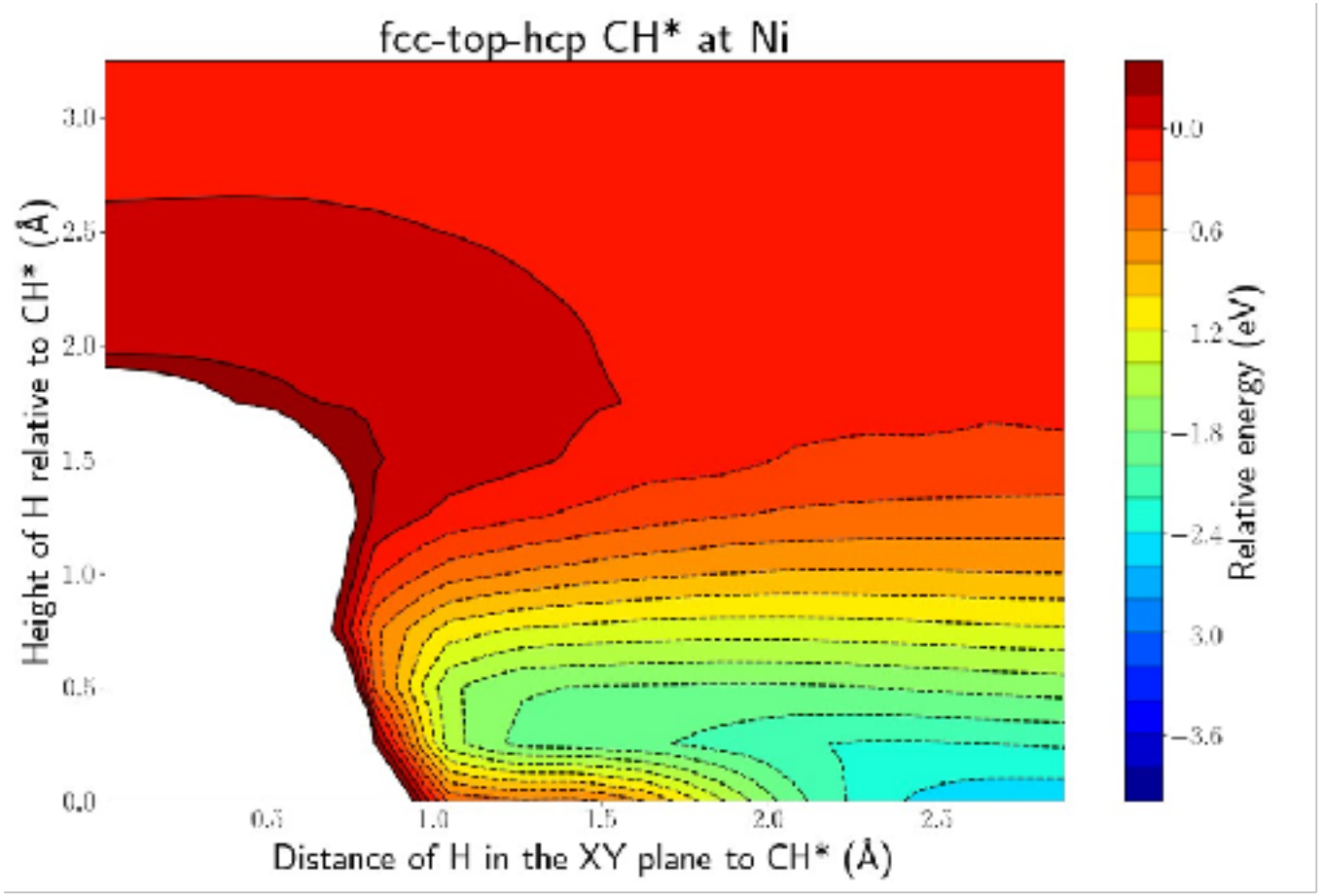
Where does an incoming H-atom end up?



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

How important is Eley-Rideal?

Where does an incoming H-atom end up?

