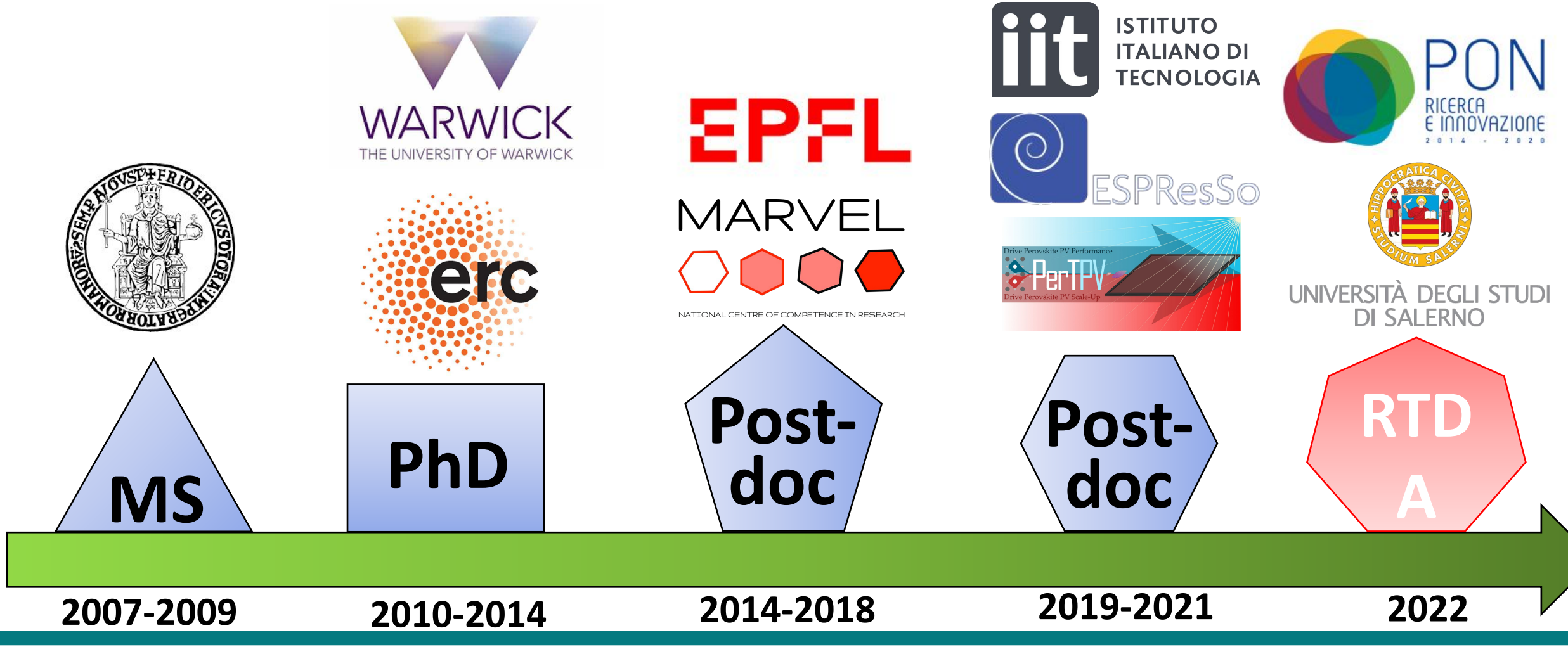
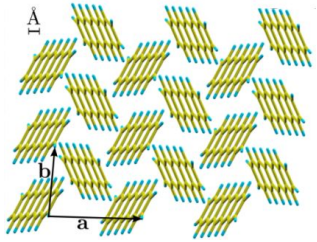

OrientaTesi
Cdl Chimica e
Scienze Chimiche
chimica_unibas
CdL Chimica Unibas
"Scegli i tuoi
esperimenti"

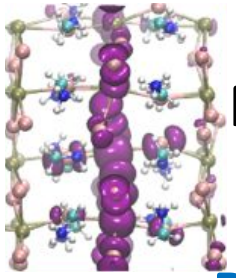
Introducing myself first…



The **«fil rouge»** of my research activity



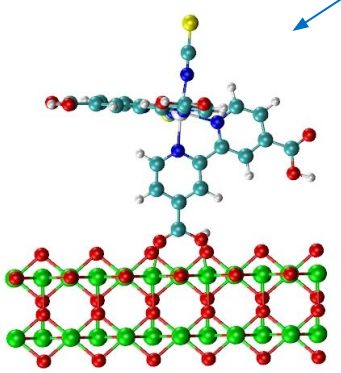
Organic crystals



Metal halide perovskites

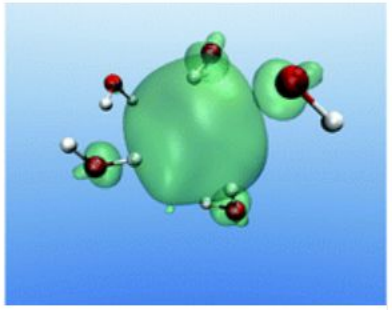
PHOTOVOLTAICS

Dye-sensitized solar cells



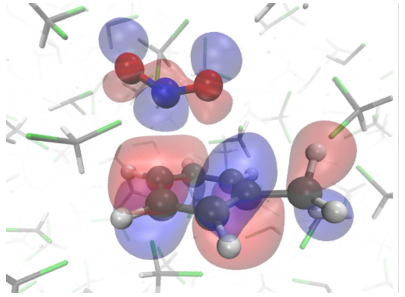
Charge transfer

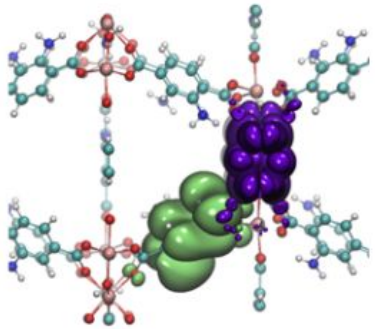
REACTIVITY IN SOLUTION



Hydrated electron

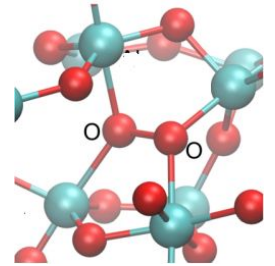
Aromatic nitration



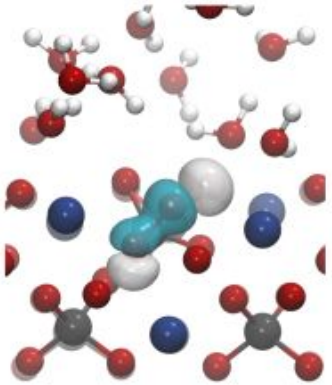


Metal-organic frameworks

Barrier-type amorphous oxides



PHOTOCATALYSIS



Semiconductor-water interfaces

The **«tools of the trade»** of my research

Pen and paper

OTTENGO ALLORA

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2 l(l+1)}{2m_e r^2}\right]u = Eu$$

HO QUINDI UN PROBLEMA UNIDIMENSIONALE CON POTENZIALE EFFICACE $V_{EFF}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2m_e r^2}$

HO ALLORA:

