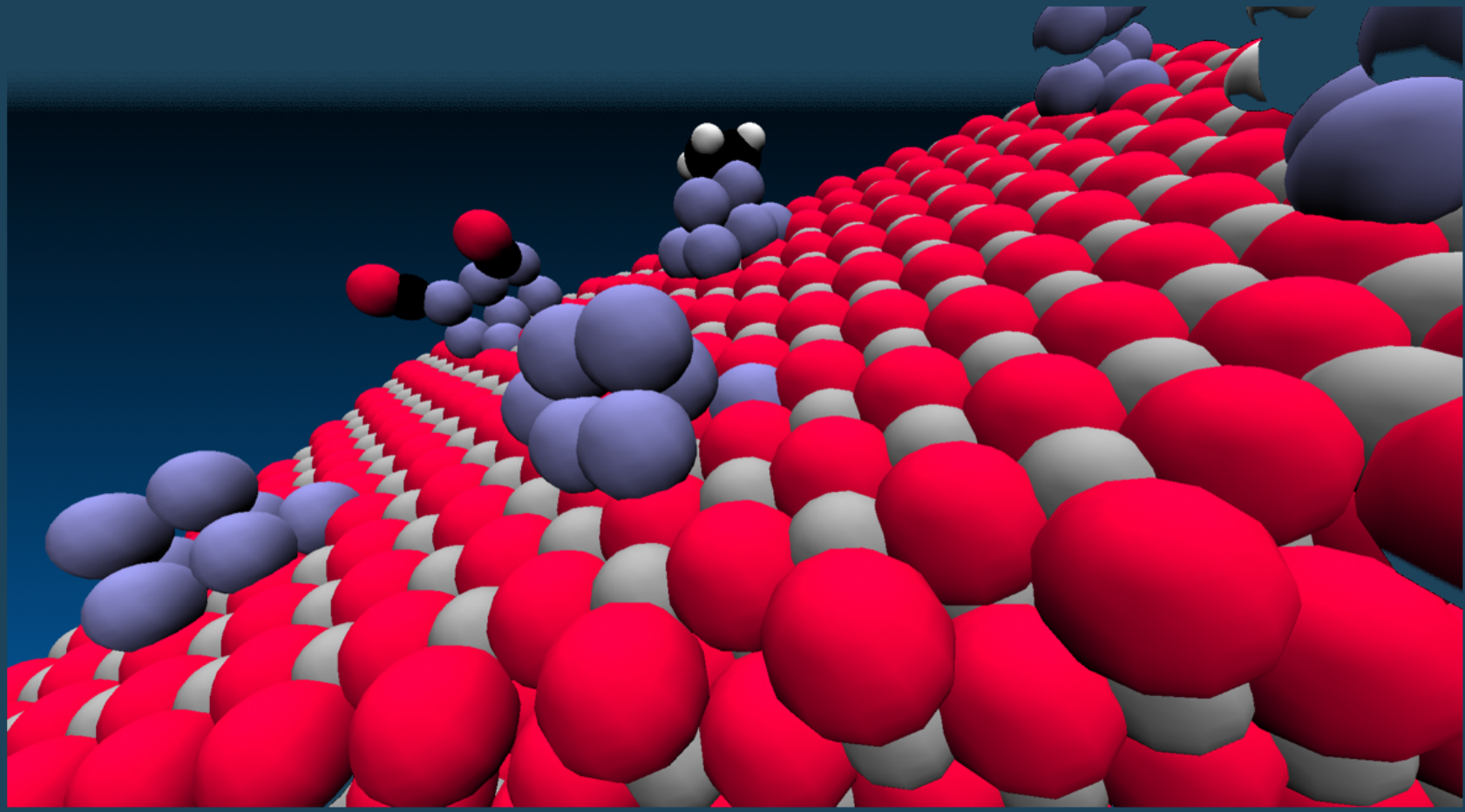
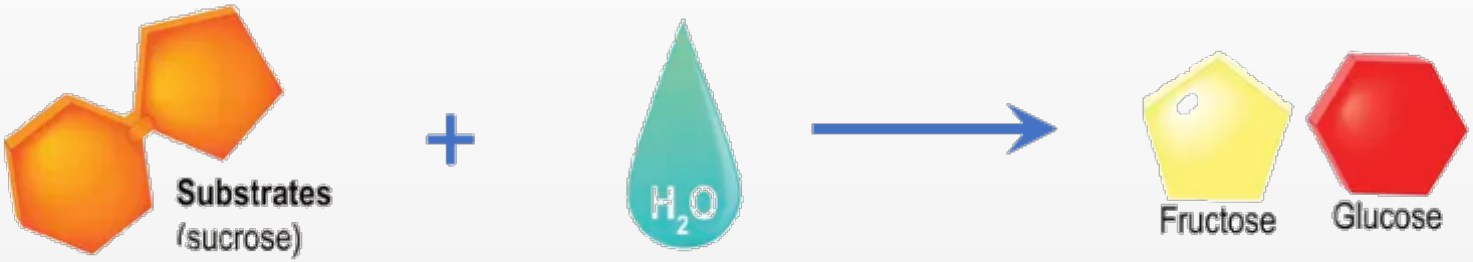
Designing Novel Platinum Based Efficient Catalysts



Jose M. Mercero

Introduction



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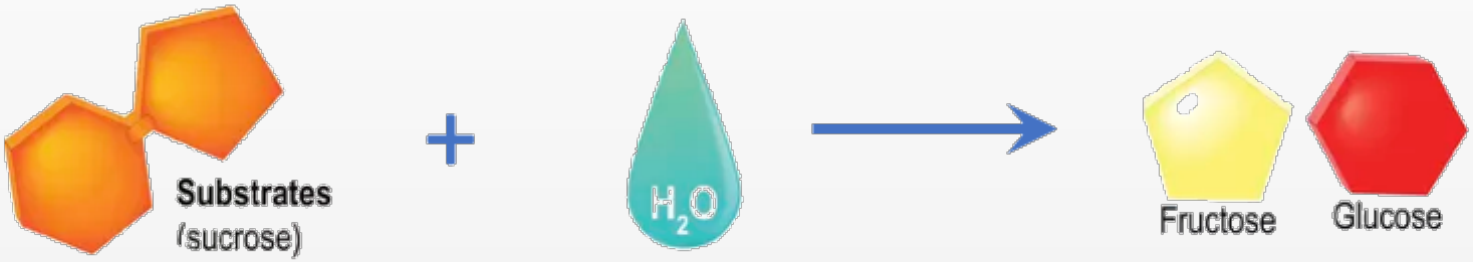
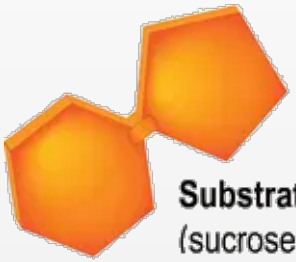


This reaction to happen will need around 460 years

Introduction



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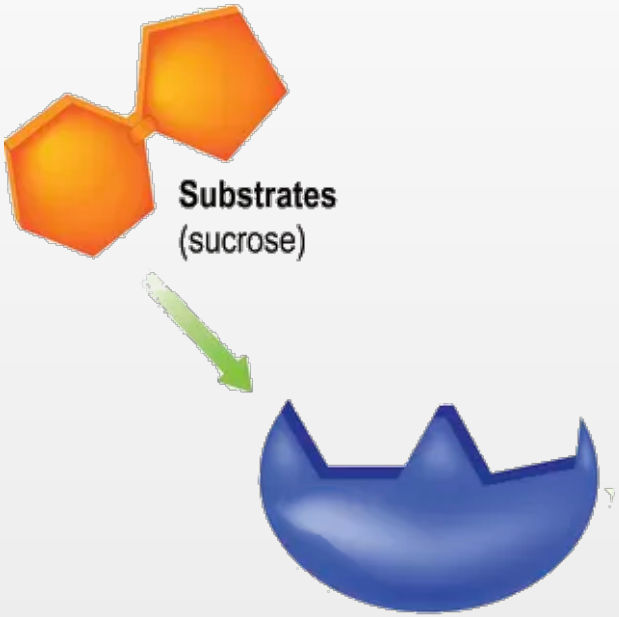

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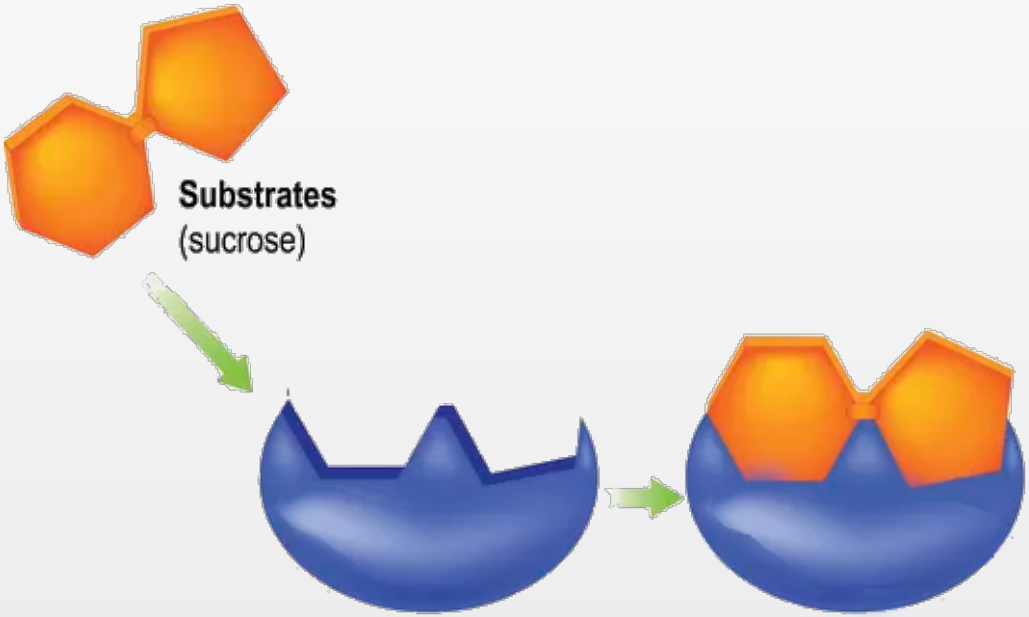

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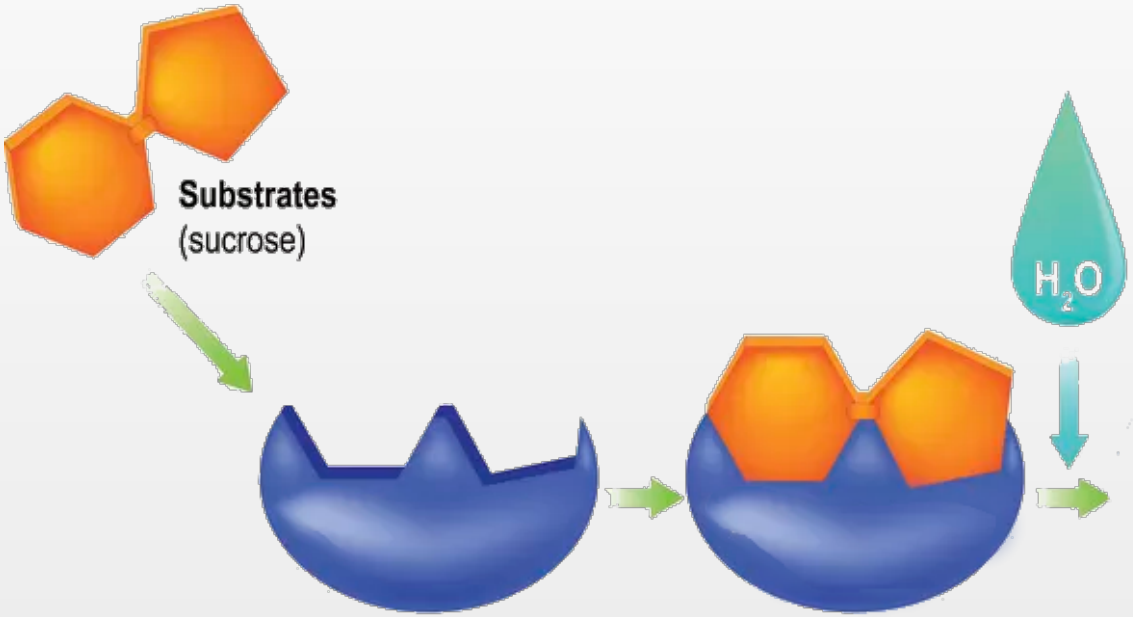

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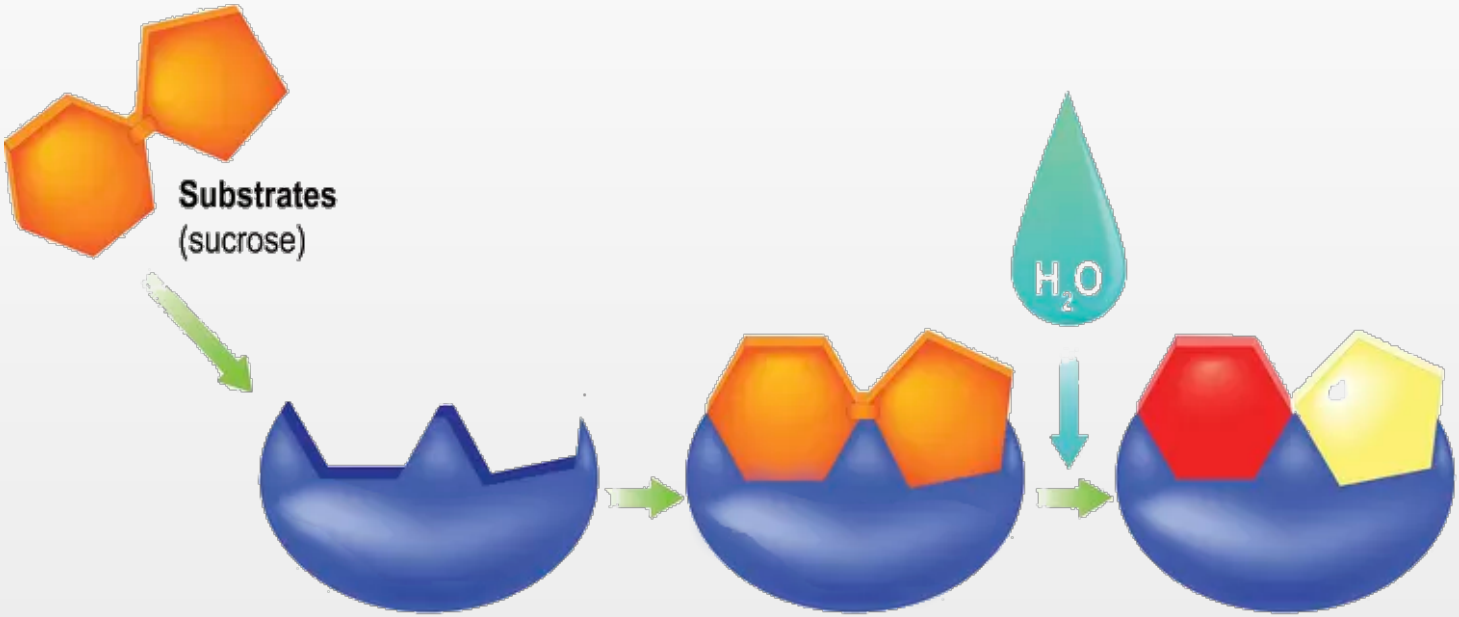

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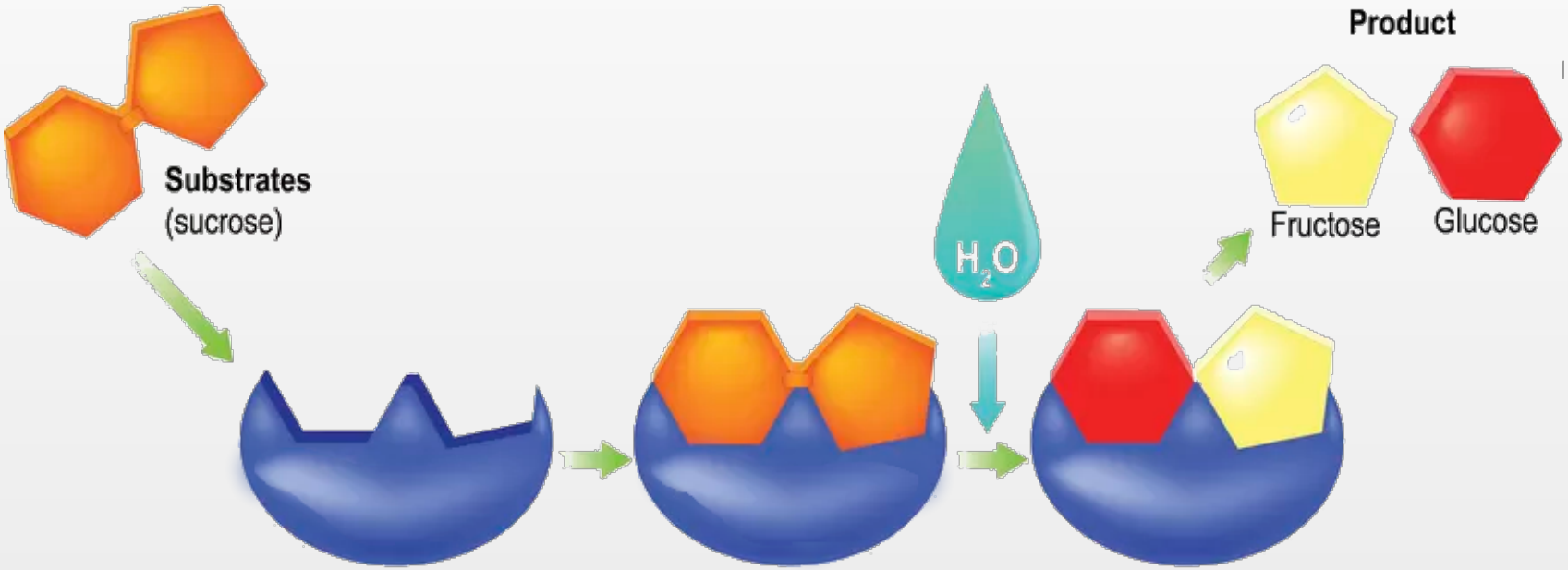