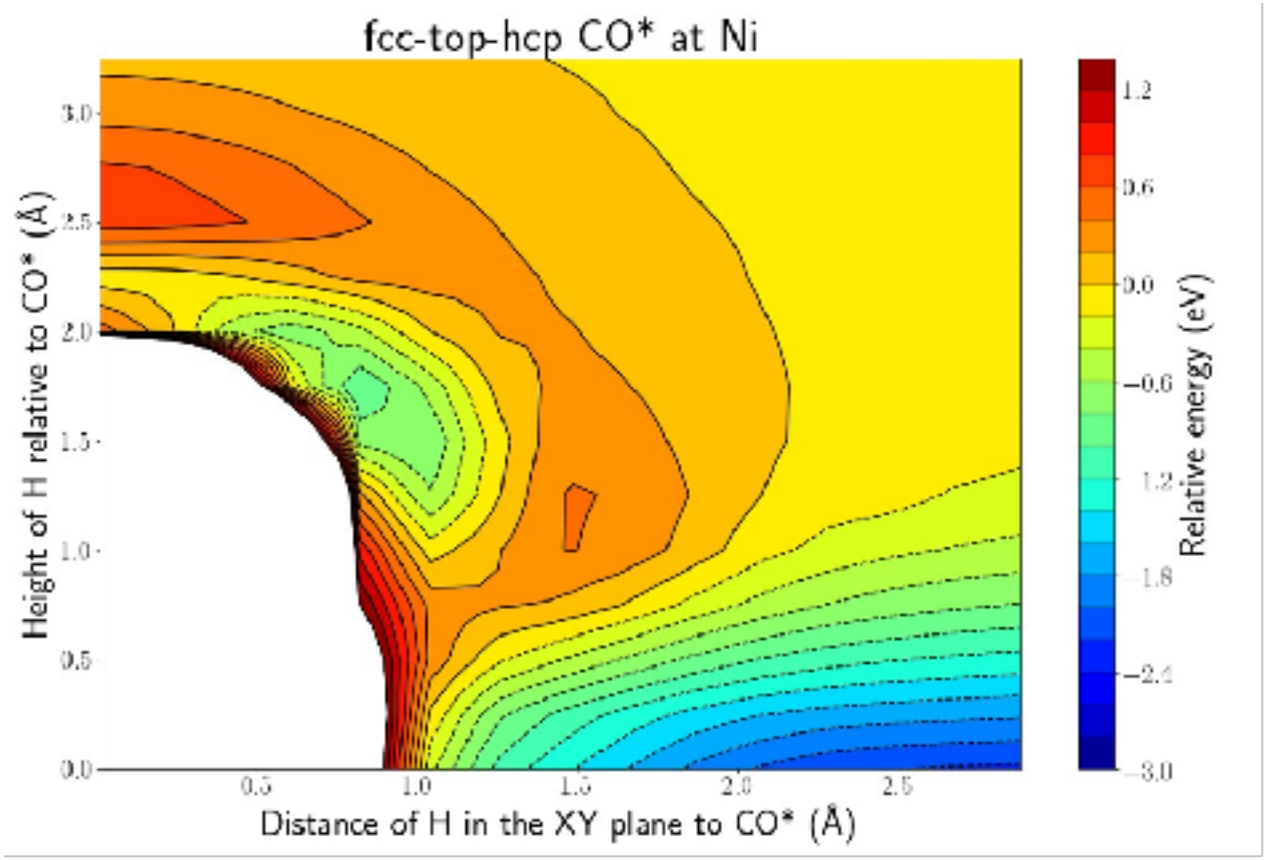


On CH*: H (surprisingly) DOES NOT adds to the CH-fragment

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

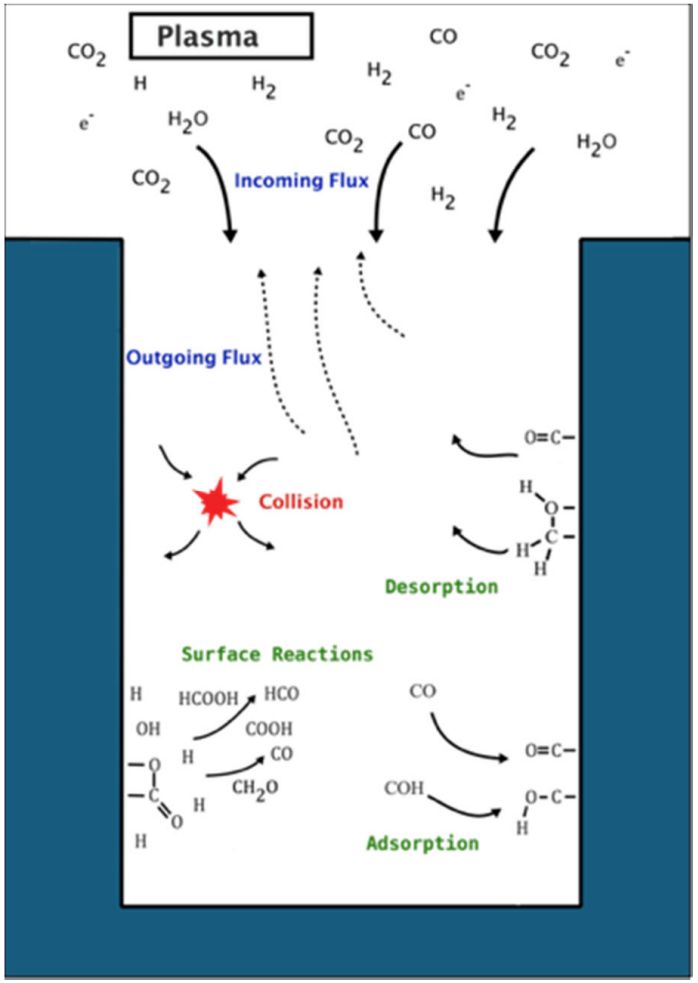
How important is Eley-Rideal?

Where does an incoming H-atom end up?



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

How far should we re-entangle?



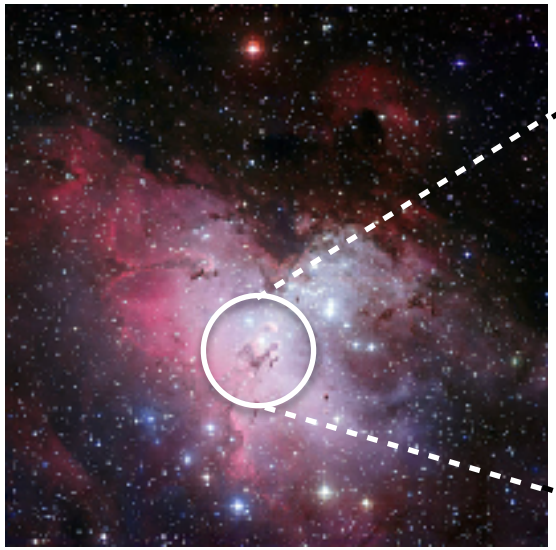
Reality is highly complex,
due to cross-interactions