- $E>0$ => STATI DI DIFFUSIONE
- $E<0$ => STATI LEGATI => LIVELLI QUANTIZZATI

IL CASO INTERESSANTE È DATO DAGLI STATI LEGATI => STUDIO $E<0$

RICORDANDO CHE ABBIAMO POSTO LA CONDIZIONE DI NORMALIZZAZIONE COME $\int_0^{+\infty}|R(r)|^2 r^2 dr = 1$

$$\Rightarrow \int_0^{+\infty}|u(r)|^2 dr = 1 \Rightarrow u(r)\xrightarrow[r\to+\infty]{} 0$$

STUDIO I CASI LIMITE:

- HO $r\to 0$

  L'EQUAZIONE È $-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2 l(l+1)}{2m_e r^2}-E\right]u = 0$, $V(r)=\frac{ze^2}{4\pi\varepsilon_0 r}$

  HO ALLORA CHE $V(r)$ ESPLODE PIÙ LENTAMENTE DI $\frac{\hbar^2 l(l+1)}{2m_e r^2}$

  => POSSO SCRIVERE $-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\frac{\hbar^2 l(l+1)}{2m_e r^2}u = 0 \Rightarrow \frac{d^2u}{dr} = \frac{l(l+1)}{r^2}u$

  $\Rightarrow u(r)\sim r^{l+1}$, $\frac{du}{dr}\sim(l+1)r^l$, $\frac{d^2u}{dr^2}\sim l(l+1)r^{l-1}$

  ALLORA SE $V=0\left(\frac{1}{r^2}\right) \Rightarrow R(r)=\frac{u(r)}{r}\sim r^l$ PER $r\to 0$

- HO $r\to+\infty$

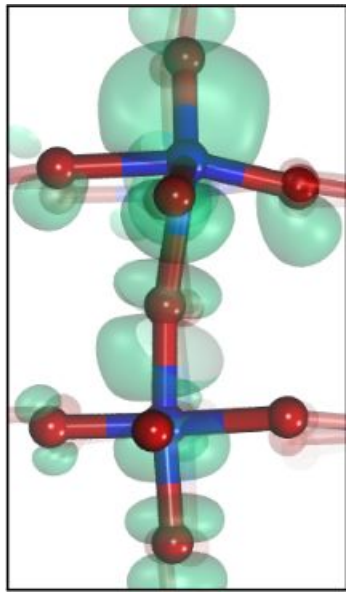
  L'EQUAZIONE È $-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2 l(l+1)}{2m_e r^2}-E\right]u = 0$. HO CHE I POTENZIALI VANNO A ZERO

$\frac{d^2u}{\quad} \quad \frac{2m_e E}{\quad}$

My laptop

Clusters of calculators

The «tools of the trade» of my research

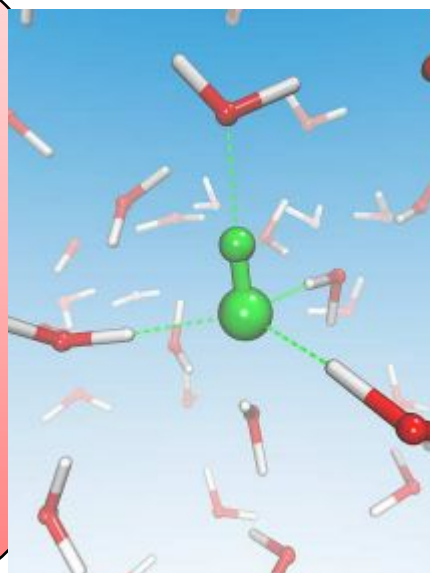


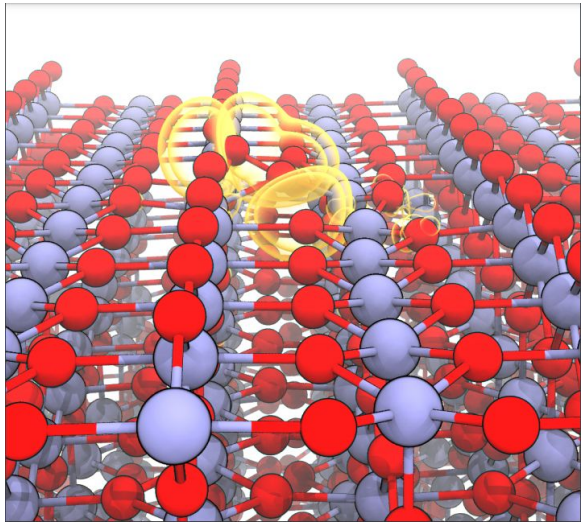
Electronic-structure calculations

- Density functional theory (DFT)
- Time-dependent DFT
- GW approximation
- Post Hartree-Fock methods

Molecular dynamics simulations

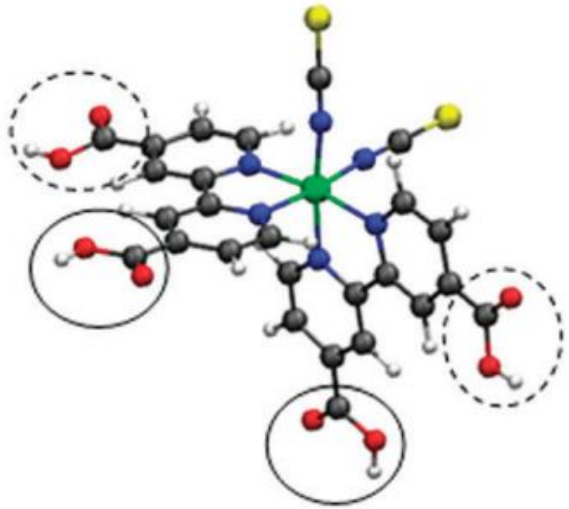
- Thermodynamic integration
- Blue Moon simulations
- QM/MM dynamics





Theoretical modeling

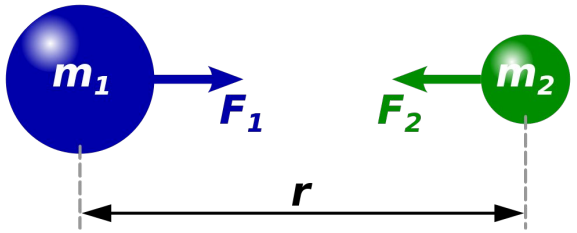
- Electron transfer theory
- Theory of defects in solids
- Model Hamiltonians