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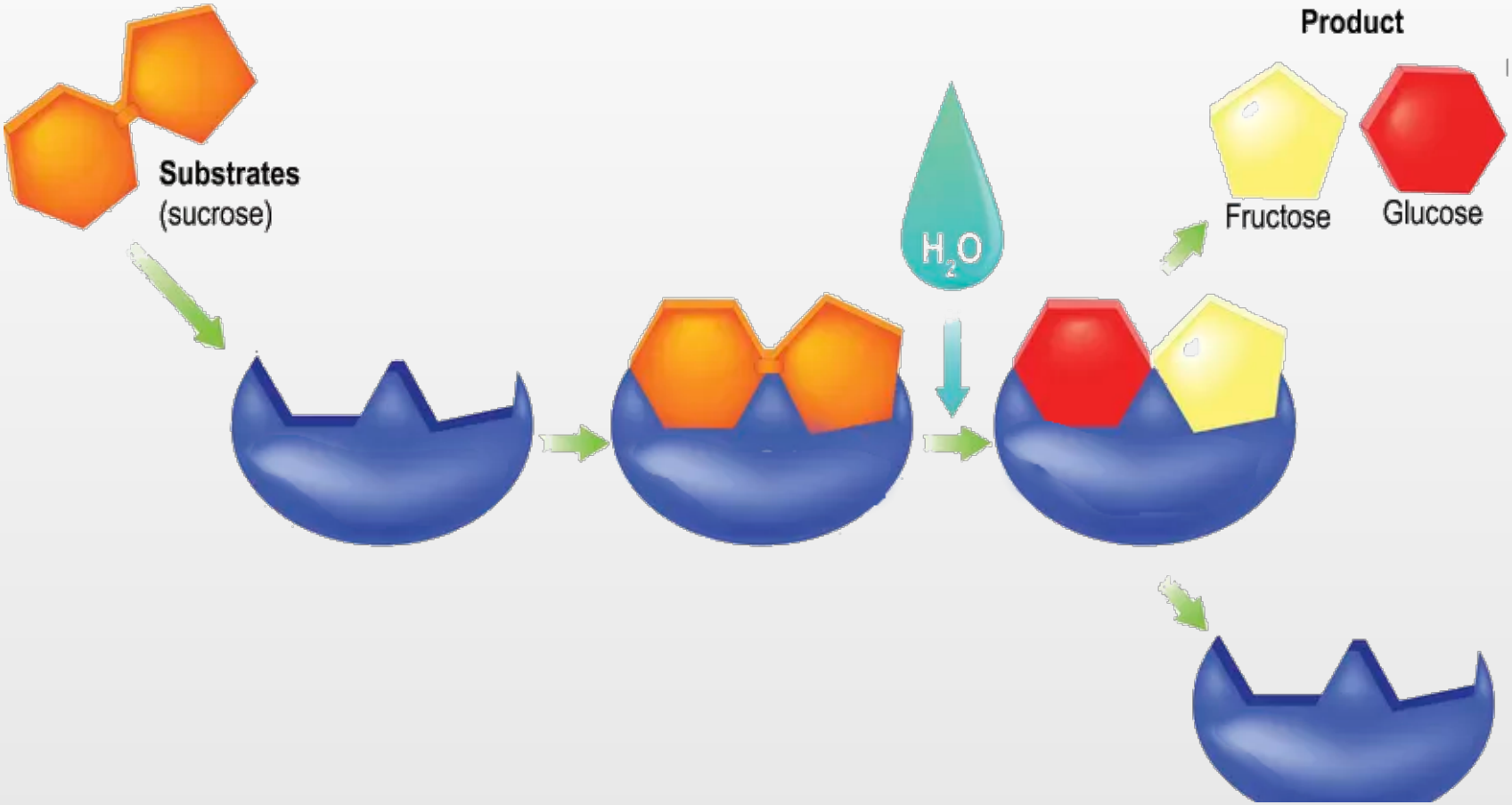

$$\text{HYDROGEN} + \text{OXYGEN} \longrightarrow \text{WATER}$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

HYDROGEN + OXYGEN ⟶ WATER

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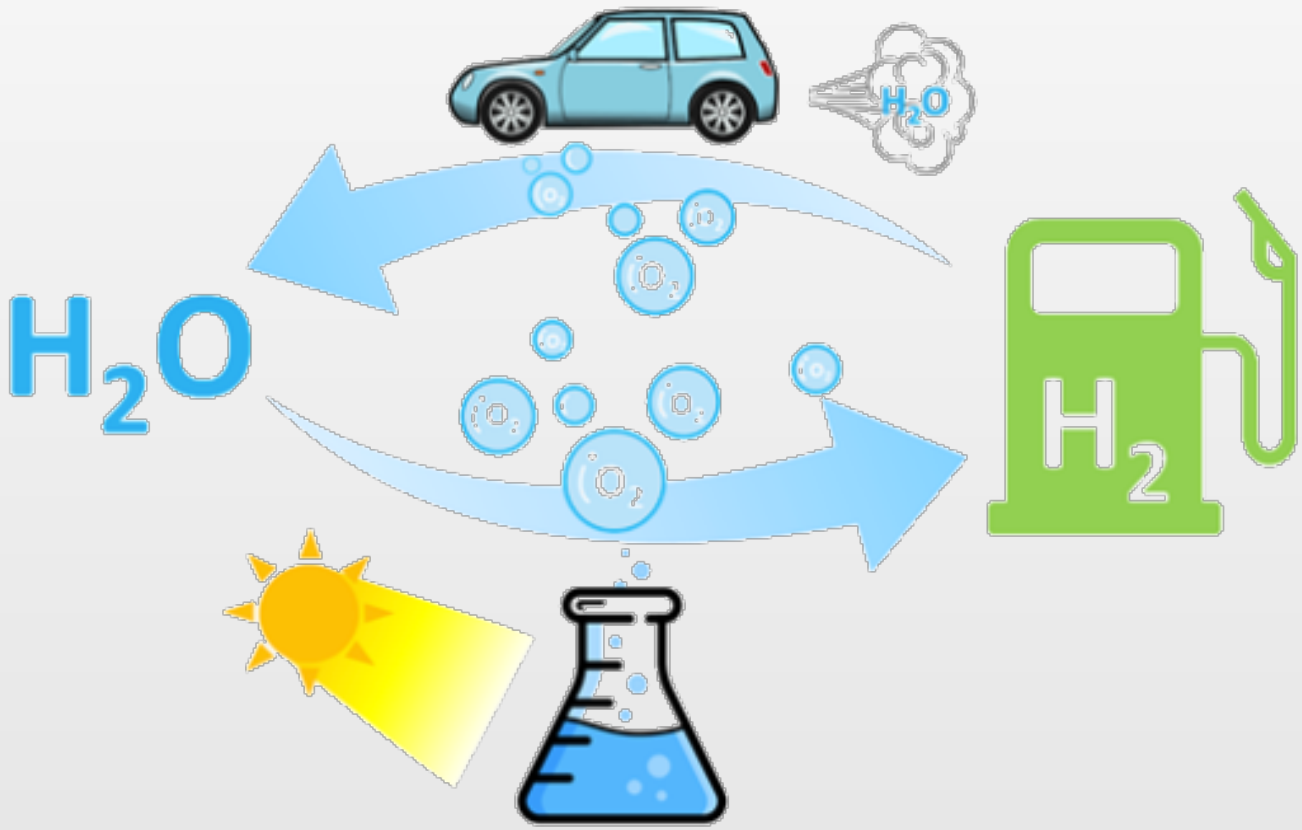

Metal nanoclusters

Metal nanoclusters

- Reduced amount of metals ⇒ greener catalysis
- High surface-to-volume ratio ⇒ superb catalysts

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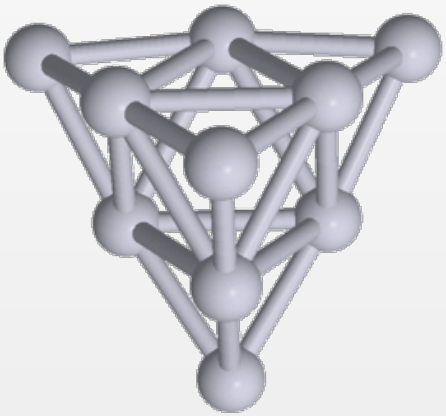

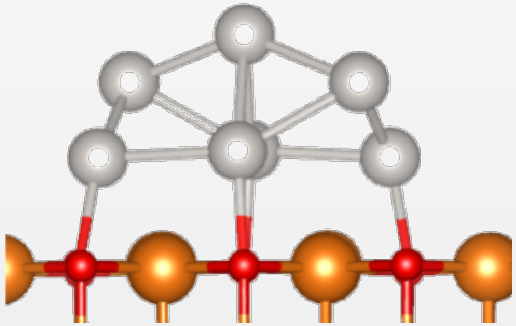

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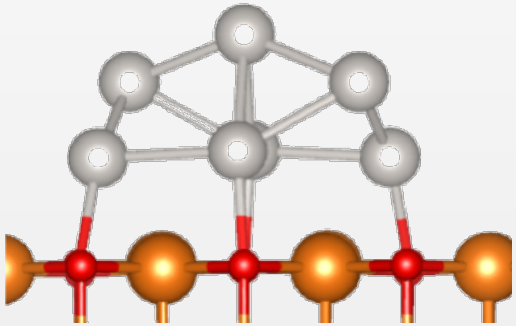

Pt nanoclusters

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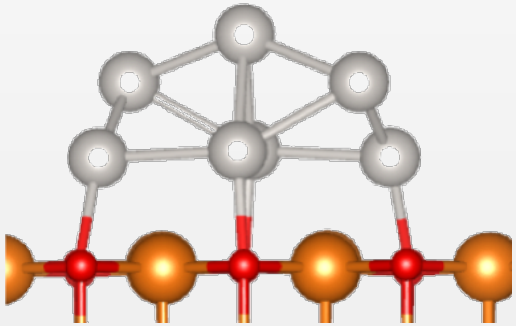
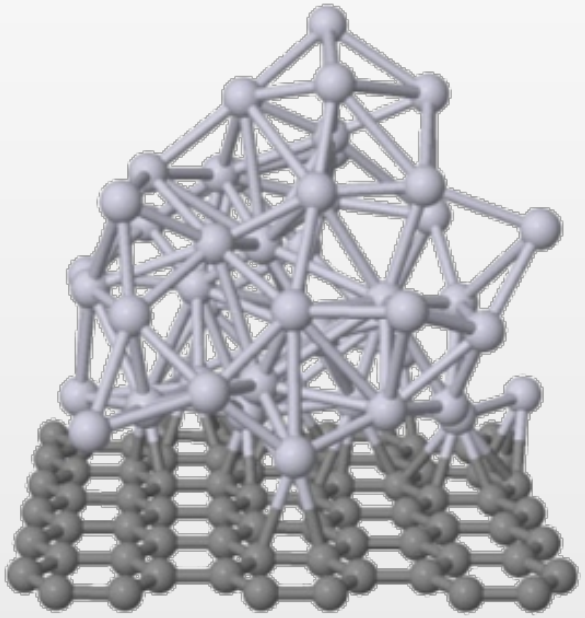