Current models are very simple
cross-interactions are absent

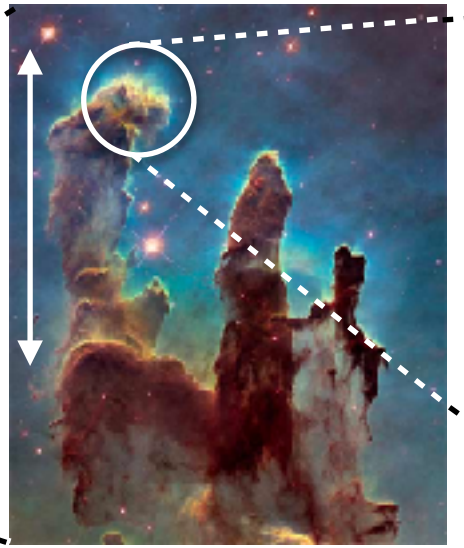
Bridge gap with experiments

Annex: plasma-surface astrochemistry

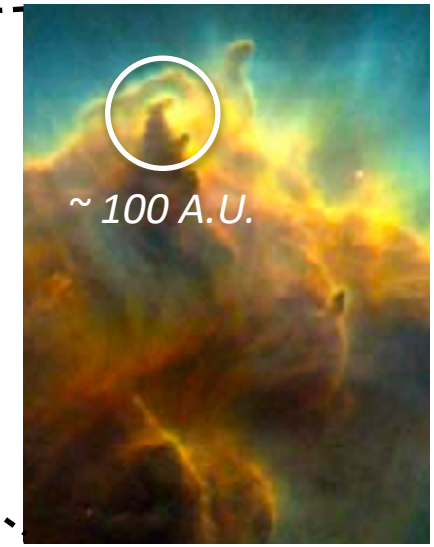
Plasmas are not confined to earth…



Eagle Nebula



Pillars of Creation

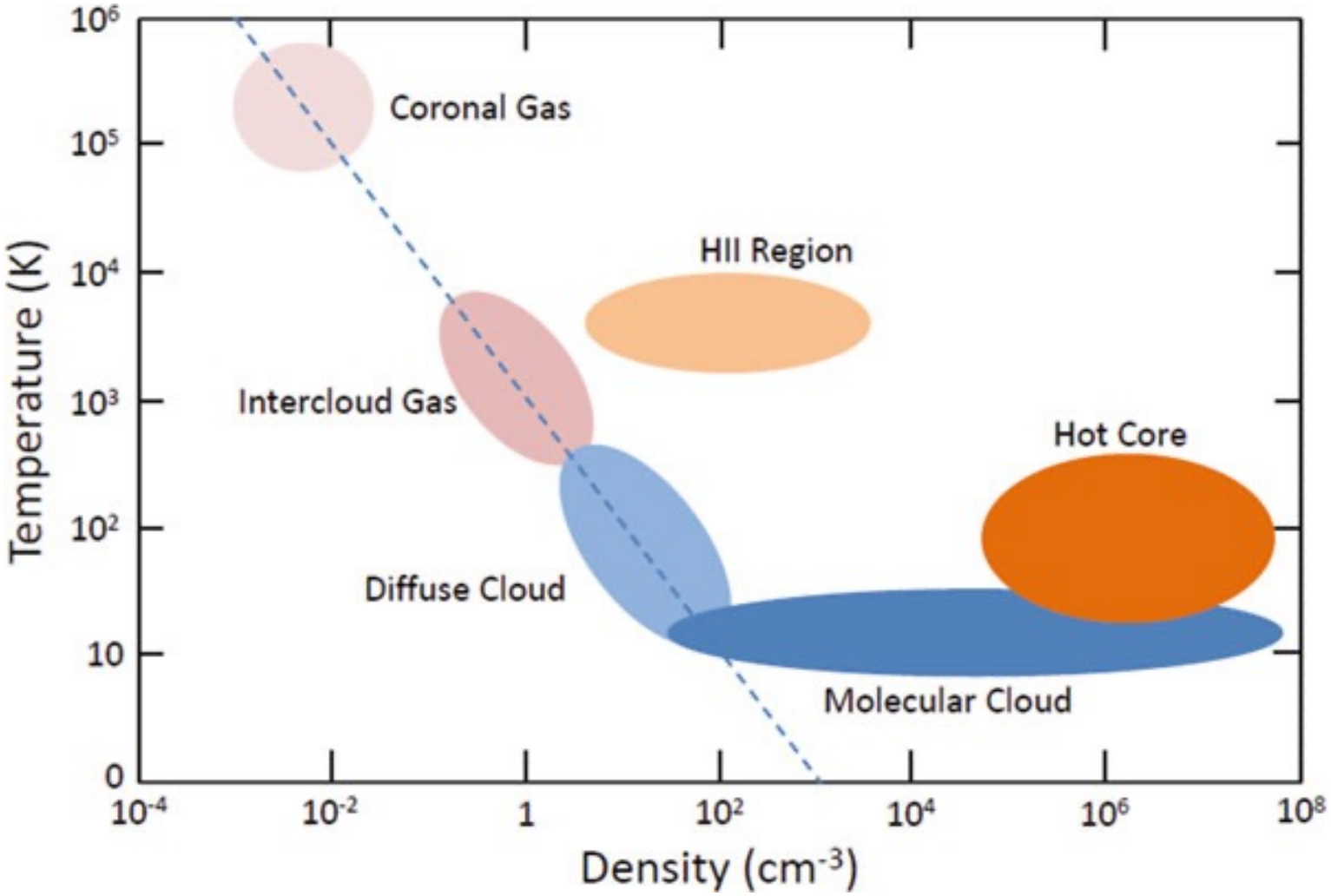


Evaporating Gaseous Globules