The «philosophia» of my research

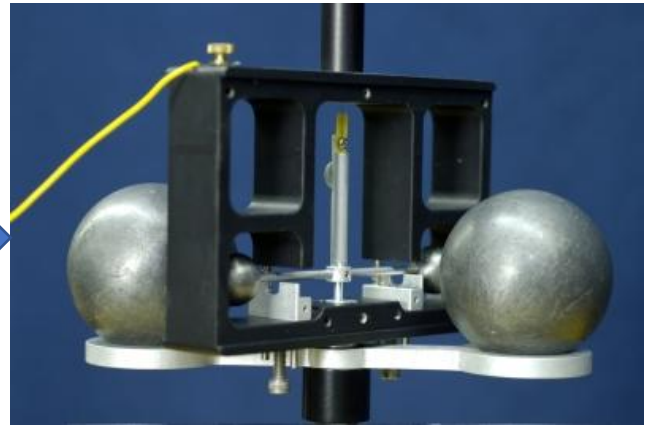
Observation of a phenomenon

Development of a theory

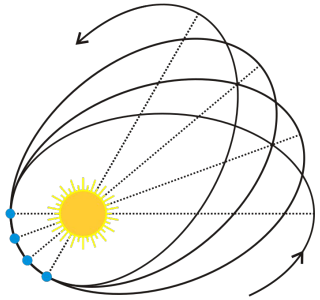


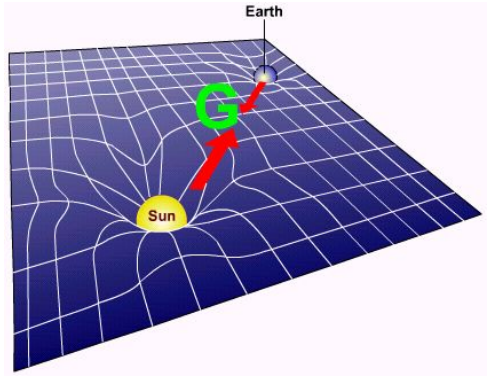
$$F_1 = F_2 = G \frac{m_1 \times m_2}{r^2}$$

Experiment

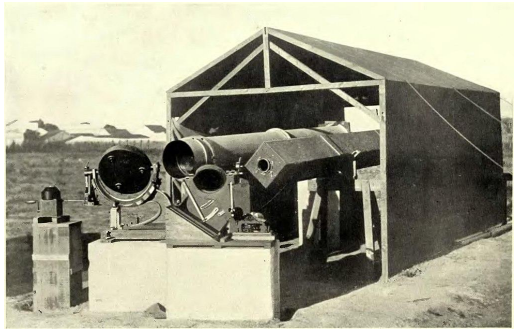


Observation of a phenomenon conflicting with theory

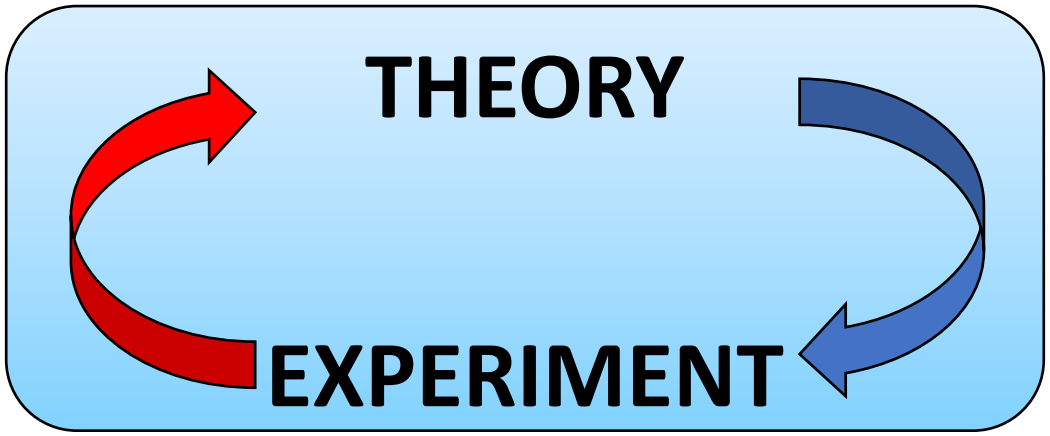




Experiment conflicting with theory



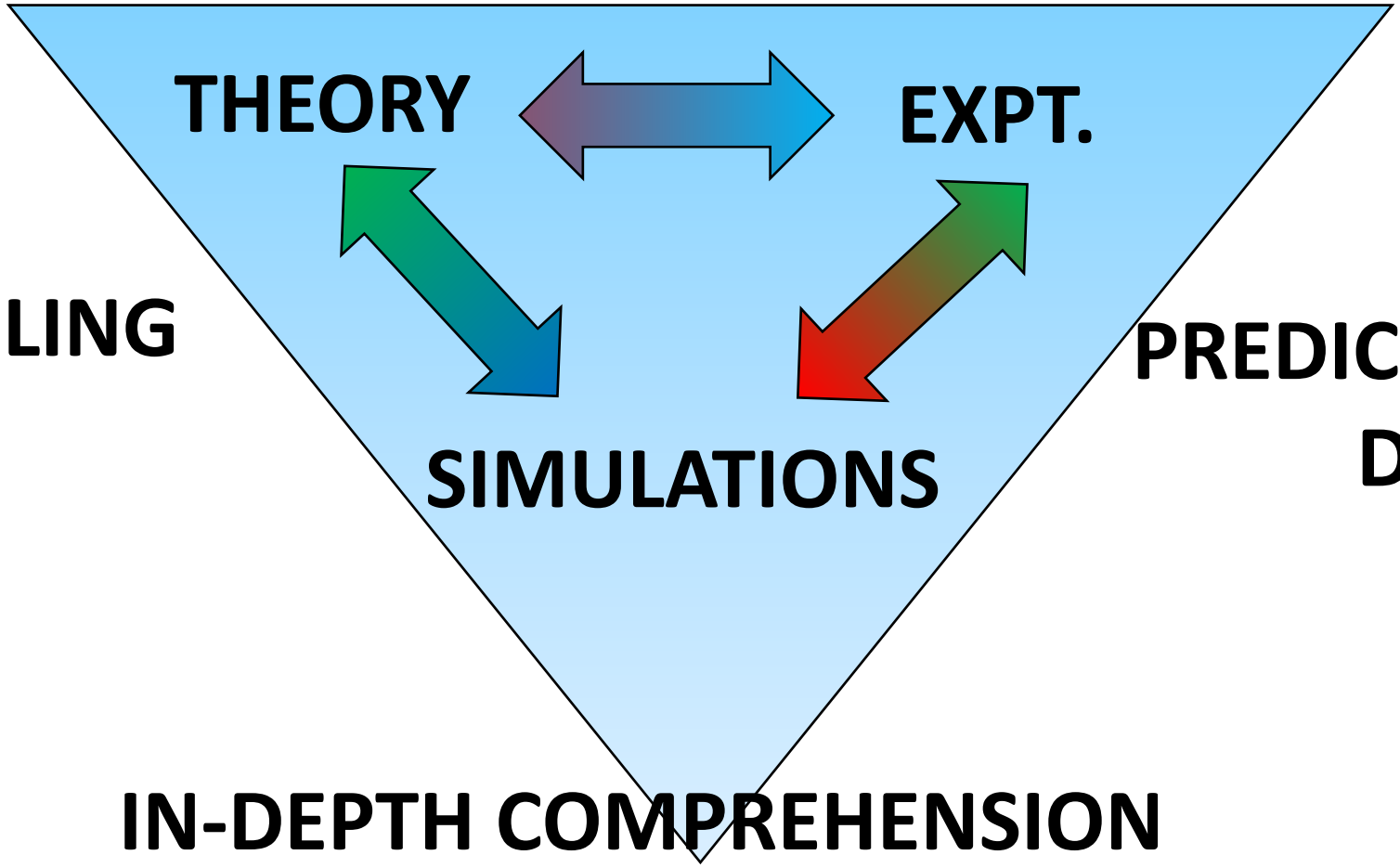
The «philosophia» of my research



HOW THE POWER OF SIMULATIONS HAS CHANGED THIS?