Pt nanoclusters

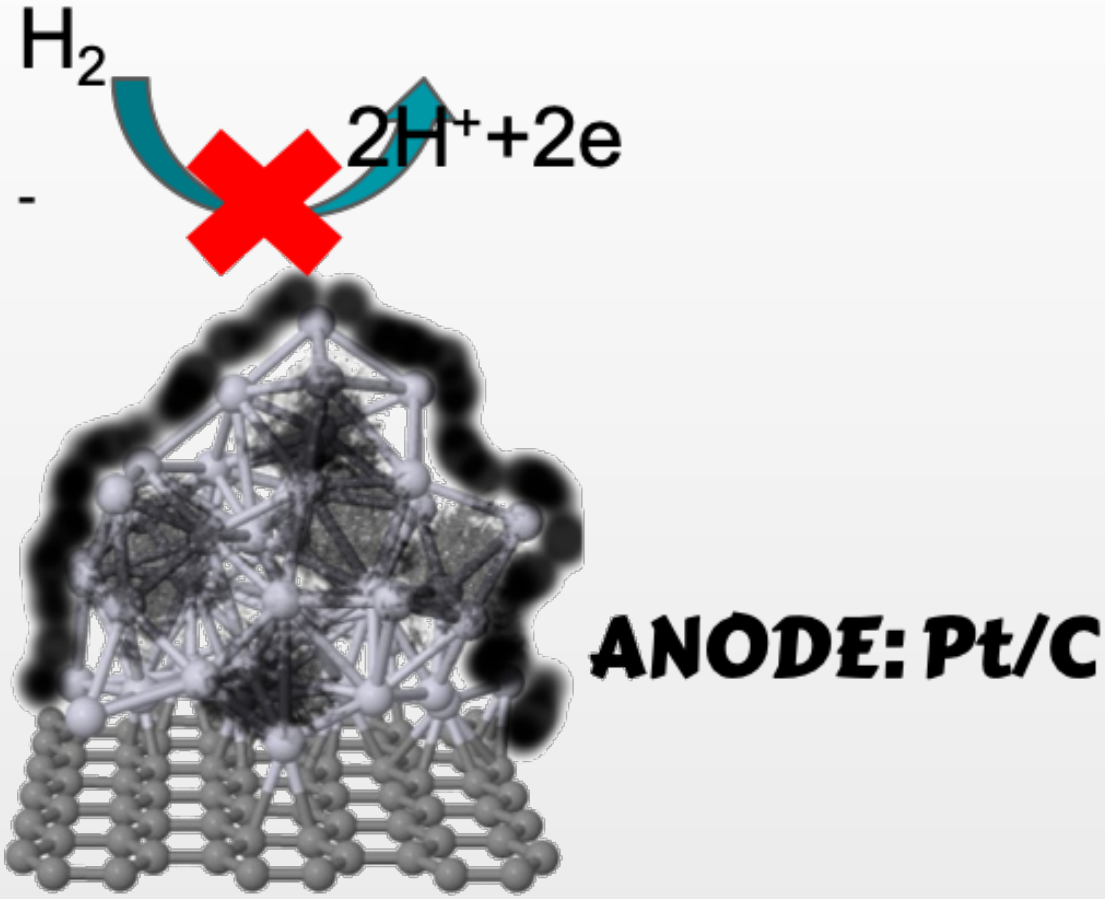
- Pt versatile catalyst

H_2 dissociation

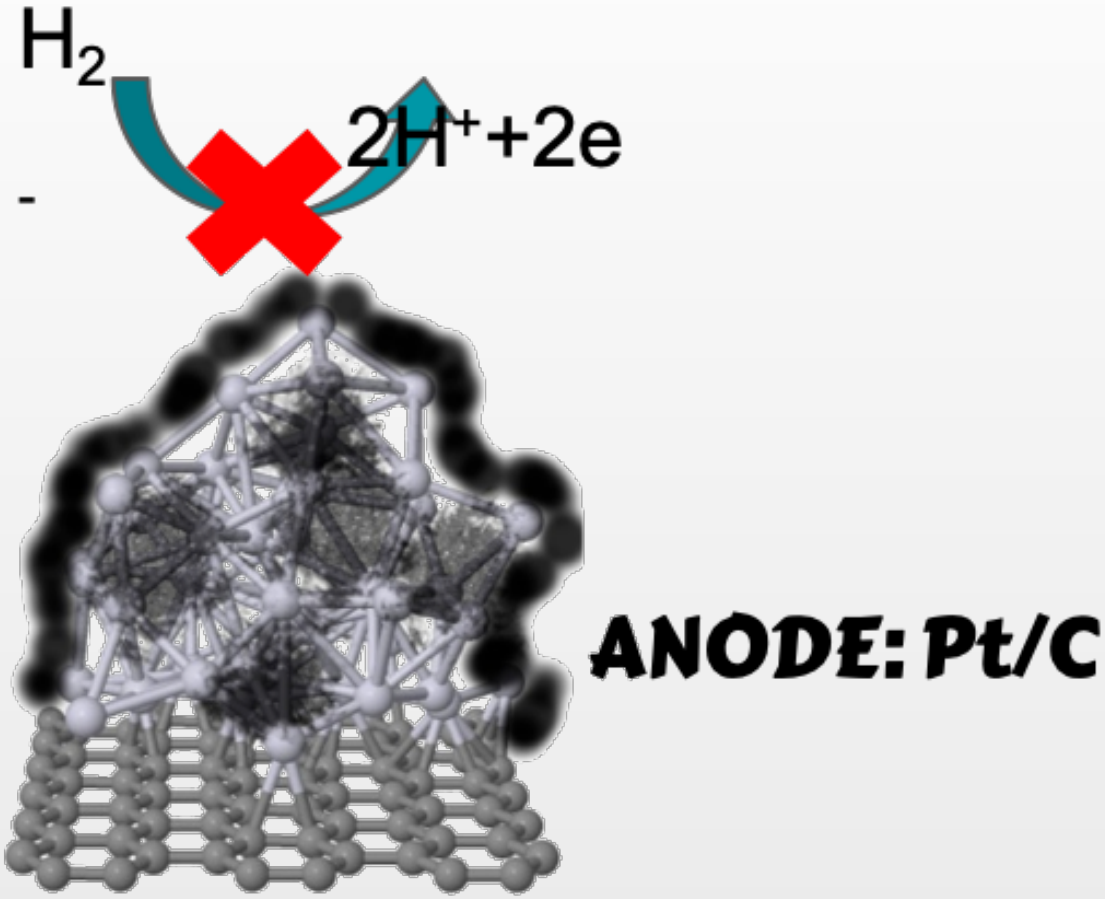


ANODE: Pt/C

H_2 dissociation

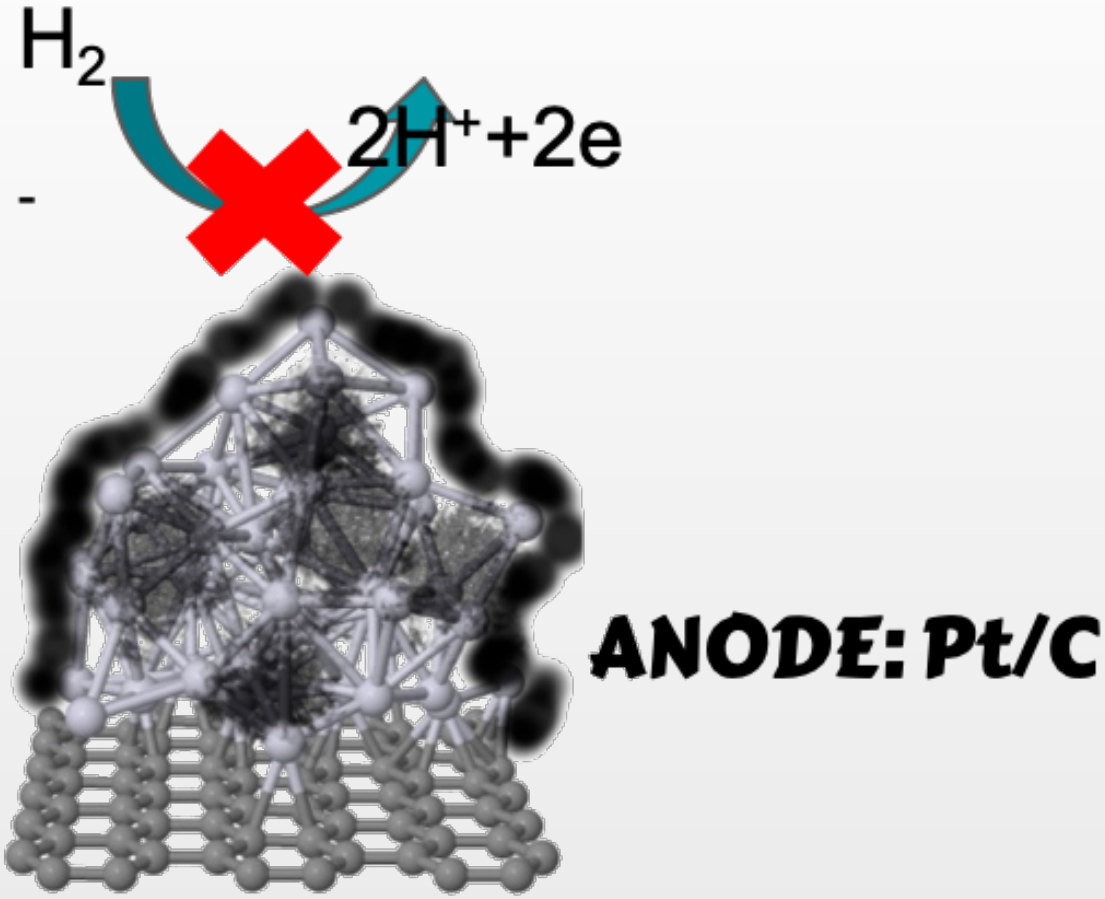


H_2 dissociation



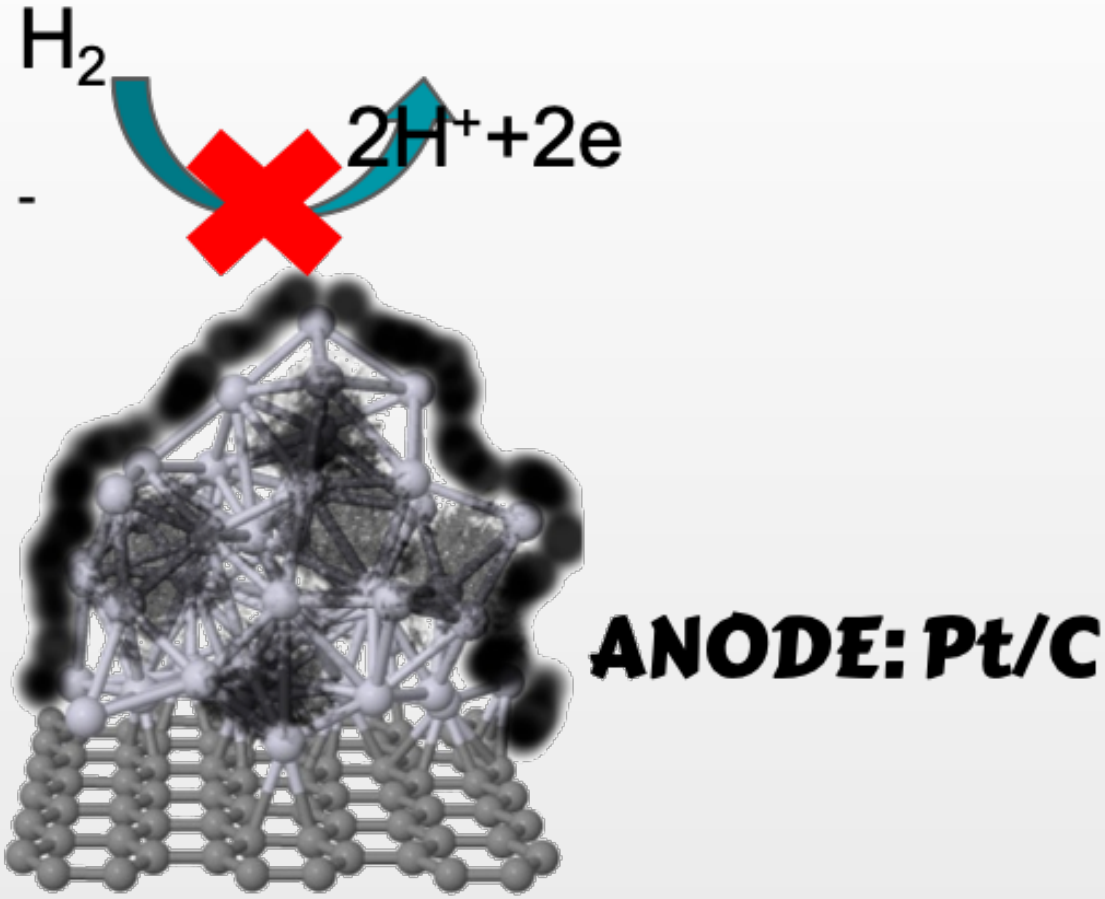
Goal:

H_2 dissociation



Goal: Design durable catalysts, resistant to deactivation

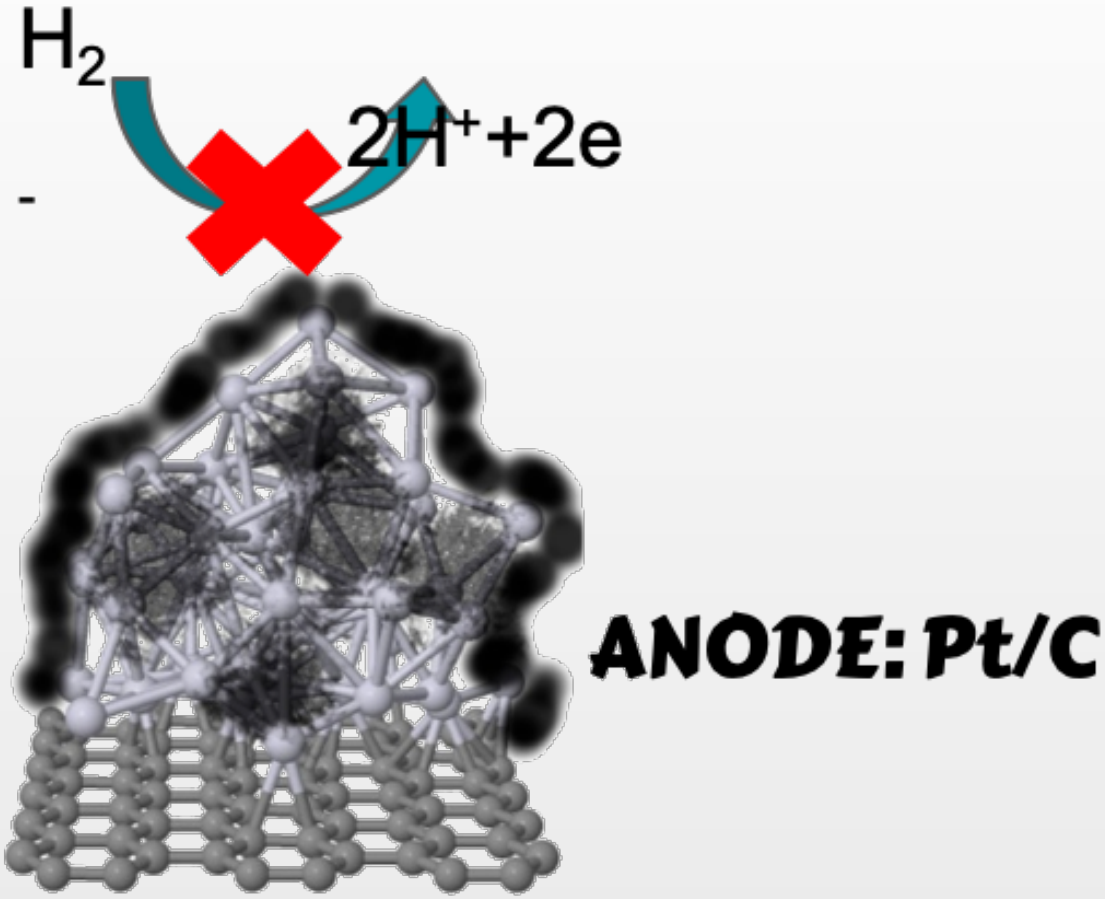
H_2 dissociation



Goal: Design durable catalysts, resistant to deactivation

How?

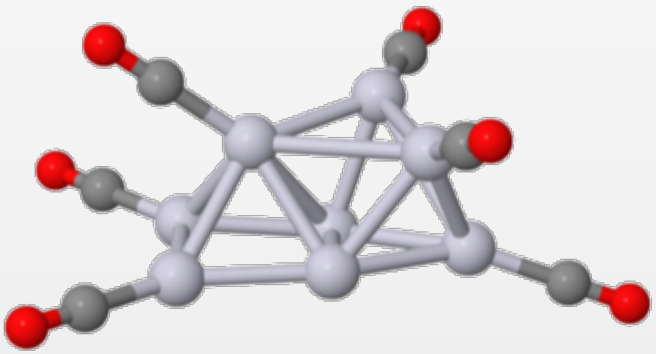
H_2 dissociation



Goal: Design durable catalysts, resistant to deactivation

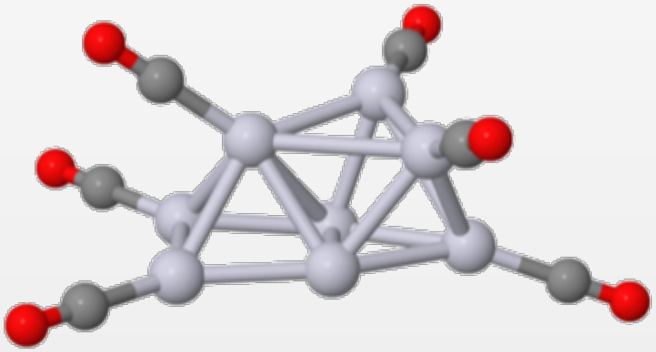
How? Doping Pt catalysts with other atoms

Conclusions



Conclusions

CO poisoned
Pt catalyst



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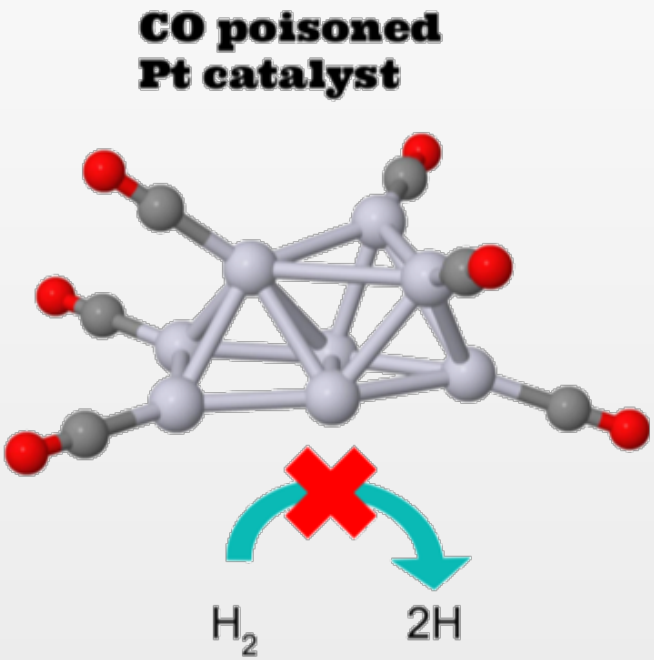

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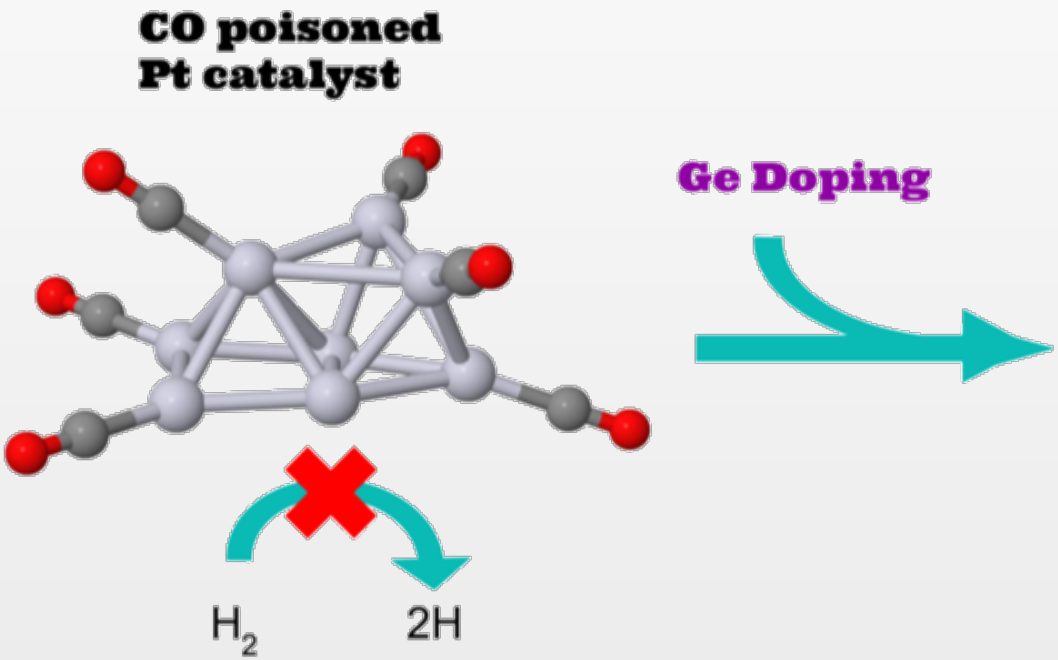

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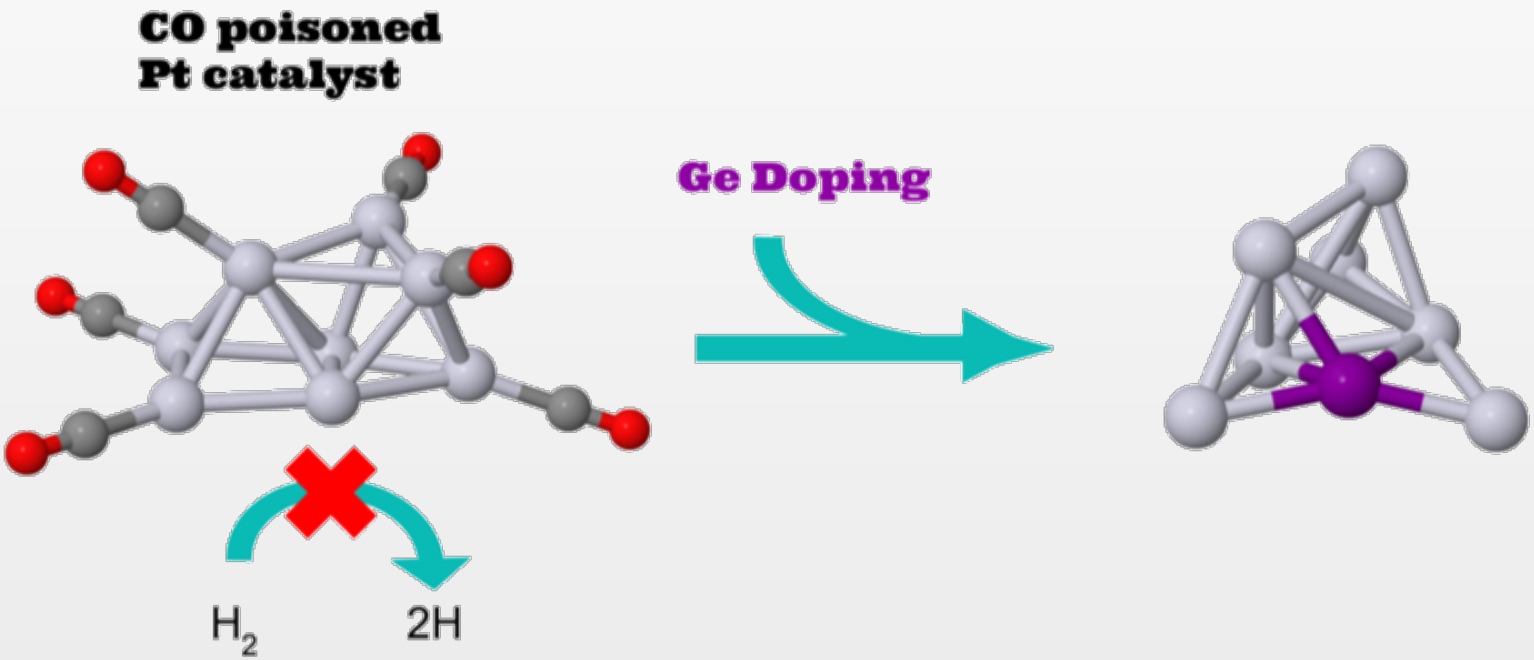

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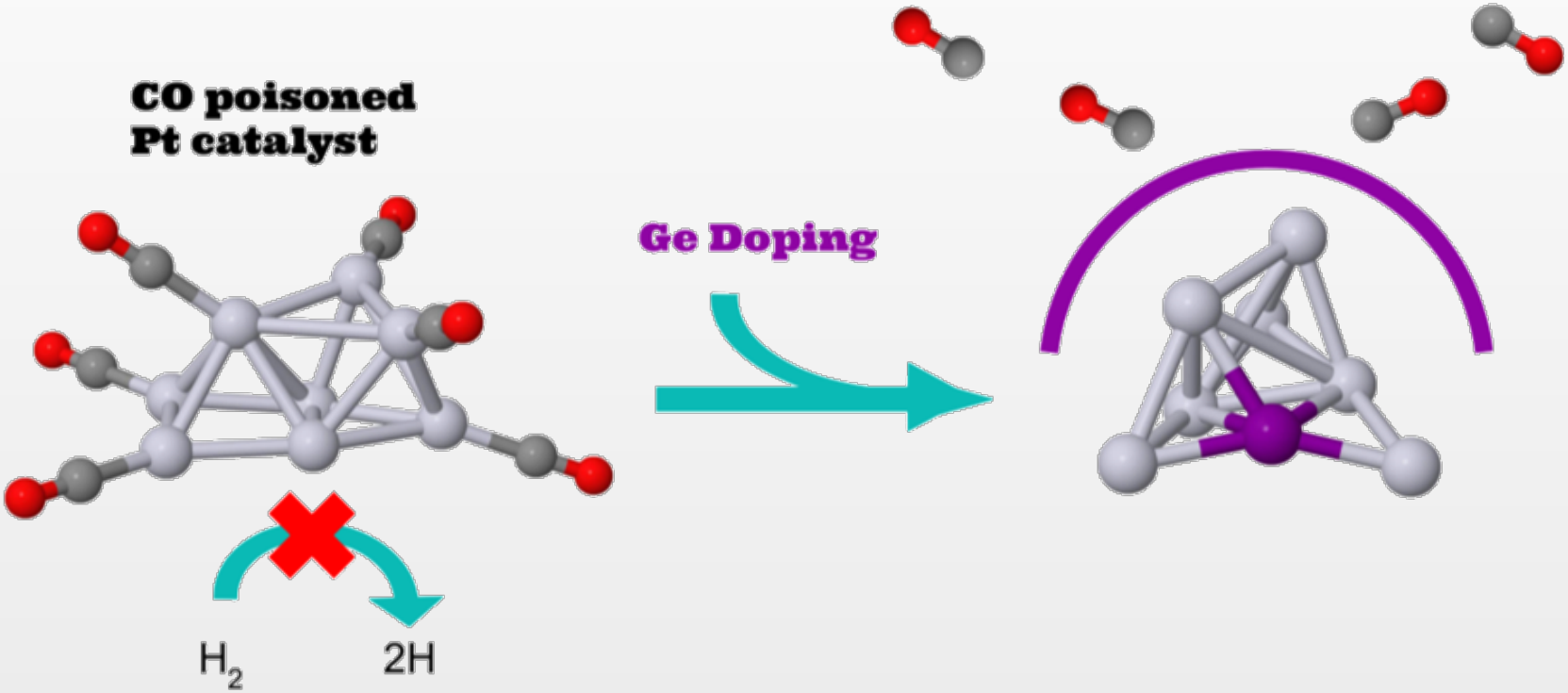