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

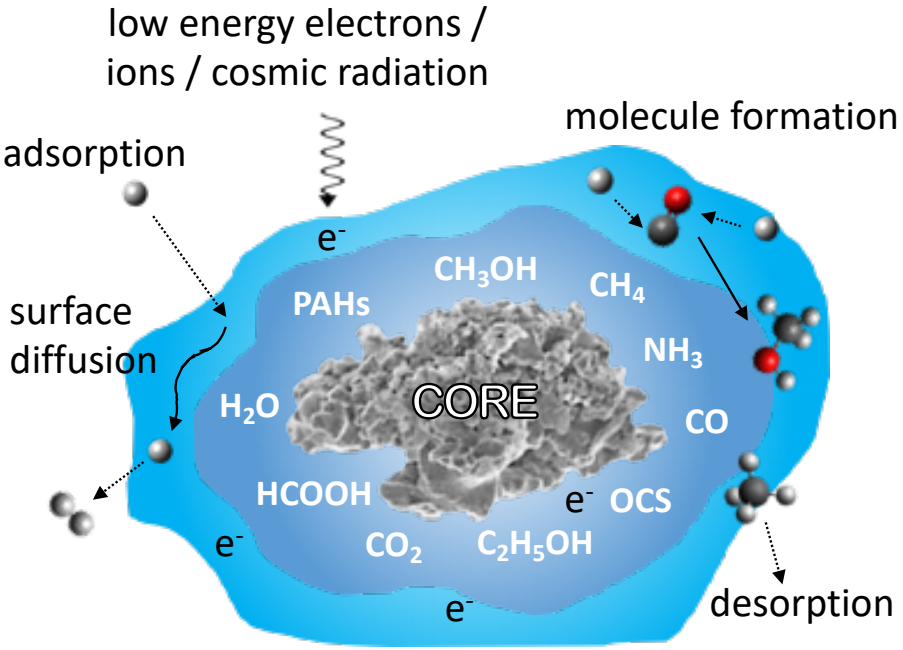
critically depend on binding energies

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

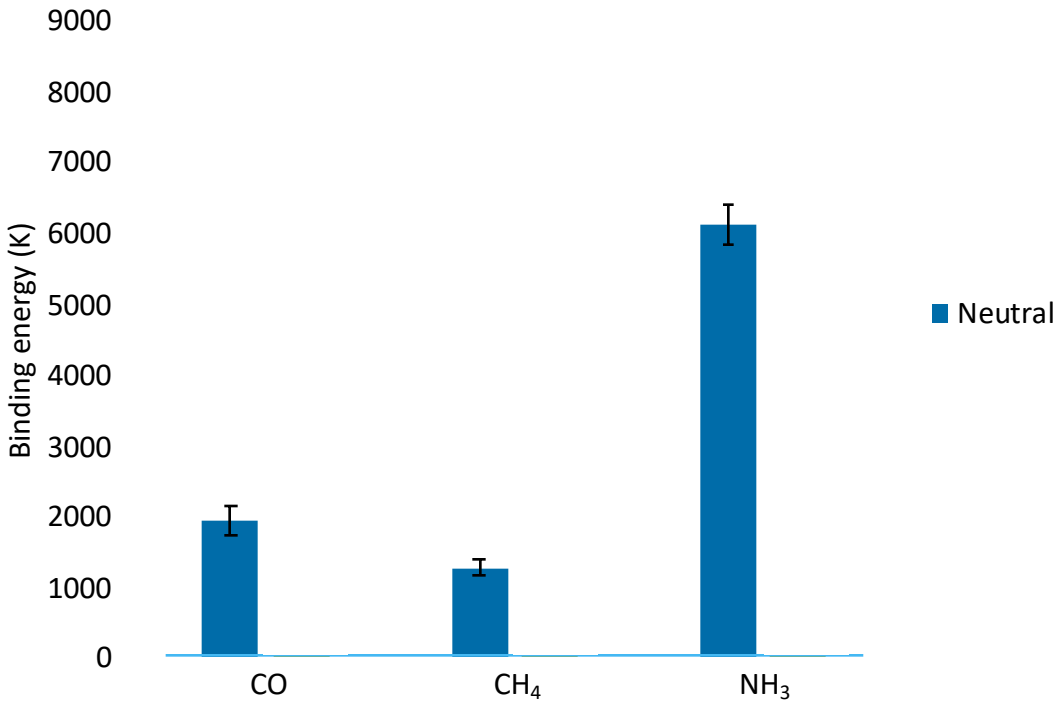
neutral: 1975 ± 195 K

CH_4: no dipole, no H-bonds

neutral: 1306 ± 123 K

NH_3: dipole, H-bonds

neutral: 6150 ± 278 K



DFT calculations; PBE0 functional + D3 dispersion