Professor Nicola Marzari (EPFL):
If Ptolemy had the access to a Blue Gene, he would have used it to prove that the sun moves around the Earth.

The «philosophia» of my research

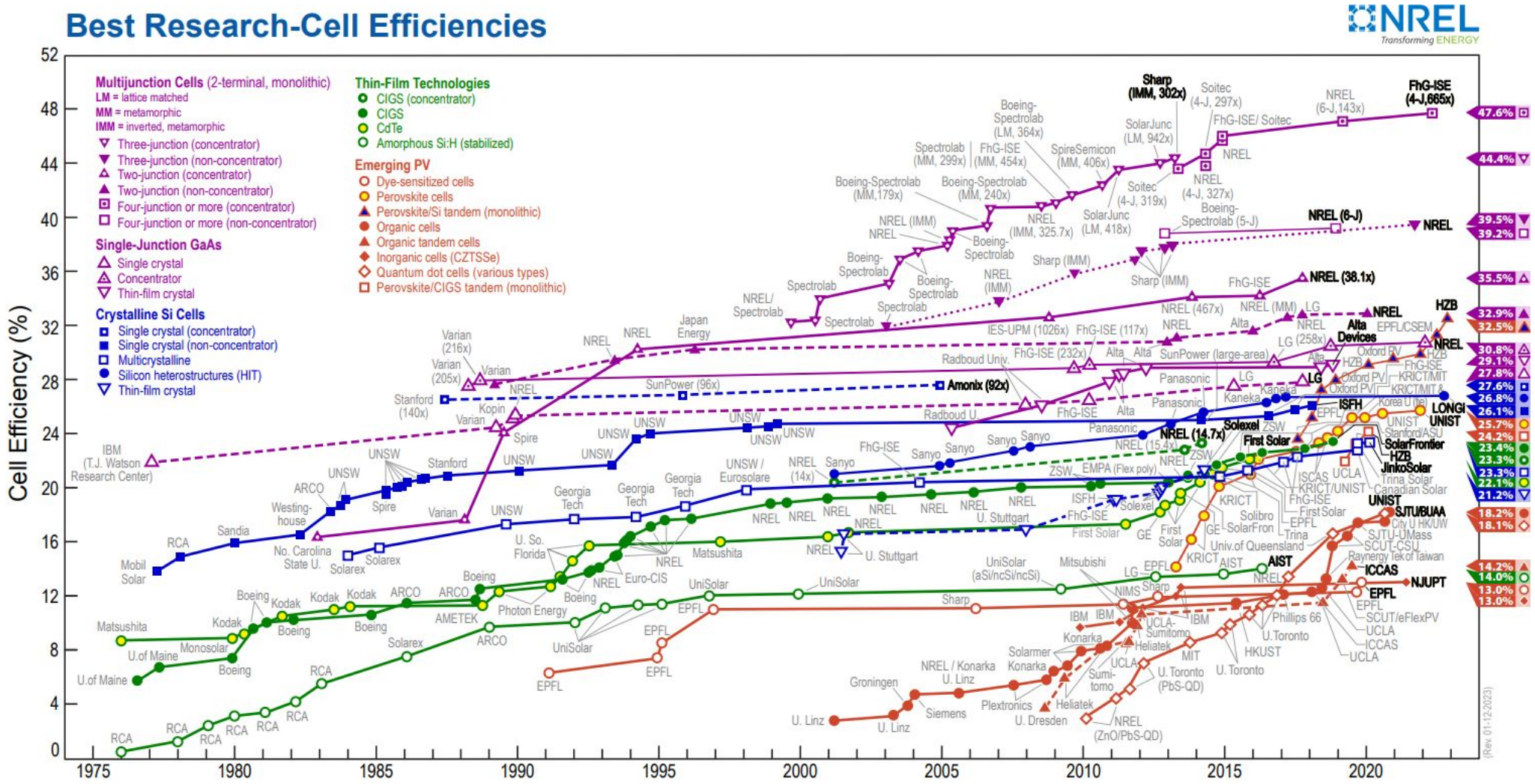


MODELING

PREDICTIVE POWER: DESIGN!