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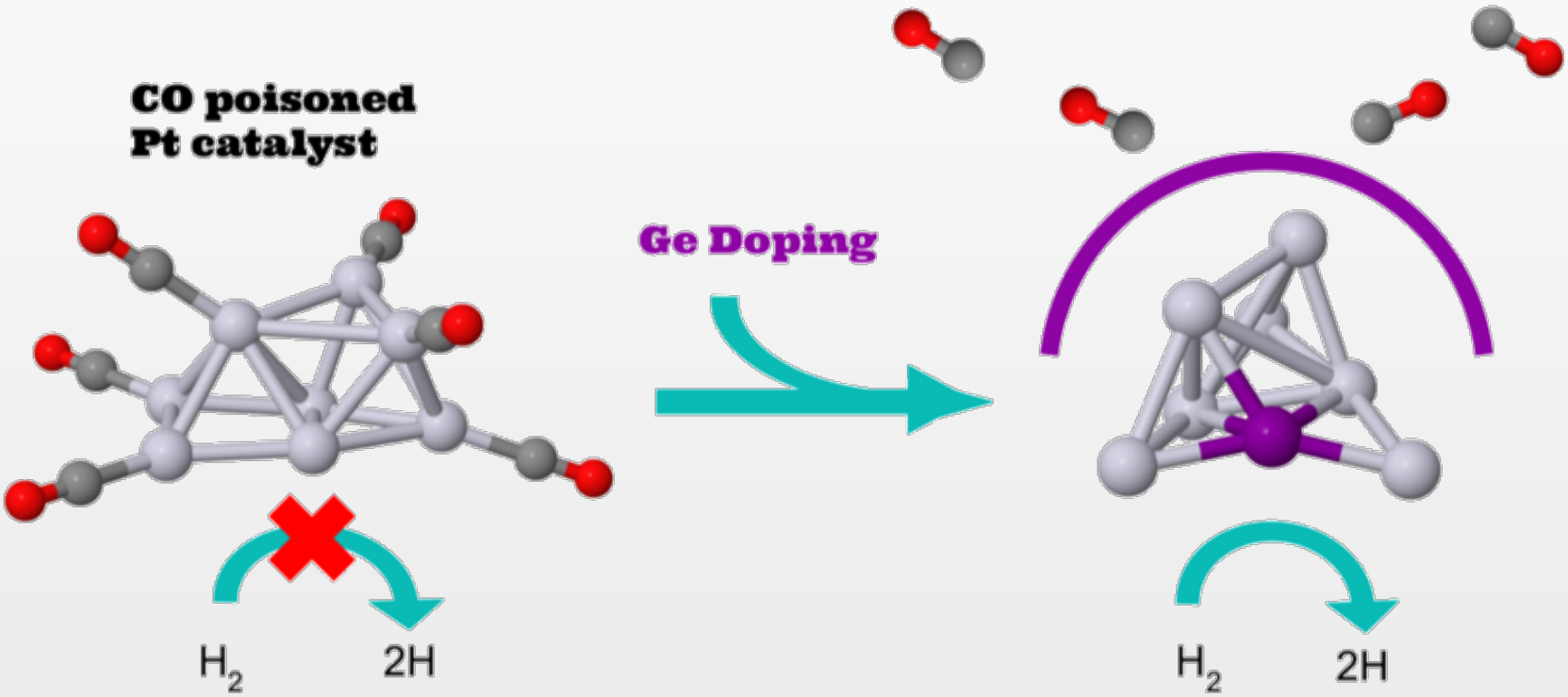

Pt_n^+ and $GePt_n^+$ clusters

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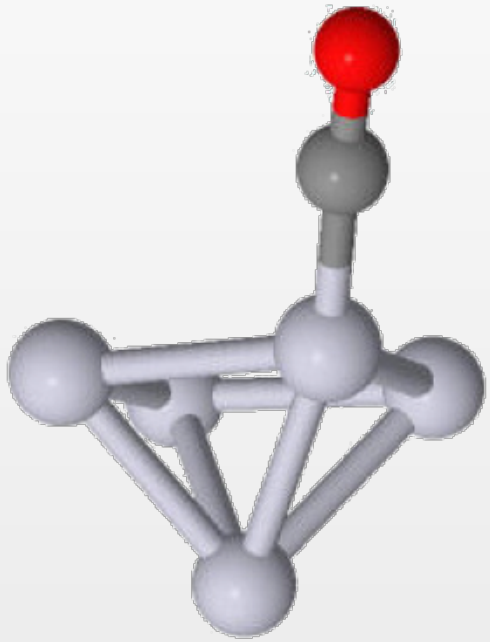
Global minima search of $CO-Pt_n^+$ and $CO-GePt_{n-1}^+$ (n = 5–9)



A. Ugartemendia, et al. *ChemPhysChem* 22, 1603 (2021)

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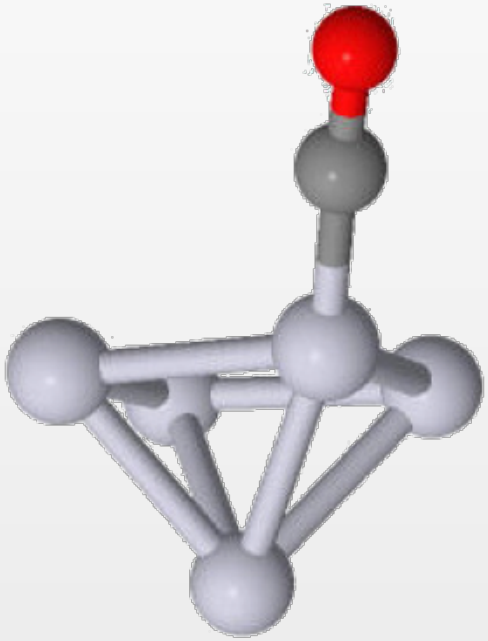

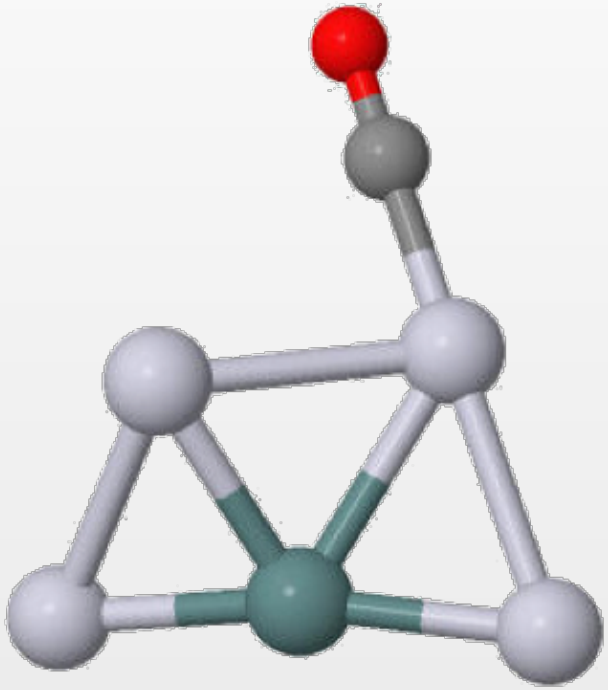

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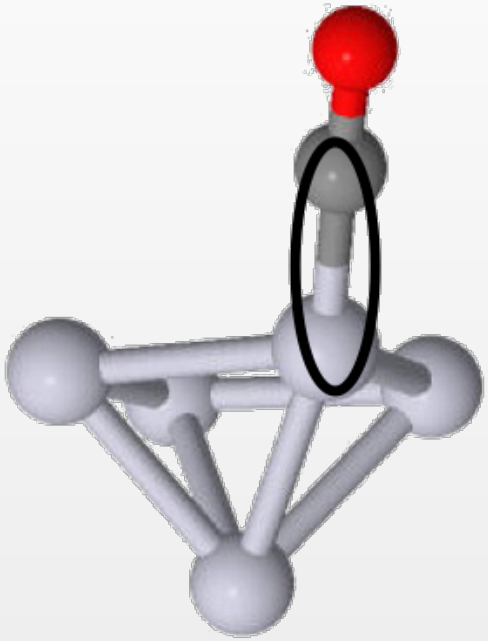

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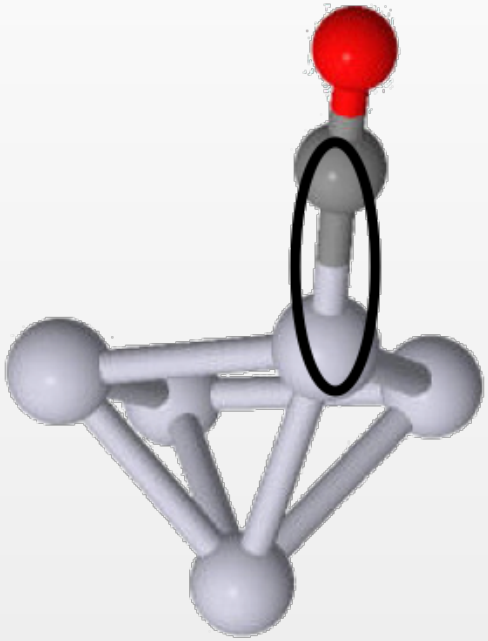
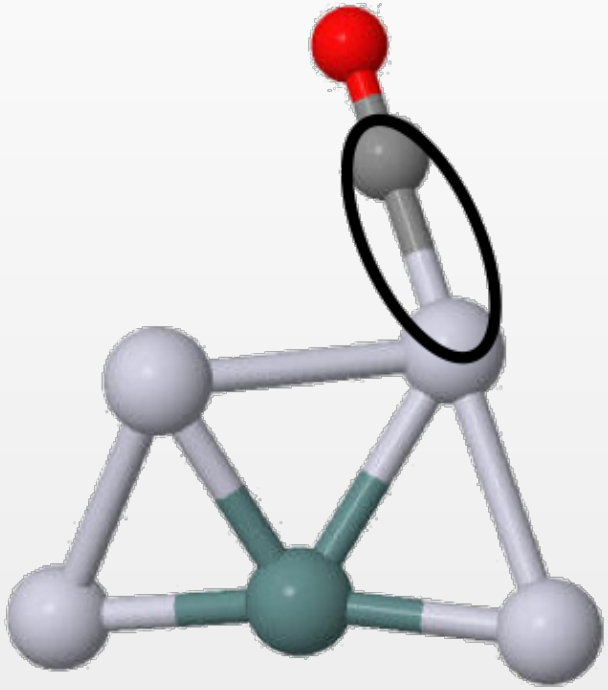
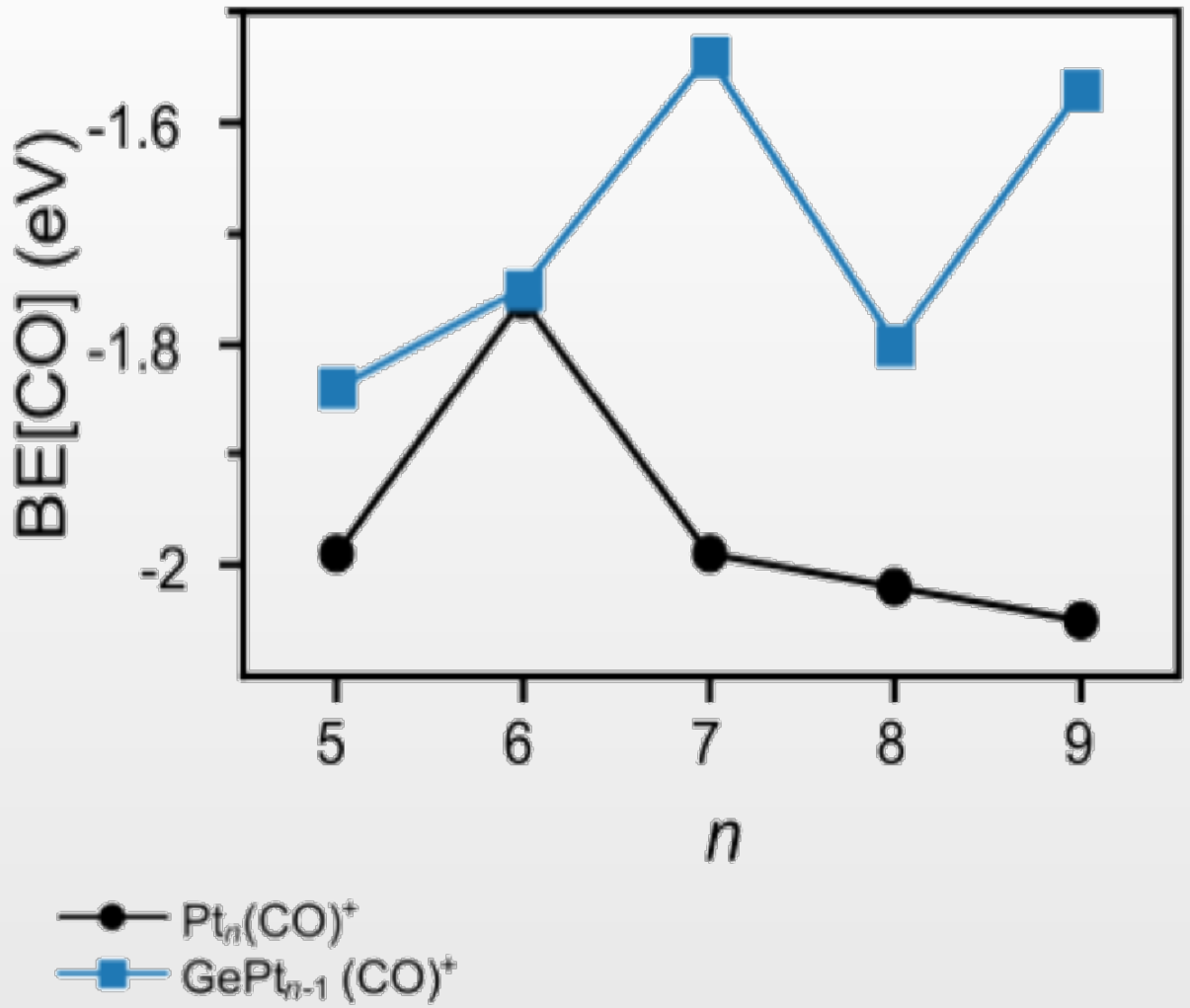




A. Ugartemendia, et al. *ChemPhysChem* 22, 1603 (2021)

Pt_n^+ and $GePt_n^+$ clusters

CO Binding Energy



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CO Binding Energy

Blyholder model:

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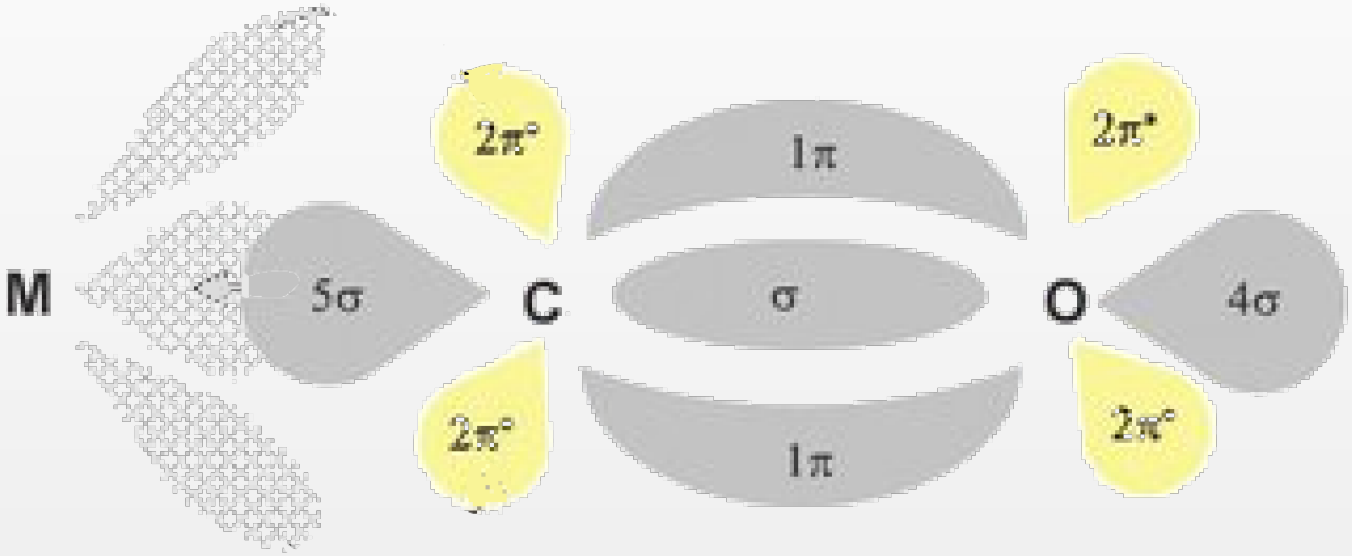