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

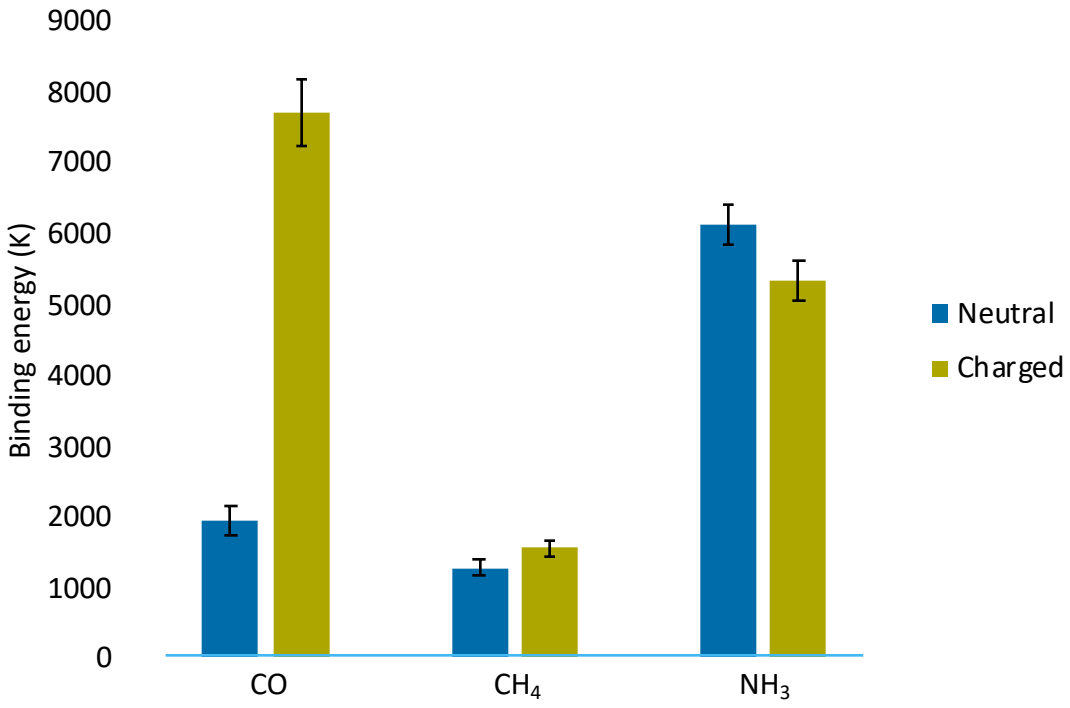
neutral: 1306 ± 123 K

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

Acknowledgments

People involved in this work

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head of PLASMANT group

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