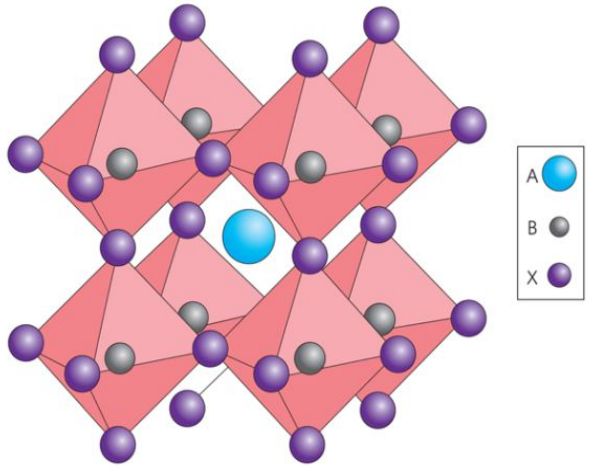
IN-DEPTH COMPREHENSION

Third-generation photovoltaics



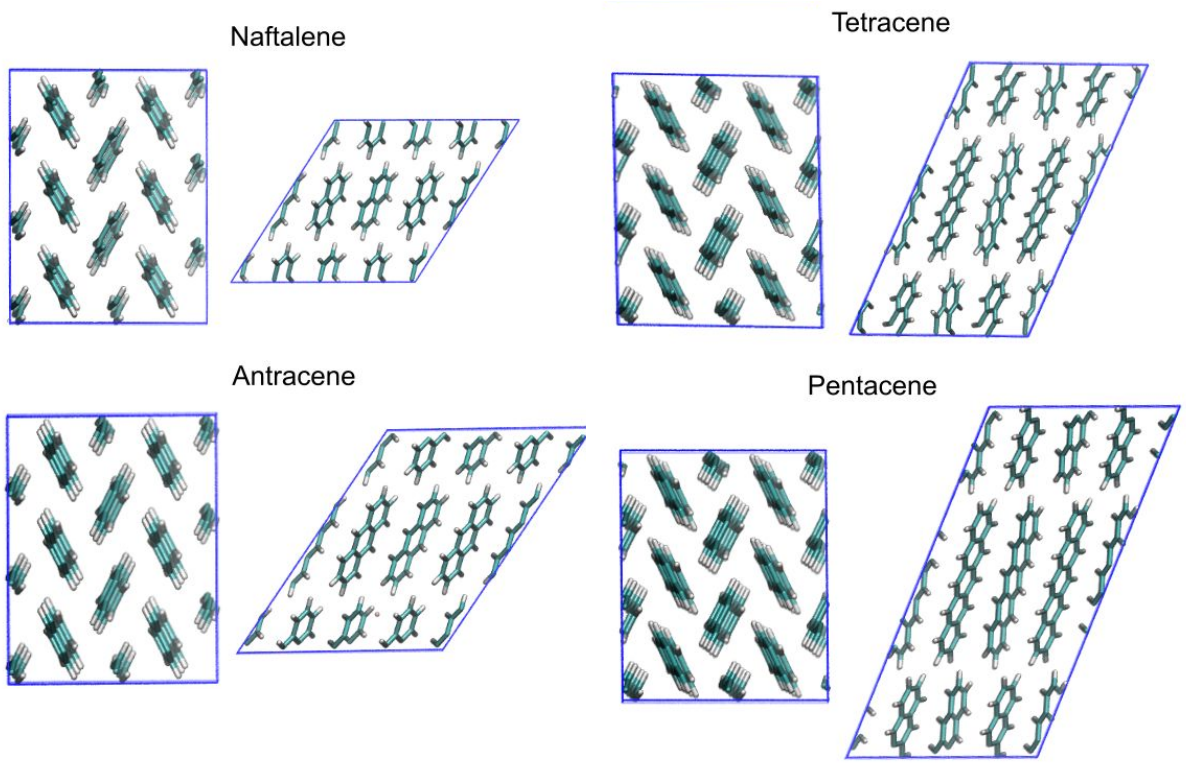
Alternatives to crystalline Si

Metal halide perovskites



A= Cs^+, $CH_3NH_3^+$
B=Pb^{2+}, Sn^{2+}
X=I^-, Br^-, Cl^-

Organic semiconductors

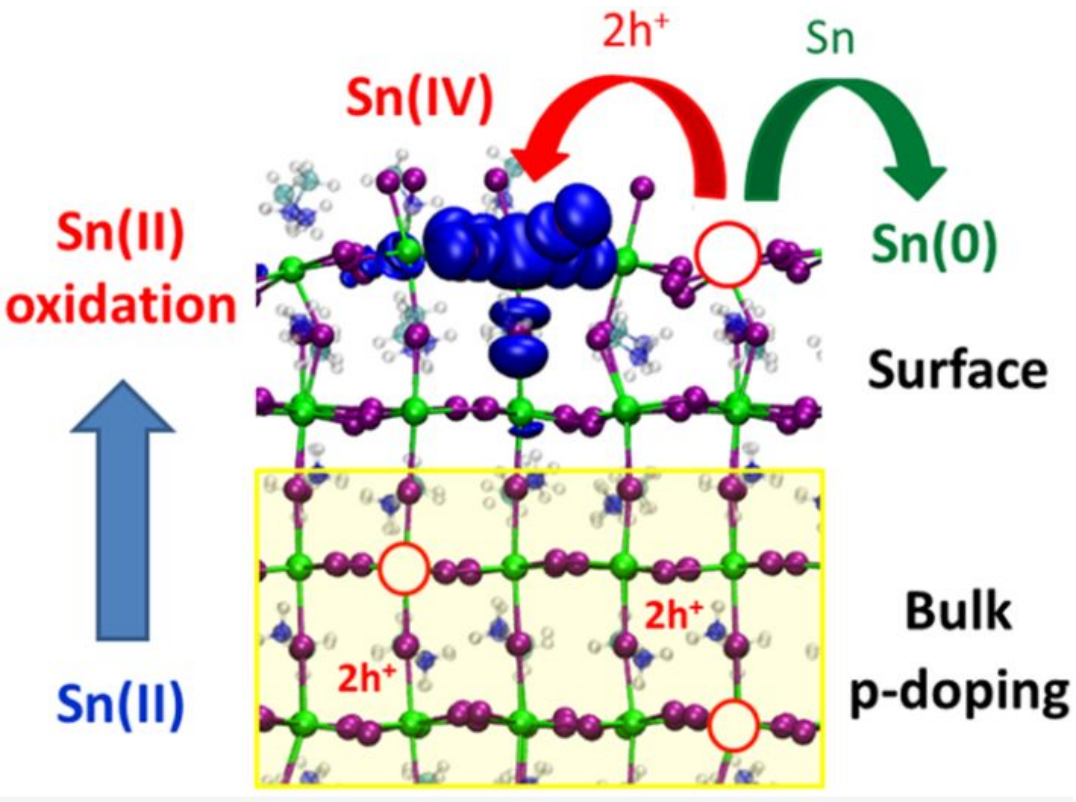


Acene crystals

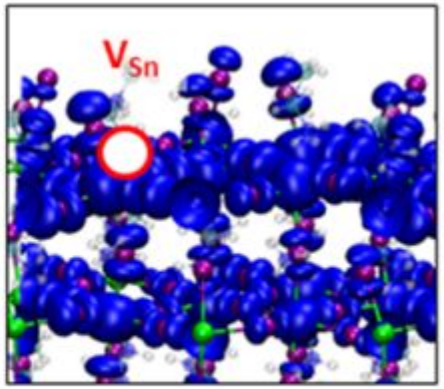
An example of project

Motivation: Oxidation of Sn(II) to Sn(IV) deteriorates the performance of Sn-based perovskites and ultimately induces degradation of the material.

Tools: Electronic-structure calculations, theory of defects in semiconductors.



What we learn: Oxidation of Sn(II) is a surface process that can be eventually hindered using appropriate additives (e.g. SnF_2) in the synthesis of the material.



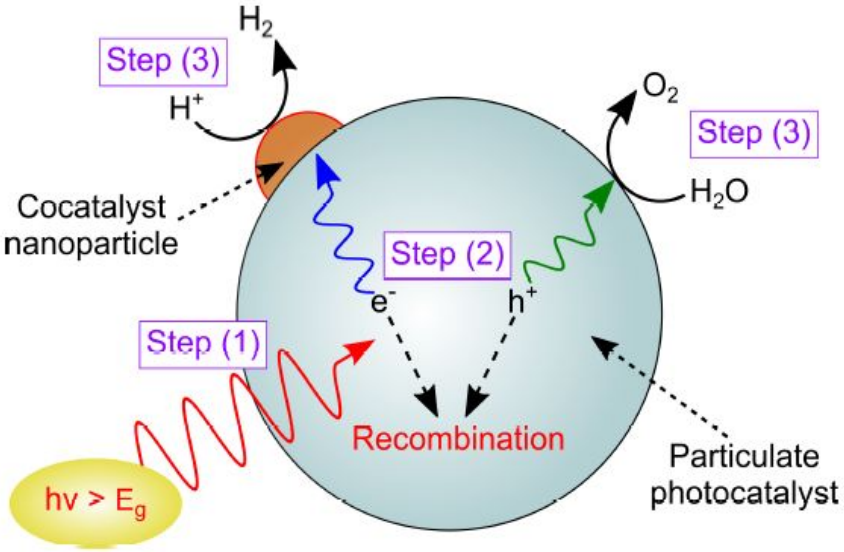
UNIVERSITÀ DEGLI STUDI DI PERUGIA

ISTITUTO ITALIANO DI TECNOLOGIA

ACS Energy Lett. **2020, 5, 9, 2787– 2795**

Artificial photocatalysis

Principle: **Breaking/forming chemical bonds by solar energy conversion as done by nature**