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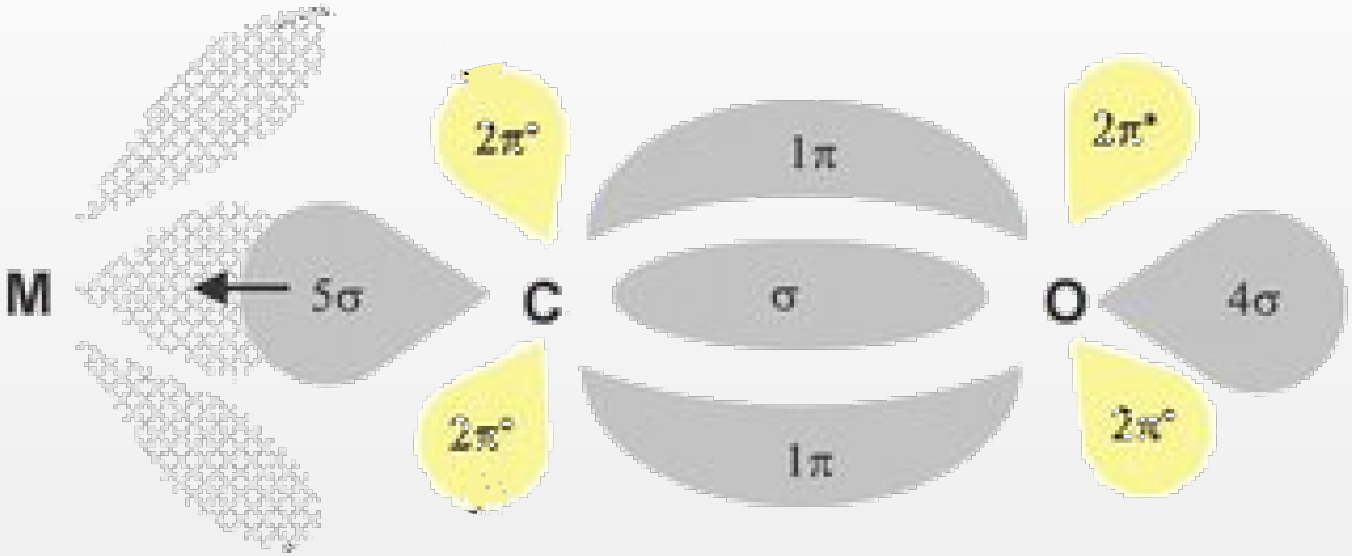
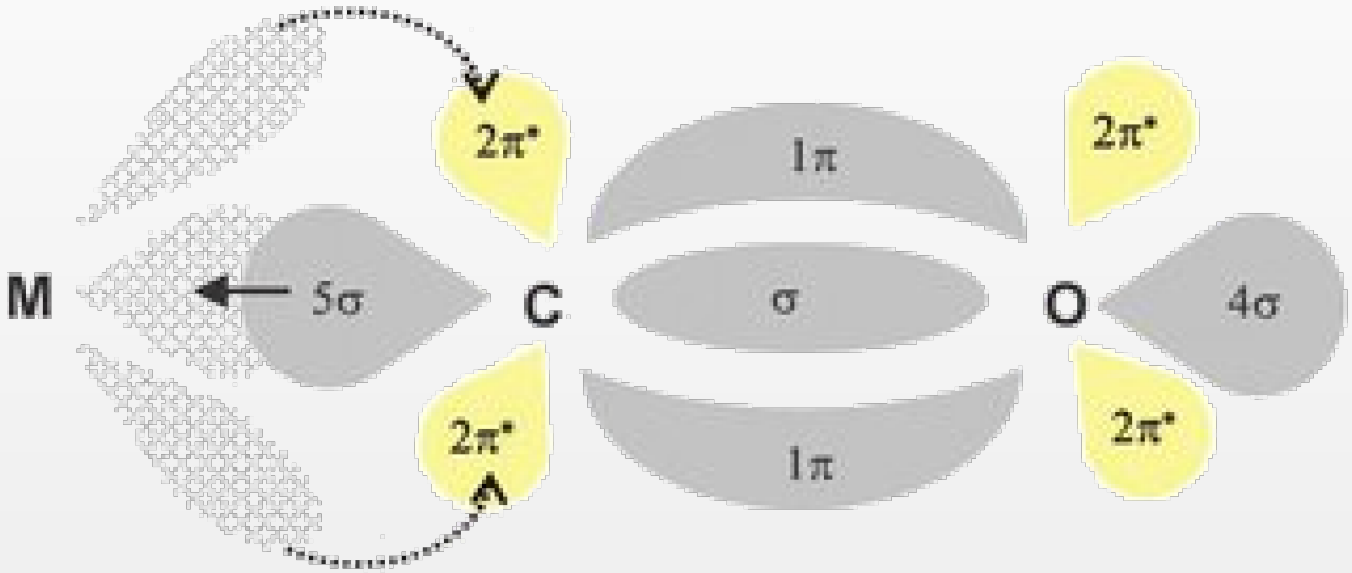


Donation:
CO 5σ (HOMO)
$\Downarrow$
Pt d_{z^2}

CO Binding Energy

Blyholder model:



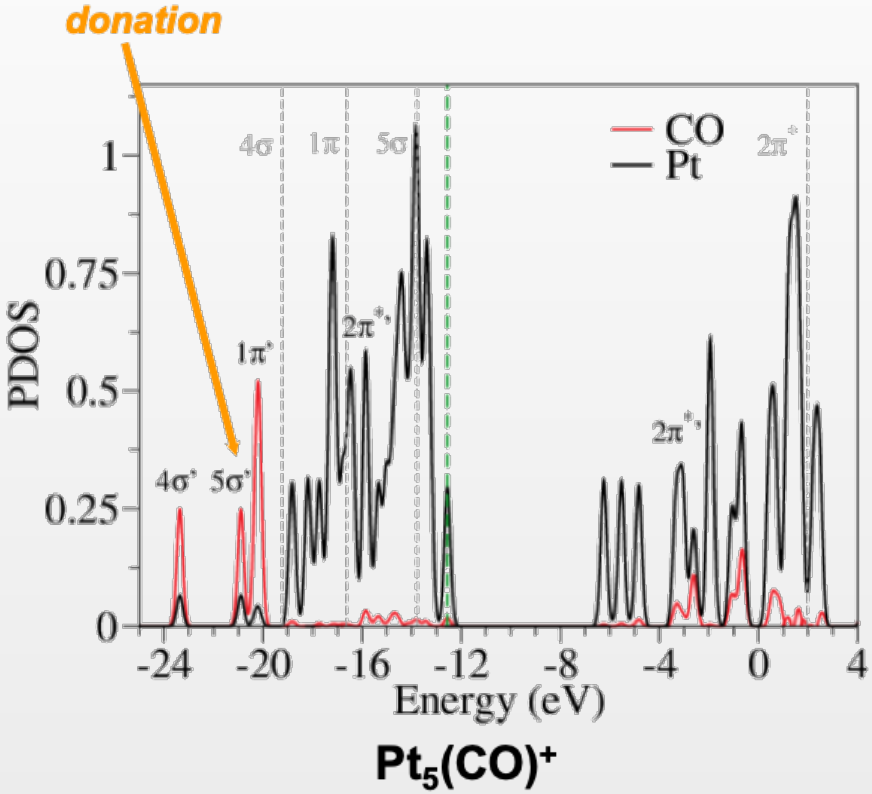
Donation:
CO 5σ (HOMO)
$\Downarrow$
Pt d_{z^2}

Back-Donation:
Pt $d_{xz,yz}$
$\Downarrow$
CO $2\pi^*$ (LUMO)

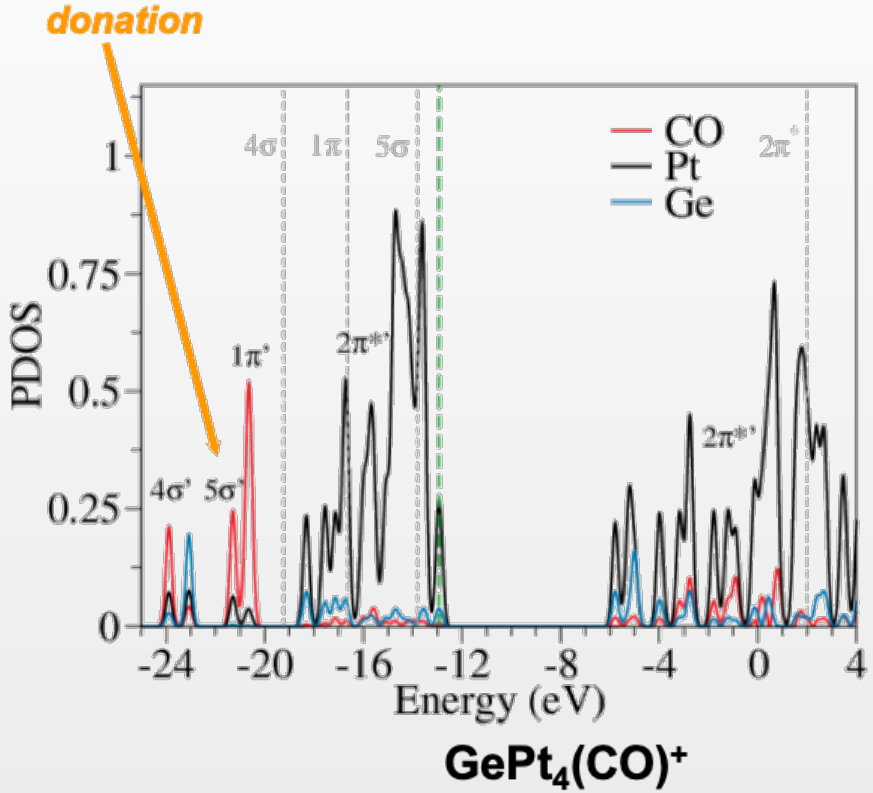
Projected Density of States

CO Binding Energy

Projected Density of States



$Pt_5(CO)^+$



$GePt_4(CO)^+$

CO Binding Energy

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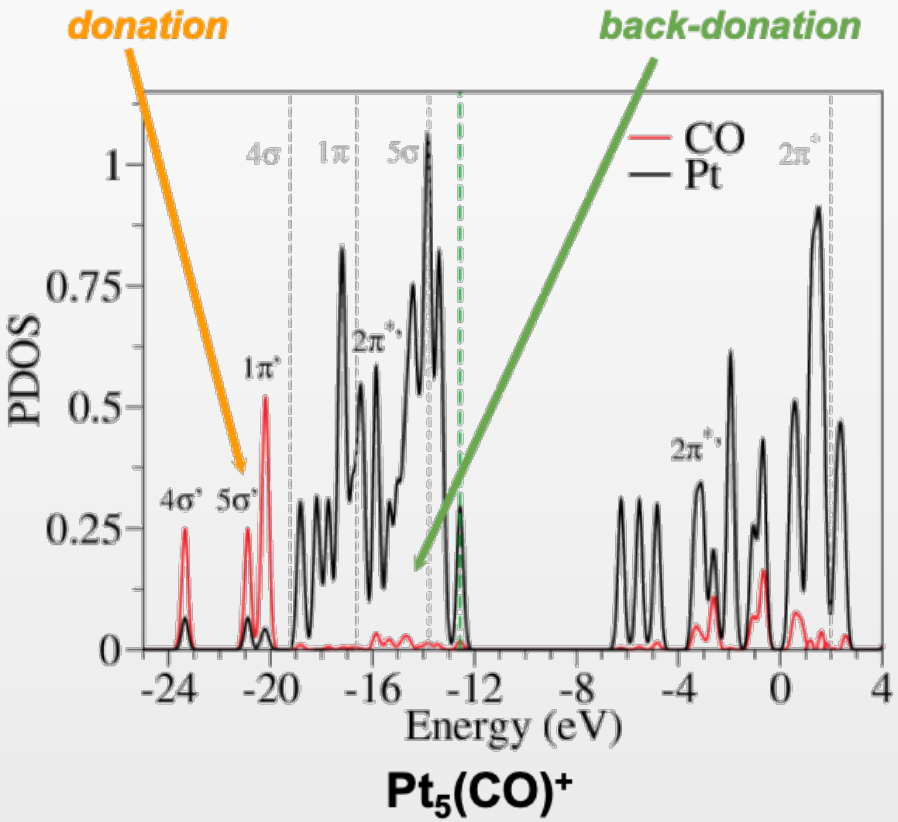

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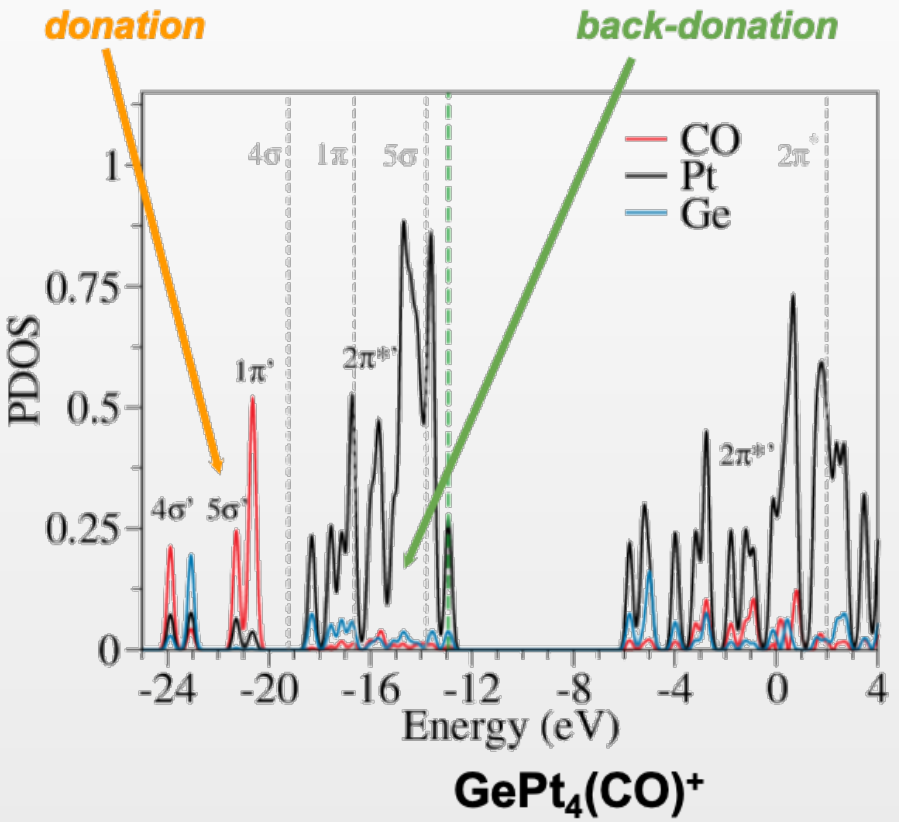

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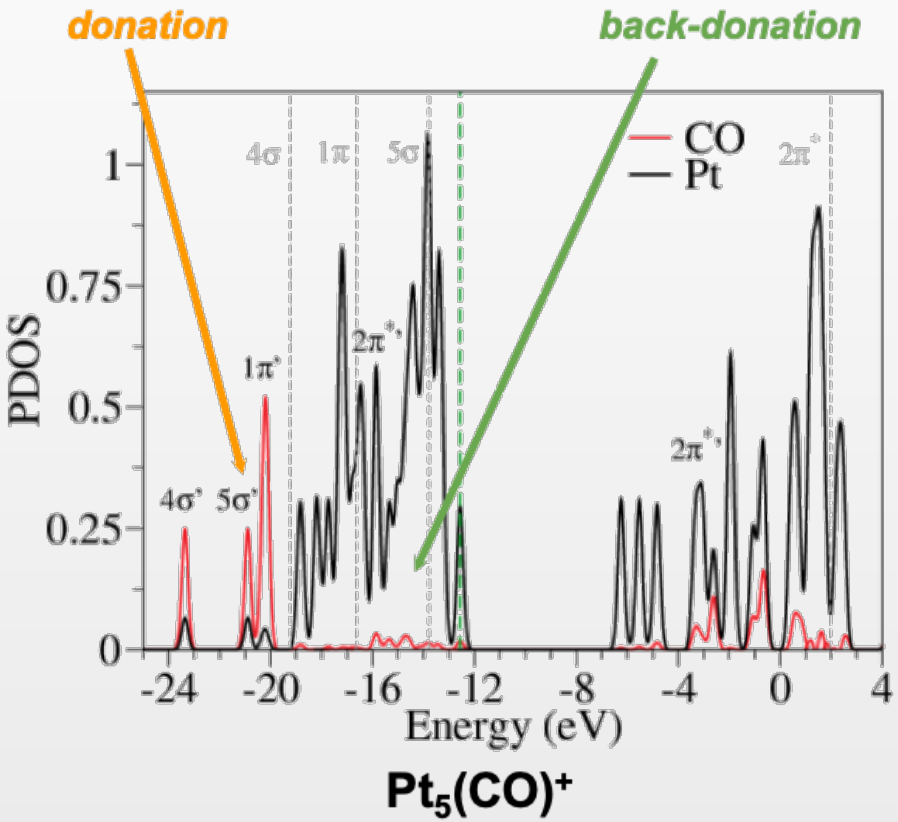
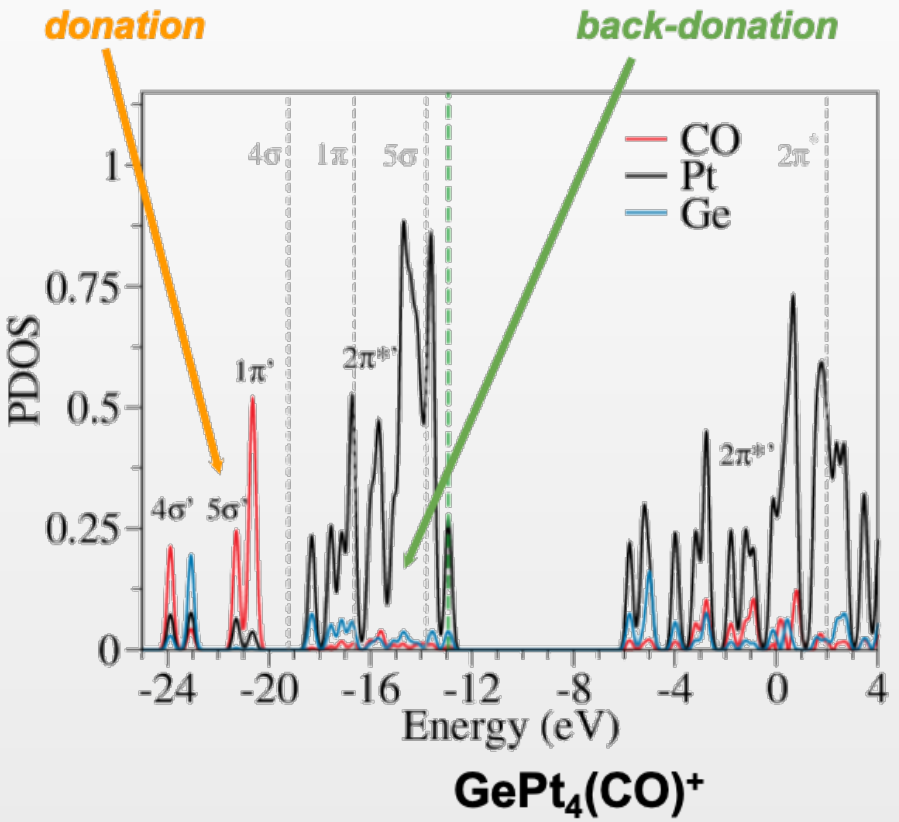
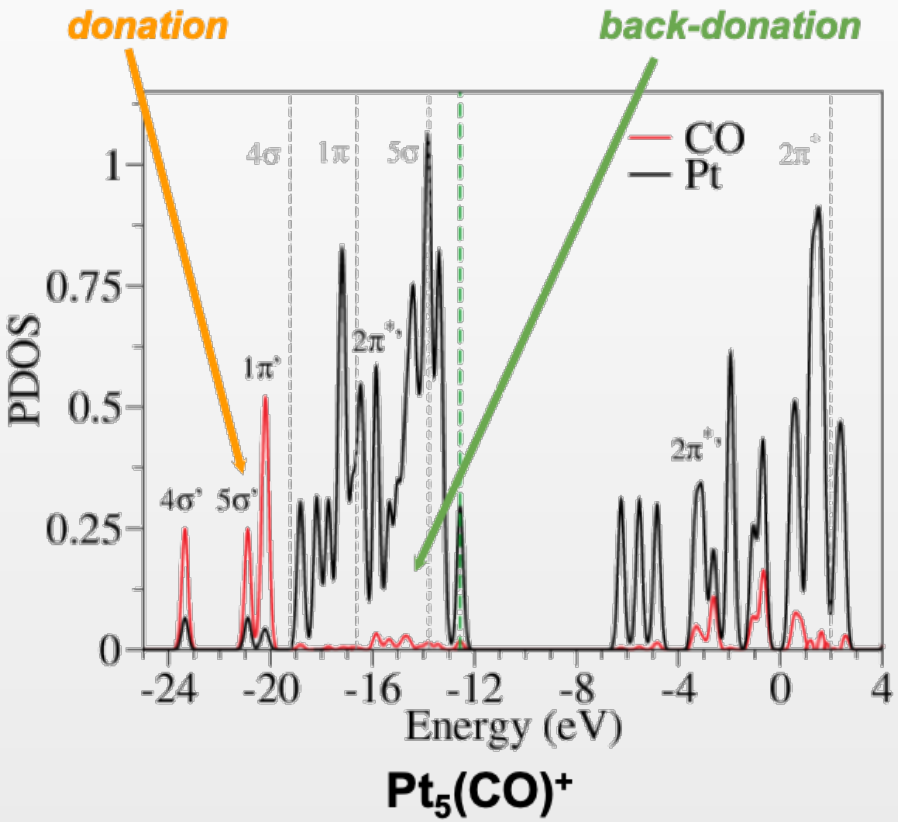


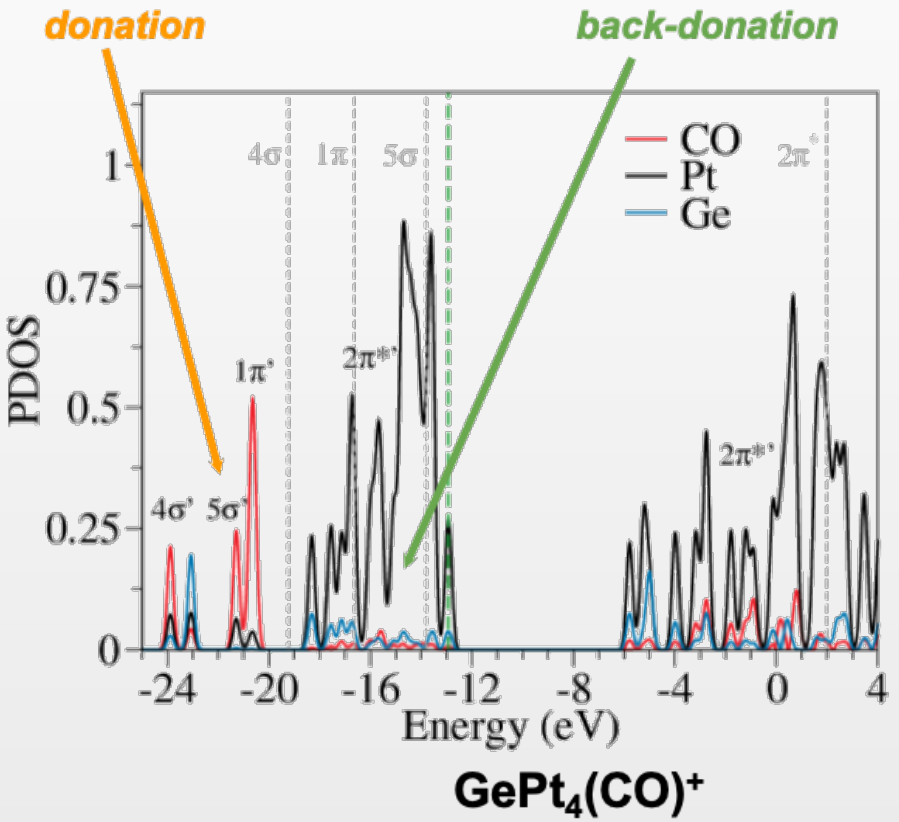


- Smaller back-donation

CO Binding Energy

Projected Density of States





- Smaller back-donation
- Availability of Pt *d* orbitals is reduced

CO Binding Energy

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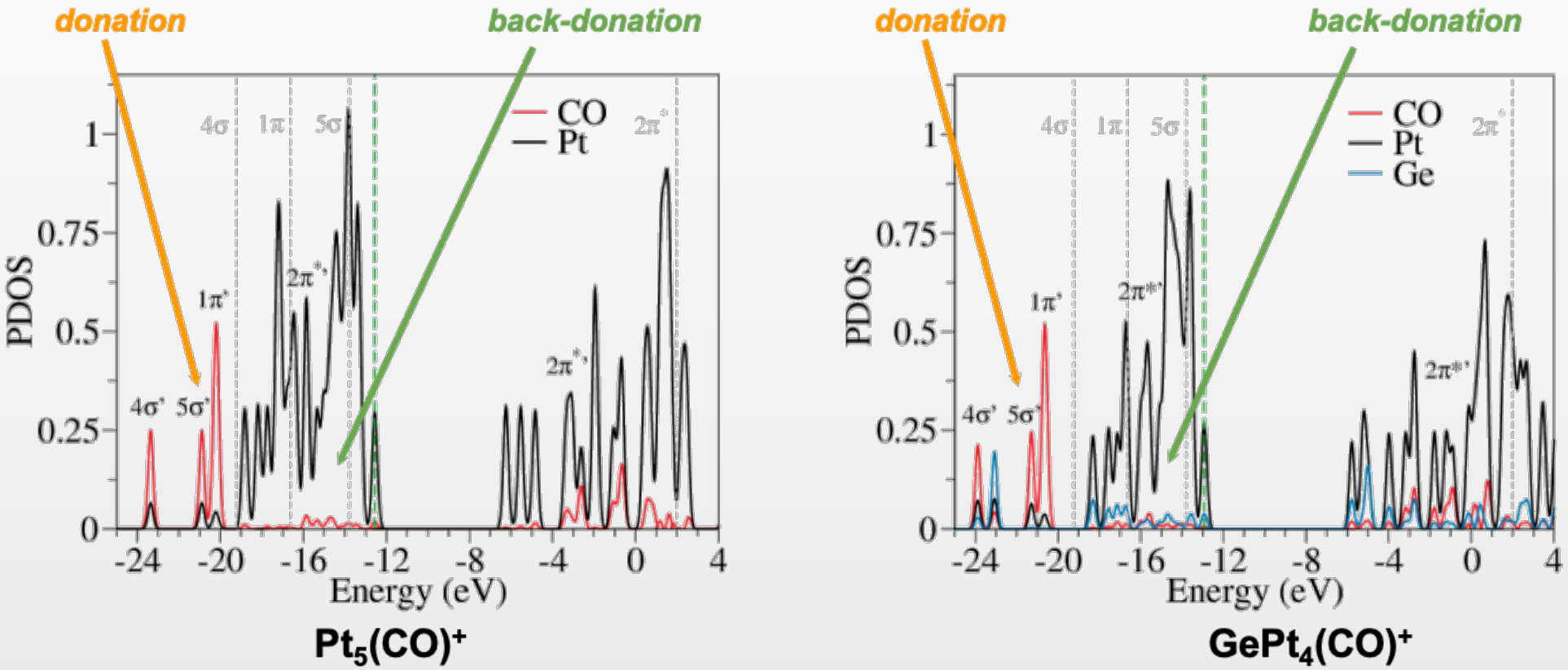
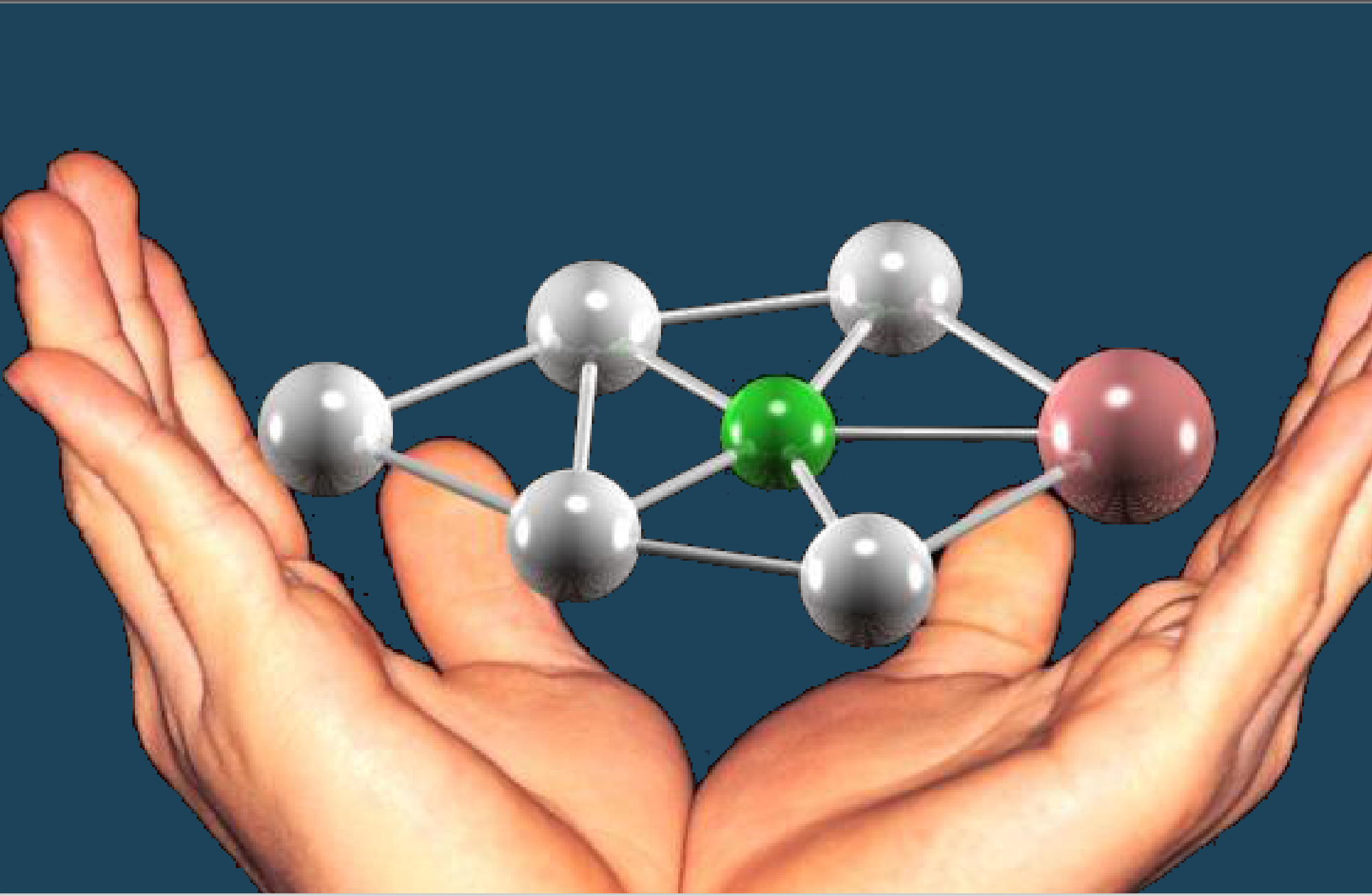


- Smaller back-donation
- Availability of Pt *d* orbitals is reduced
- NBO analysis: smaller $2\pi^*$ population in doped clusters

Playing with the dopant concentration



Playing with the dopant concentration

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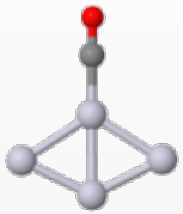

Pt_4 ... $PtGe_3$

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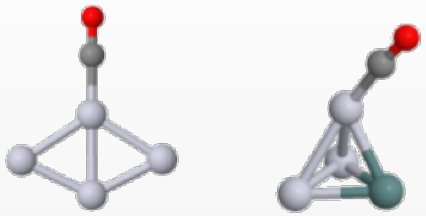

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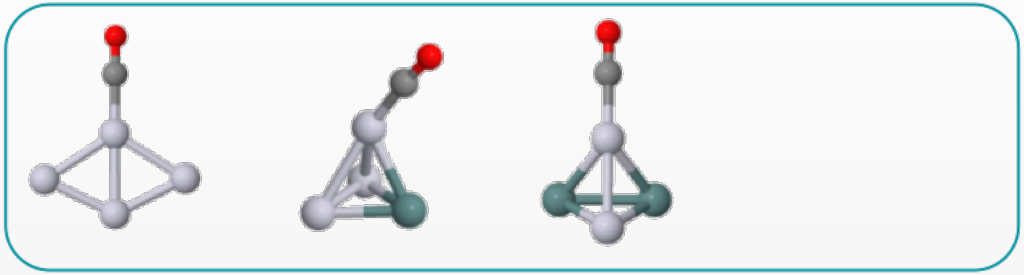

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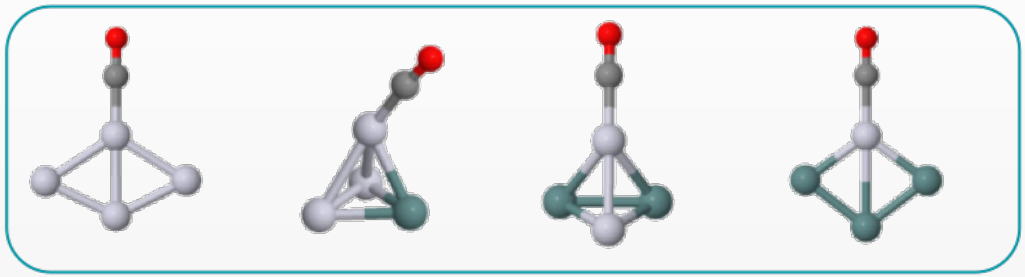

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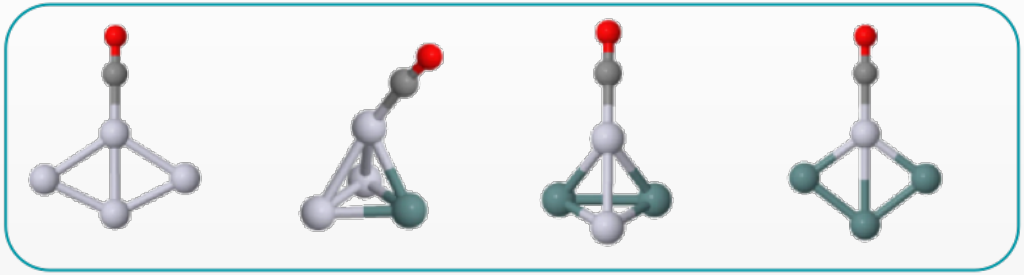

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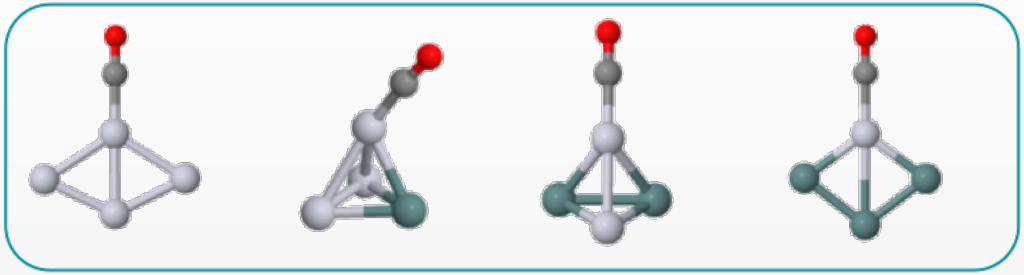
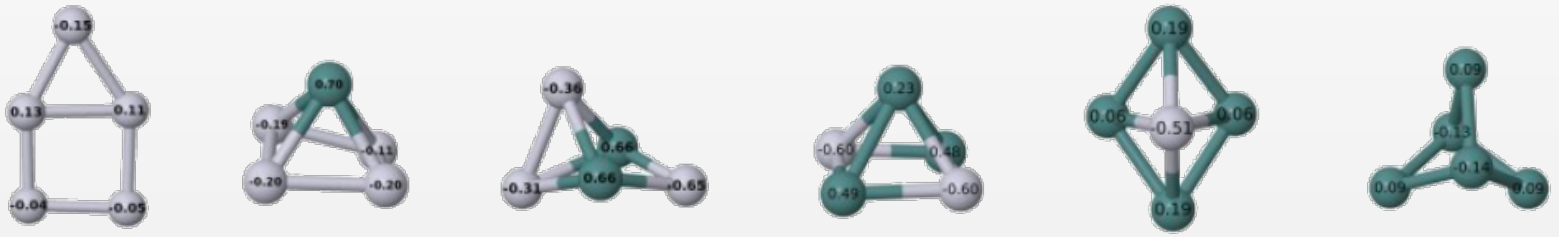
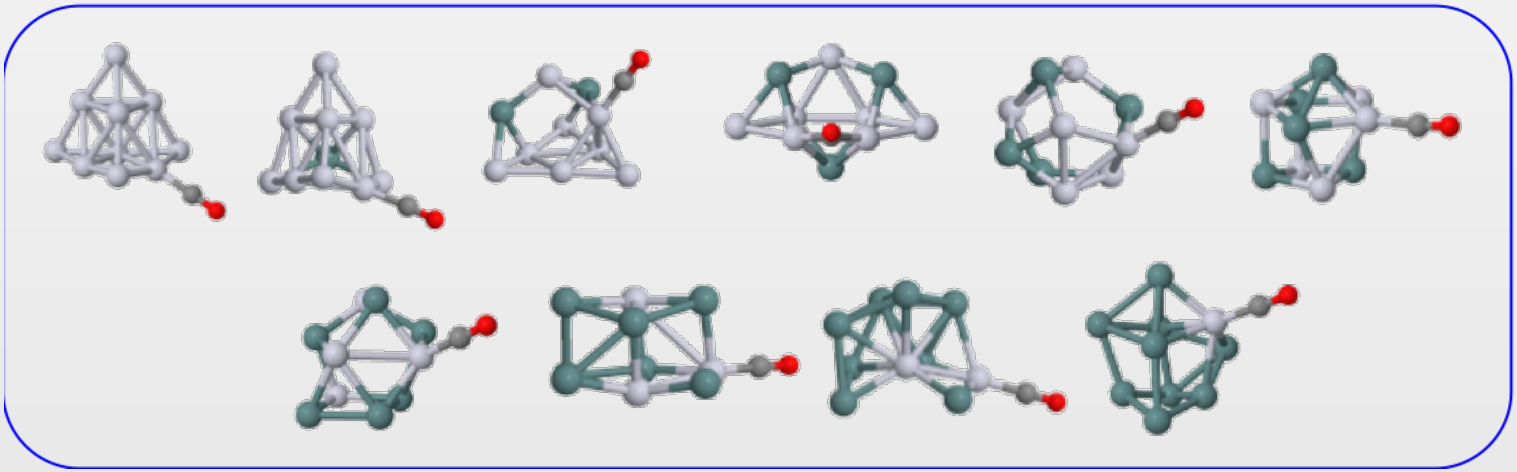