Goals

H_2 from H_2O splitting

NH_3 from N_2 fixation

Clean production of fuel/chemicals

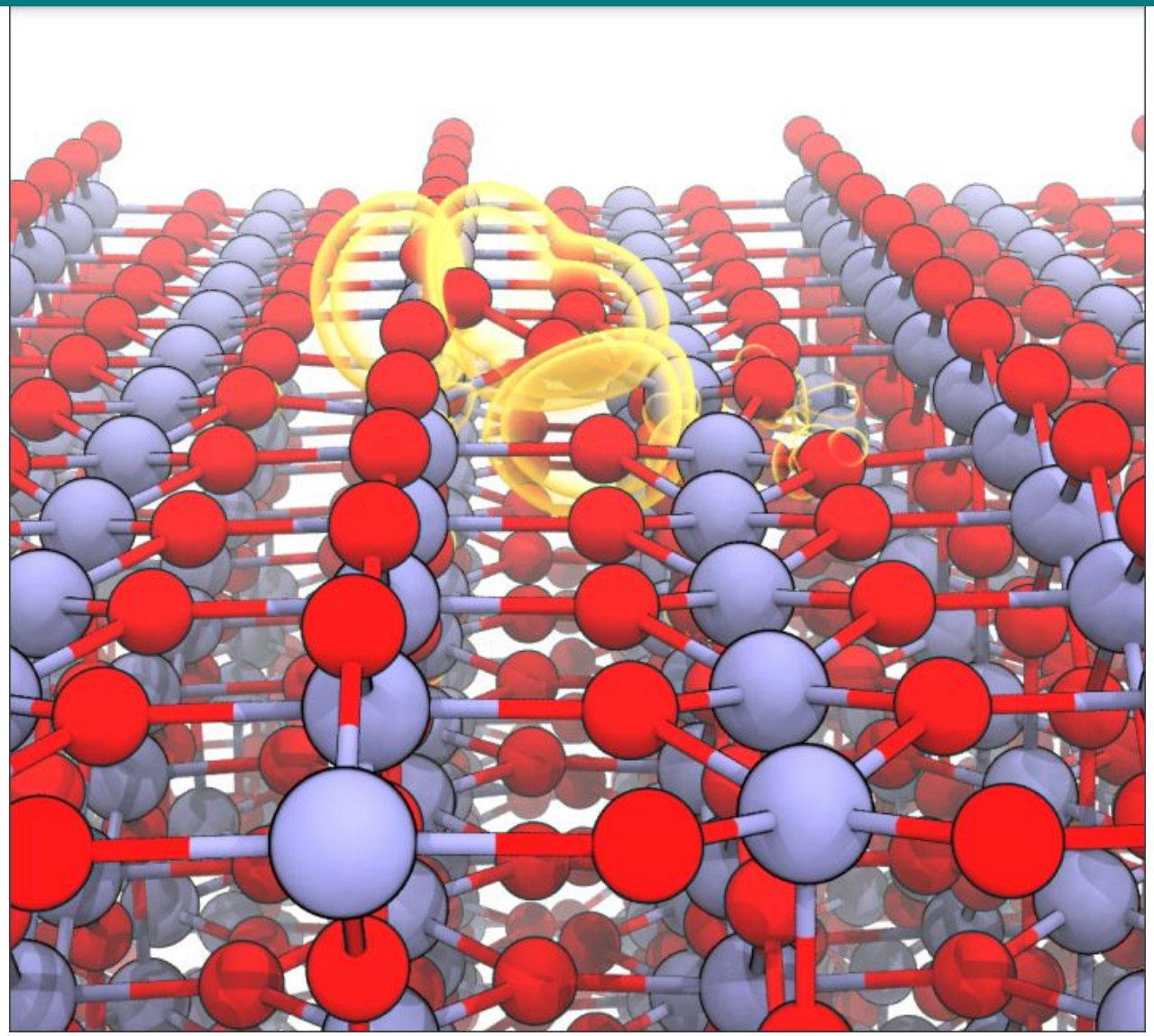
Degradation of pollutants

CO_2 reduction

Organic pollutants

Ecological transition!

Another example of project…



Another example of project…

Motivation: Standard mechanism of photocatalytic water splitting are inherently inefficient. Is it possible to overcome this?

Tools: Molecular dynamics simulations**, c**omputational electrochemistry.

Standard mechanism of water oxidation reaction

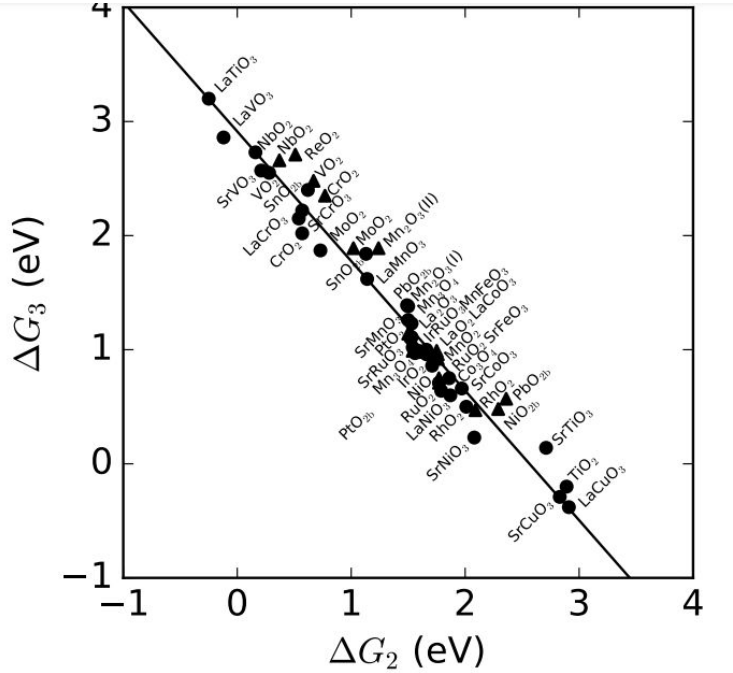
$$* + H_2O \rightarrow OH_{ads} + H^+ + e^-$$

$$OH_{ads} \rightarrow O_{ads} + H^+ + e^-$$

$$O_{ads} + H_2O \rightarrow OOH_{ads} + H^+ + e^-$$

$$OOH_{ads} \rightarrow * + O_{2g} + H^+ + e^-$$

Linear scaling relationship



Because of linear scaling, there is an *overpotential* and so the reaction is slower

Another example of project…

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Standard mechanism of water oxidation reaction