Pt_4 ... $PtGe_3$

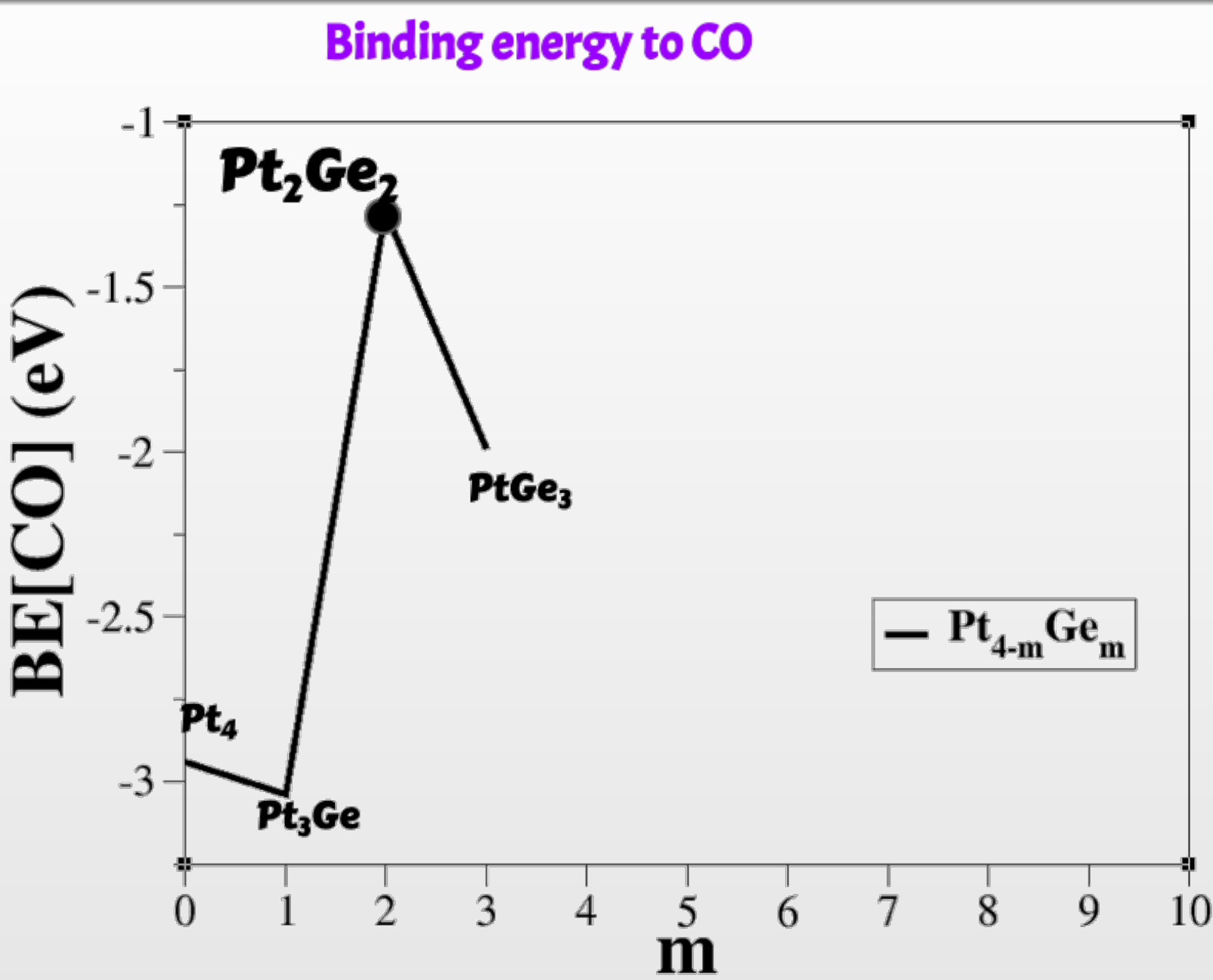




Pt_{10} ... $PtGe_9$

A. Ugartemendia, et al. *J. Chem. Phys.* 156, 174301, (2022)

Playing with the dopant concentration



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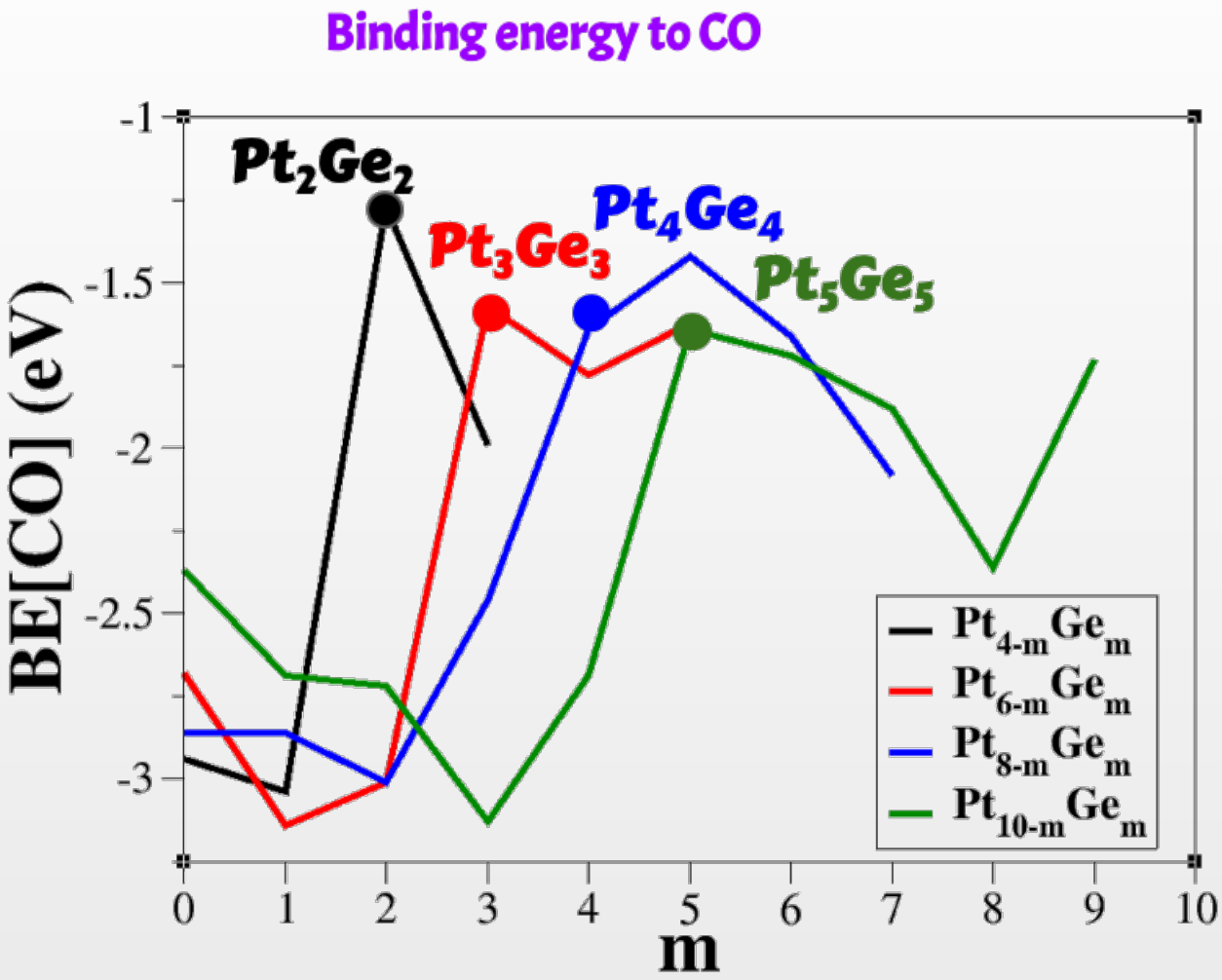
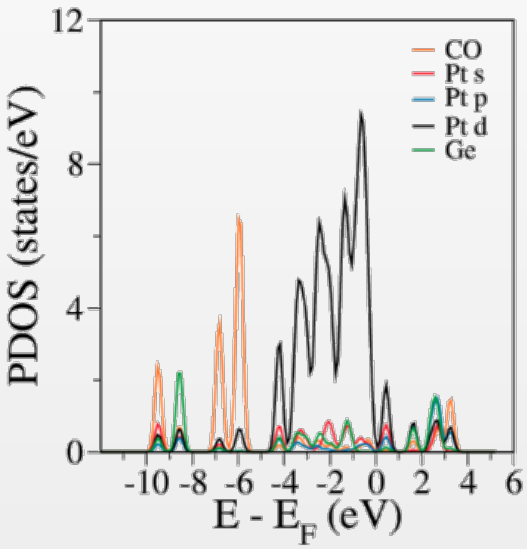
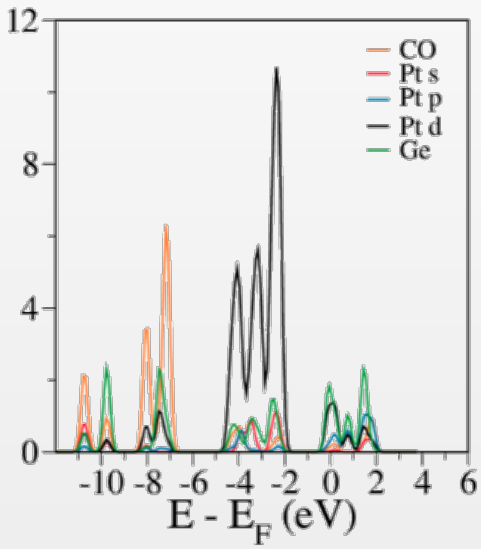


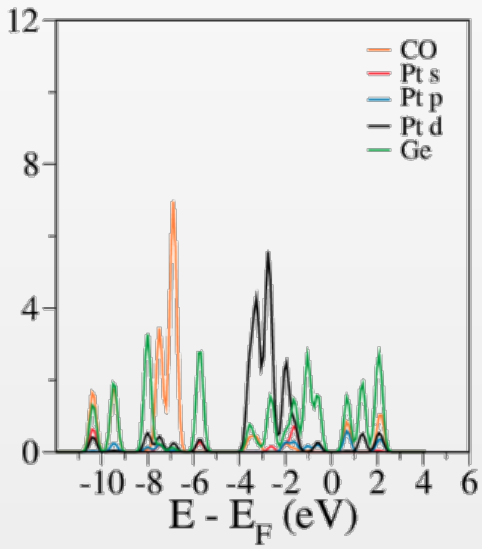
- Equimolar Pt_nGe_n alloys, minimizes CO affinity