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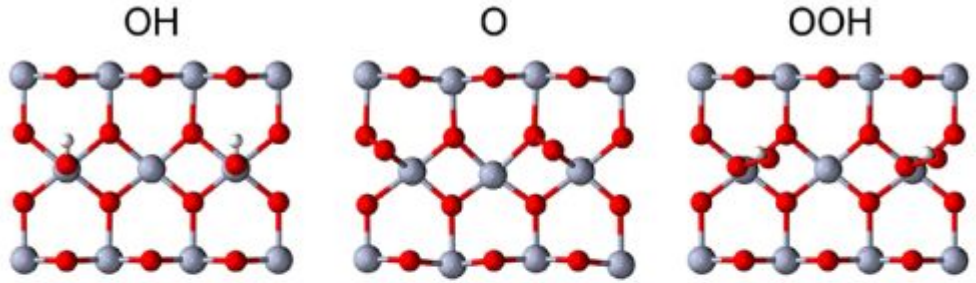
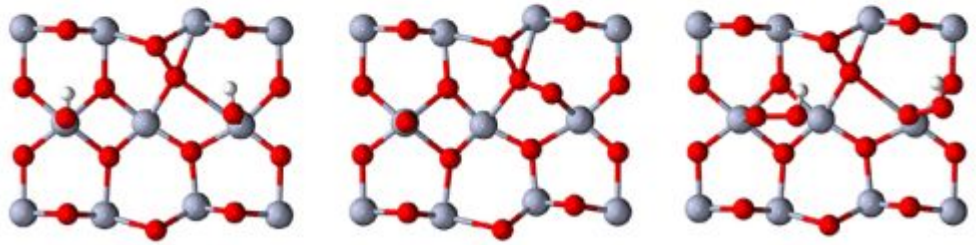
$$OOH_{ads} \rightarrow * + O_{2g} + H^+ + e^-$$

TiO_2 surface (top view)

No charge localization



Localization



What we learn: Charge localization at the semiconductor surface can bring to alternative and more efficient reaction mechanisms.

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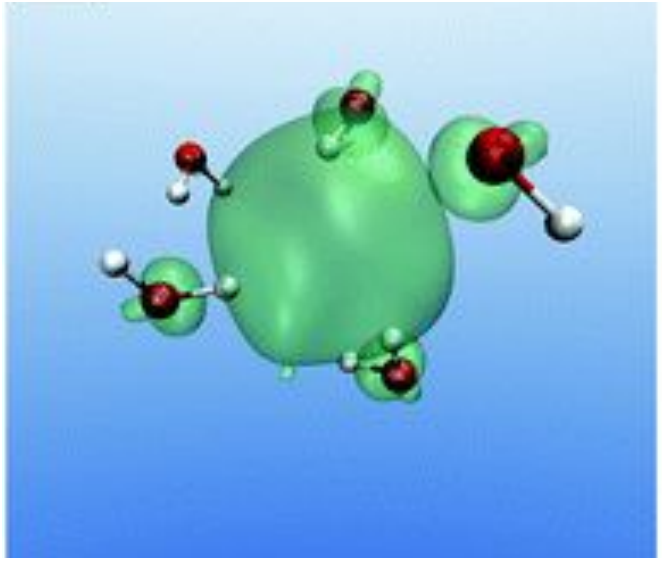
EPFL

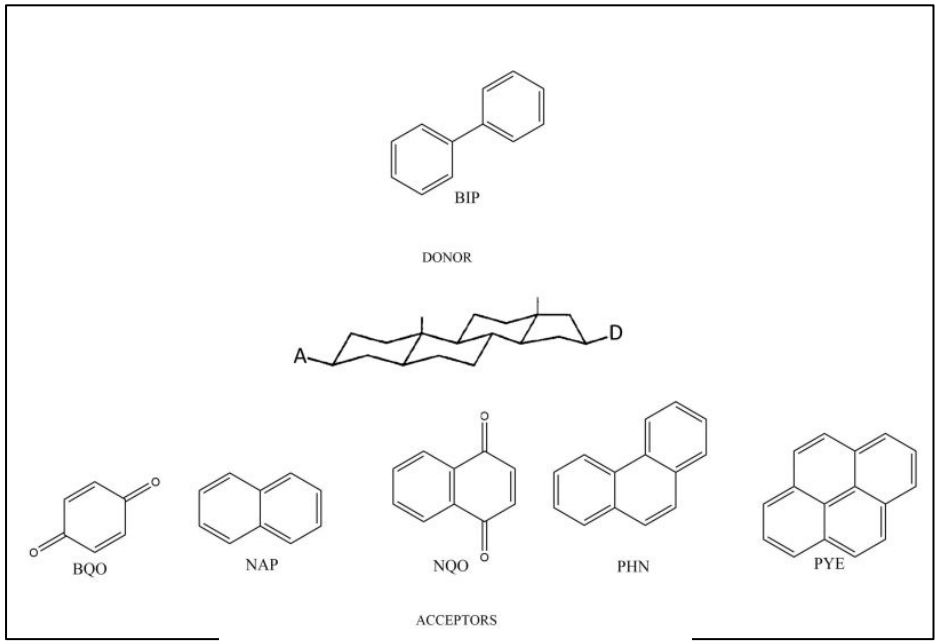
ACS Catal. 2018, 8, 7, 5847−5851

Reactivity in solution

Solvated electrons

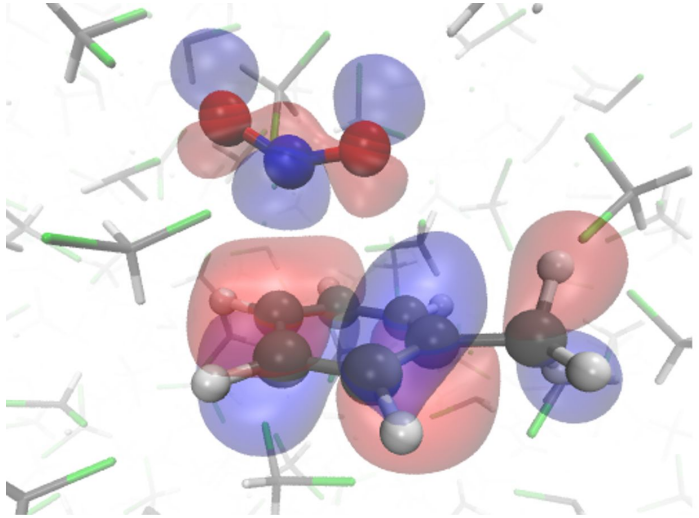


Electron transfer rates



$$k_{i\to f} = \frac{2\pi}{\hbar} F(\Delta E_{fi}, T)$$

Reaction mechanisms



The last example of project (I promise)

Motivation: The mechanism of aromatic nitration is still debated**. Can theory provide an answer?**

Tools: Electronic-structure calculations, Molecular dynamics simulations.

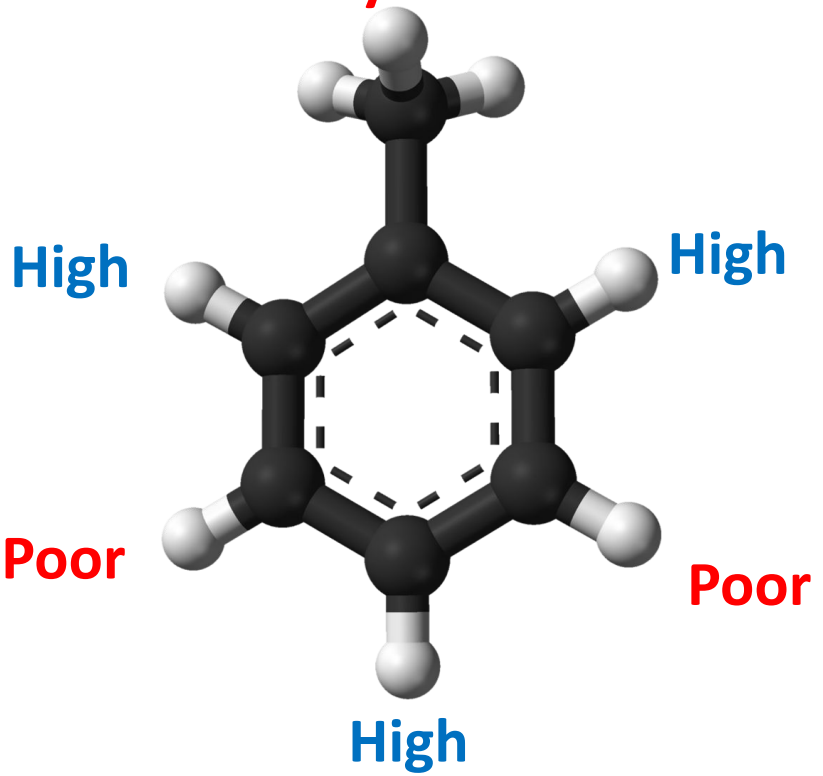
Textbook mechanism of aromatic nitration

$$NO_2^+ + ArH \rightarrow ArHNO_2^+ \xrightarrow{A^-} HA + ArNO_2$$

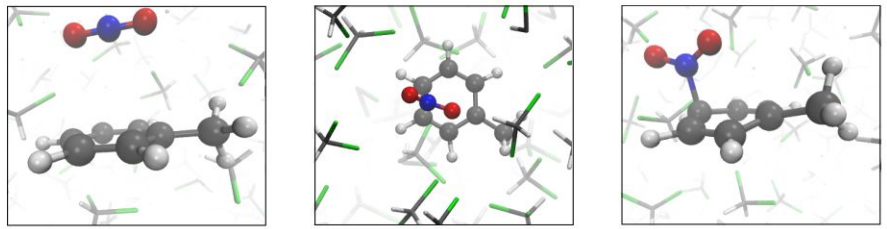
Experimental observation (Olah 1971): The high positional selectivity of products for toluene conflicts with a two-step mechanism.

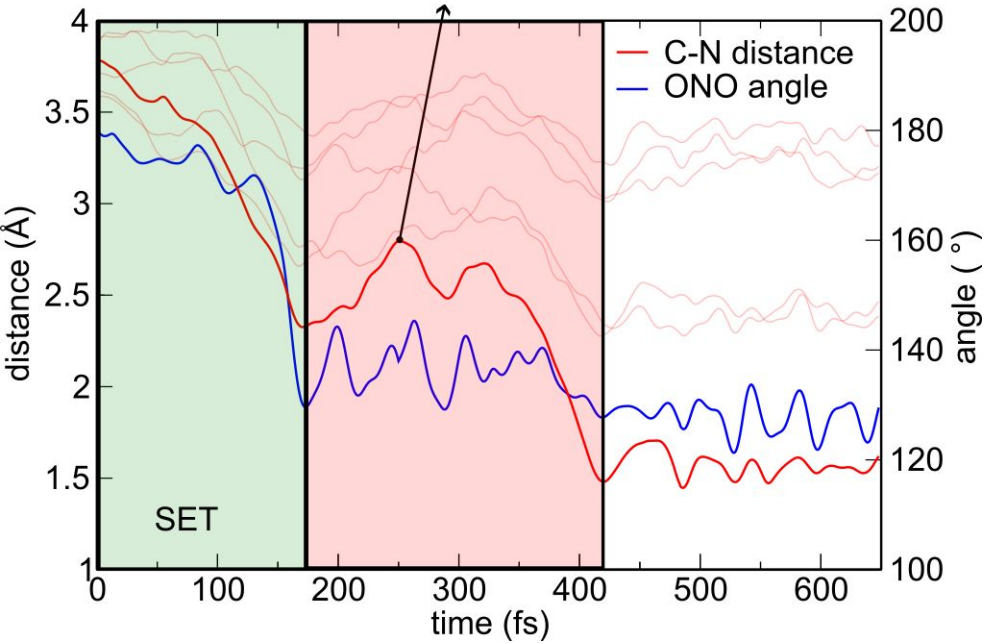
$$NO_2^+ + ArH \rightarrow \boxed{?} \rightarrow ArHNO_2^+ \xrightarrow{A^-} HA + ArNO_2$$

Reactivity of toluene



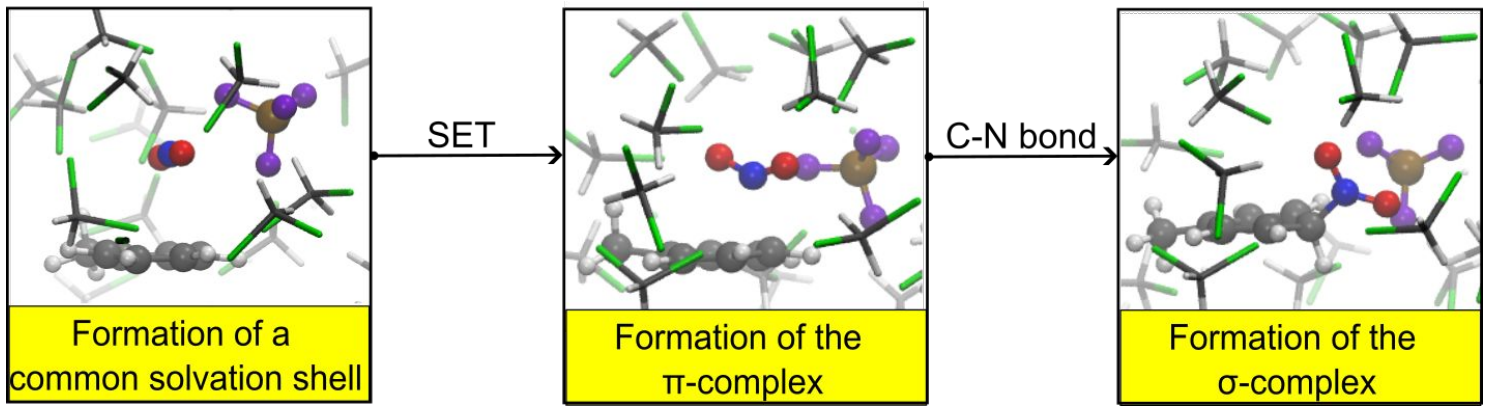
The last example of project (I promise)





What we learn: Molecular dynamics simulations show the formation a radical intermediate (the so-called π-complex) well before the formation of the C-N bond.

Proposed mechanism of aromatic nitration by NO_2BF_4 in CH_2Cl_2



Phys. Chem. Chem. Phys., 2023, 25, 2359

Acknowledgements

Thanks for you attention

Funding

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Drive Perovskite PV Performance
PerTPV
Drive Perovskite PV Scale-Up

People

- Prof. Alessandro Troisi
- Prof. Alfredo Pasquarello
- Prof. Filippo De Angelis
- Prof. Andrea Cavalli
- Dr. Annamaria Petrozza
- Prof. Andrea Peluso