Playing with the dopant concentration

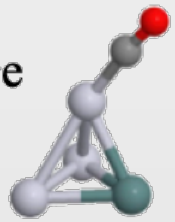
Pt-rich ***Equimolar*** ***Ge-rich***



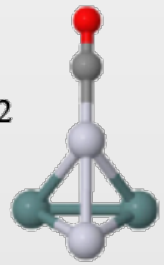




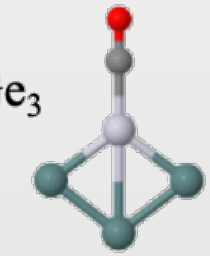
$CO\text{-}Pt_3Ge$



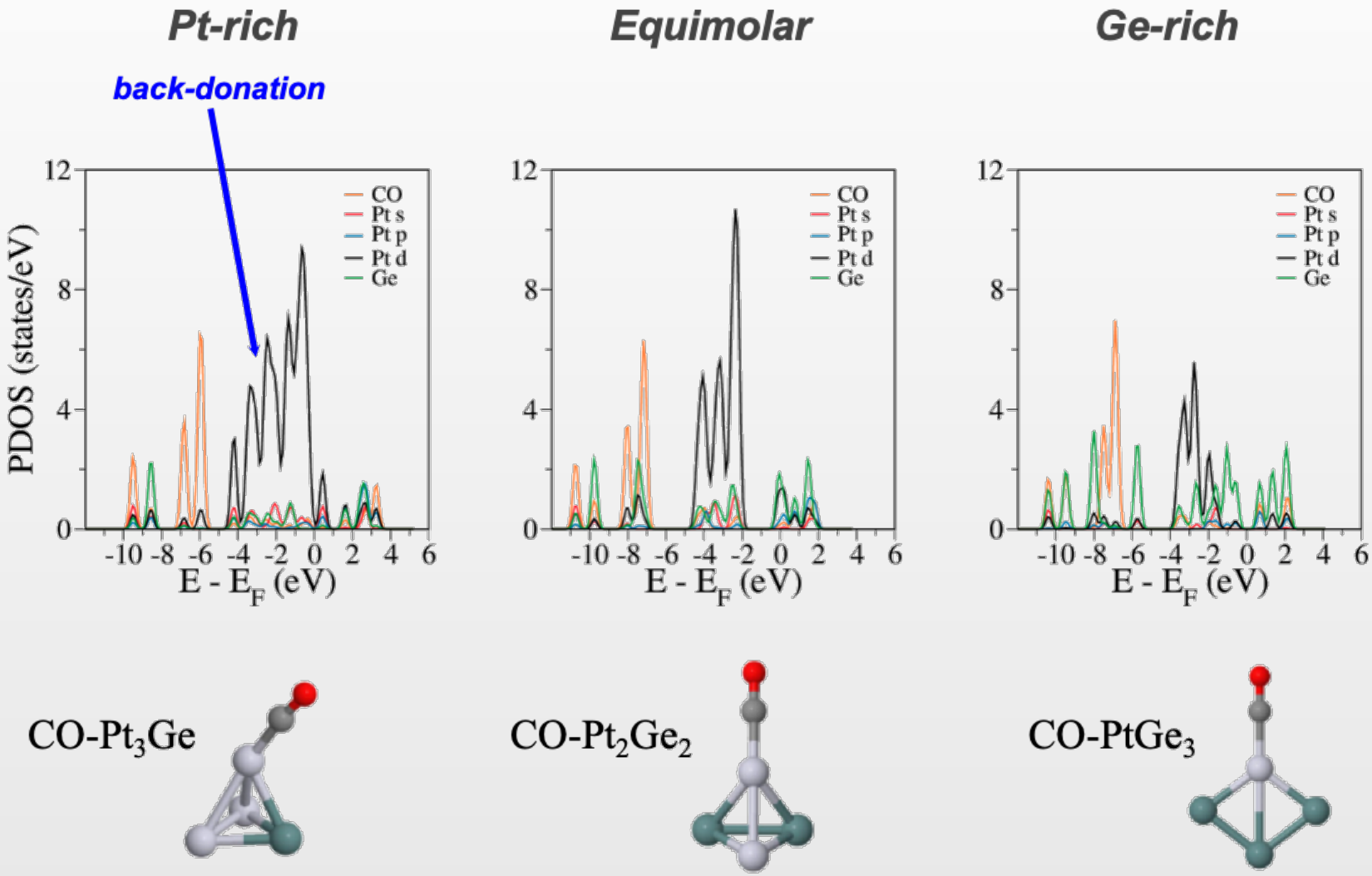
$CO\text{-}Pt_2Ge_2$



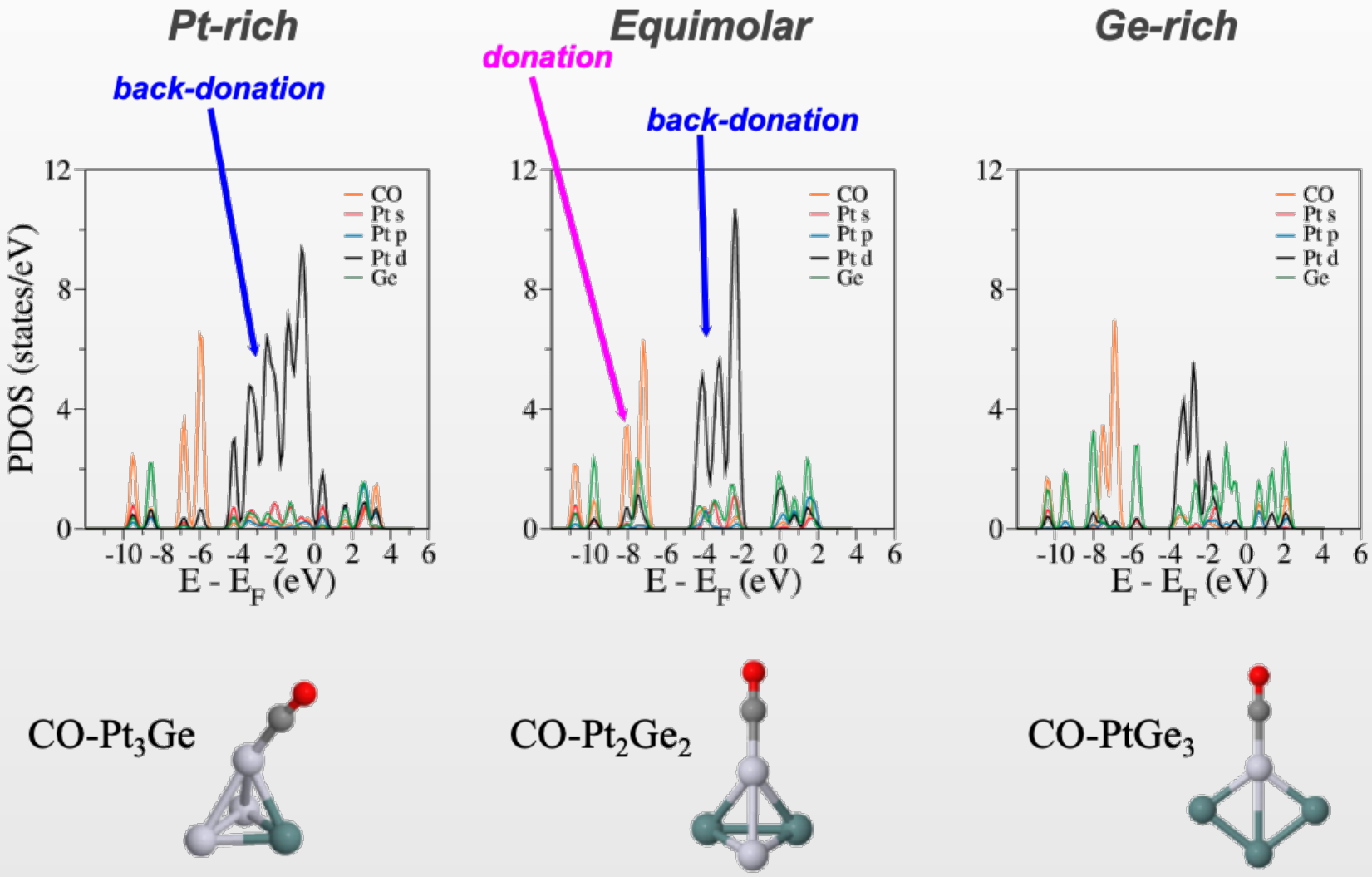
$CO\text{-}PtGe_3$



Playing with the dopant concentration



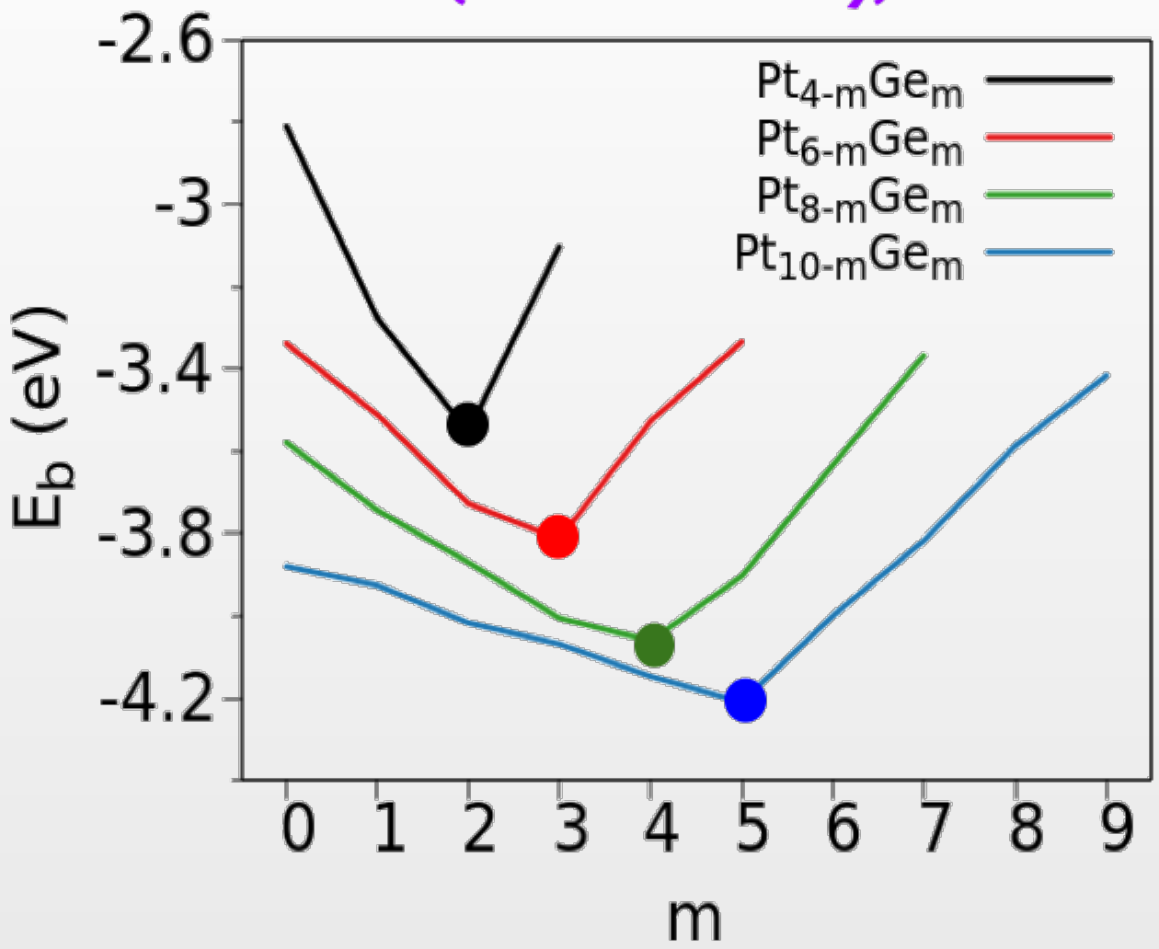
Playing with the dopant concentration



Cluster Stability

Cluster Stability

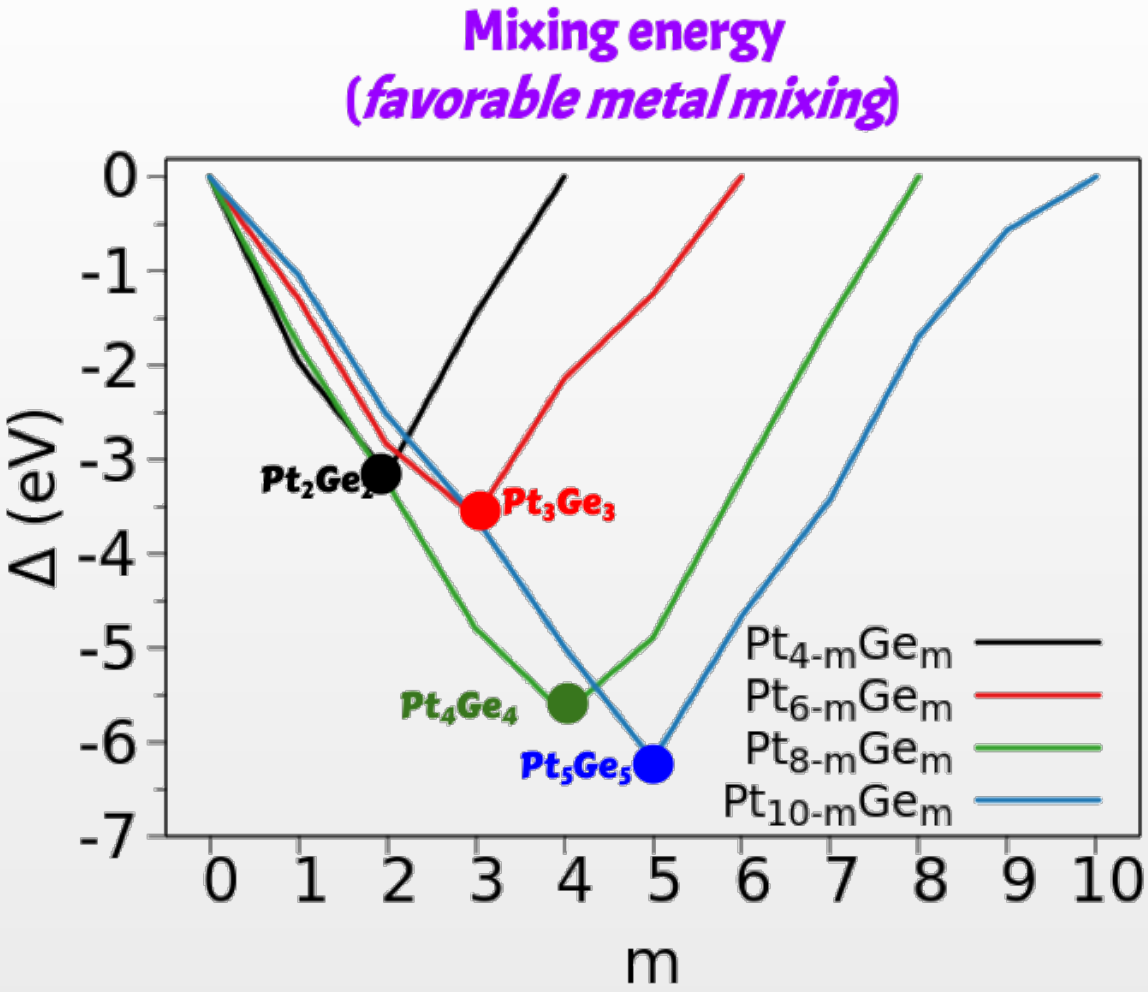
Intracluster binding energy
(*intrinsic stability*)



$$E_b = \frac{1}{N}[E(Pt_nGe_m) - nE(Pt) - mE(Ge)]; N = n + m$$

Ge/Pt Mixing

Ge/Pt Mixing



$$\Delta = E(Pt_nGe_m) - n\frac{E(Pt_N)}{N} - m\frac{E(Ge_N)}{N} \; ; \mathrm{N=n+m}$$

What makes equimolar clusters special?

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- Equimolar clusters maximize number of Pt-Ge bonds

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$\Downarrow$

CO poisoning should be reduced

What makes equimolar clusters special?

Adaptive Natural Density Partitioning (AdNDP):

What makes equimolar clusters special?

Adaptive Natural Density Partitioning (AdNDP): Description of the chemical bonding combining the simplicity of Lewis theory with the flexibility and generality of Molecular Orbital theory.

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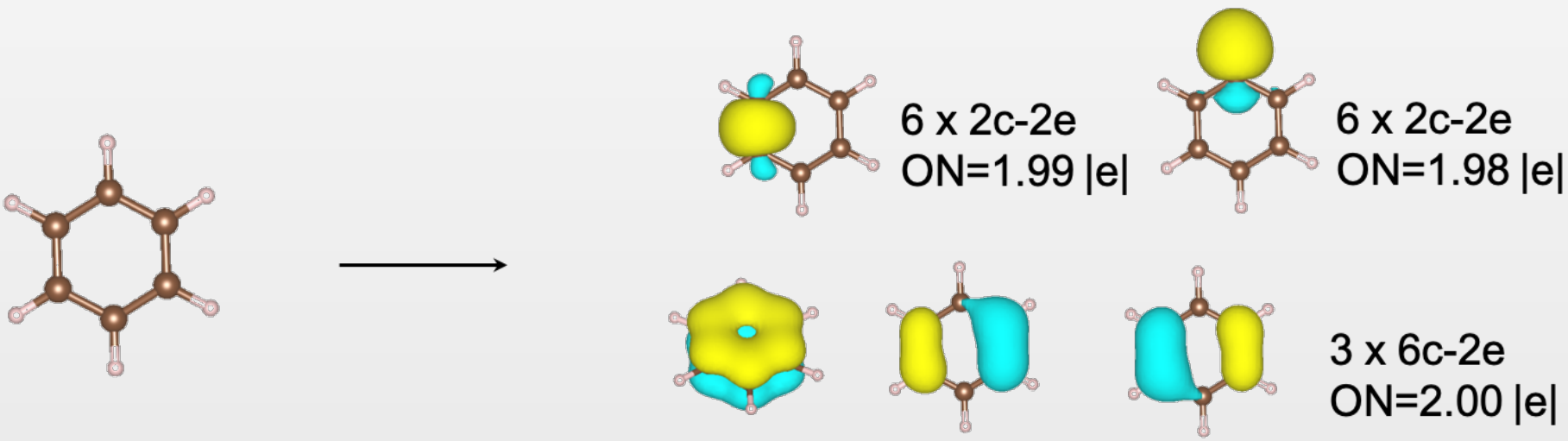

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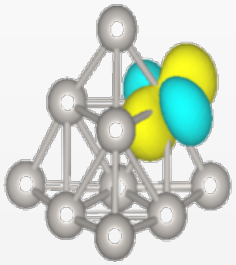
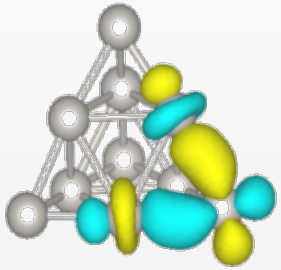
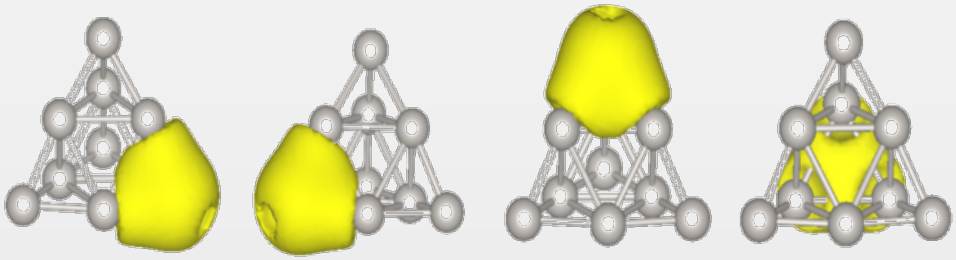
Pt_{10}



30 x **1c-2e**
ON=1.83 |e|



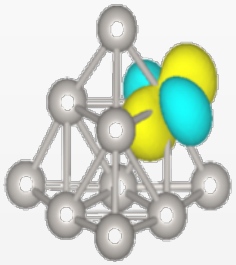
20 x **3c-2e**
ON=1.97 |e|



4 x **4c-2e**
ON=1.93
|e|

What makes equimolar clusters special?

Pt_{10}



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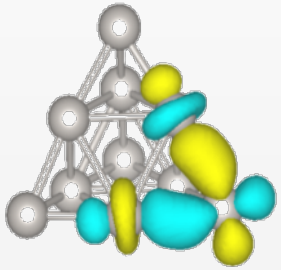

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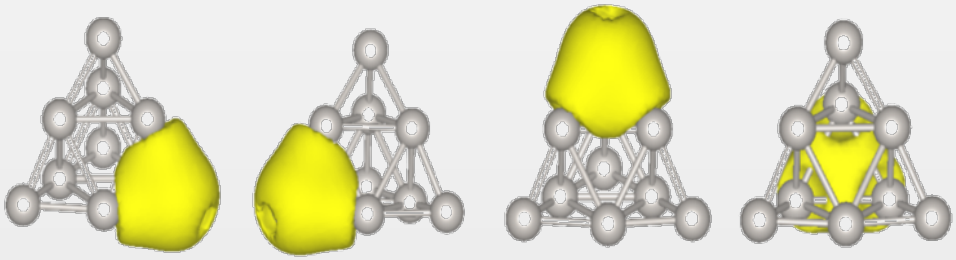
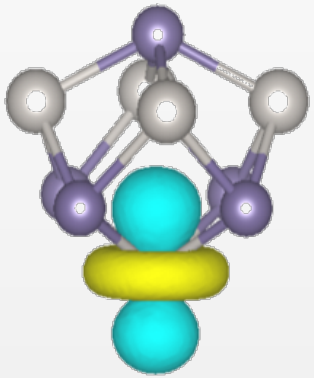
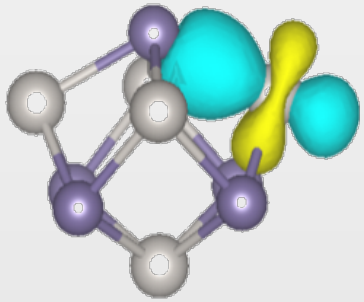


4 x **4c-2e**
ON=1.93
|e|

Pt_5Ge_5

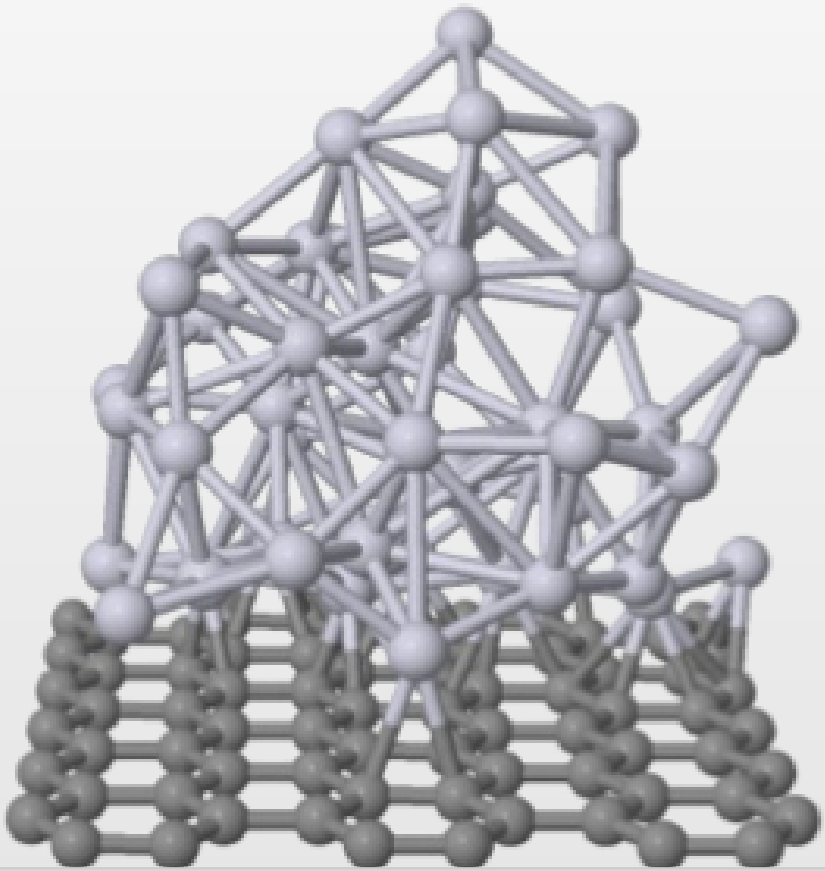


15 x **1c-2e**
ON=1.84
|e|



20 x **2c-2e**
ON=1.86 |e|

What about Catalytical Activity?



ANODE: Pt/C

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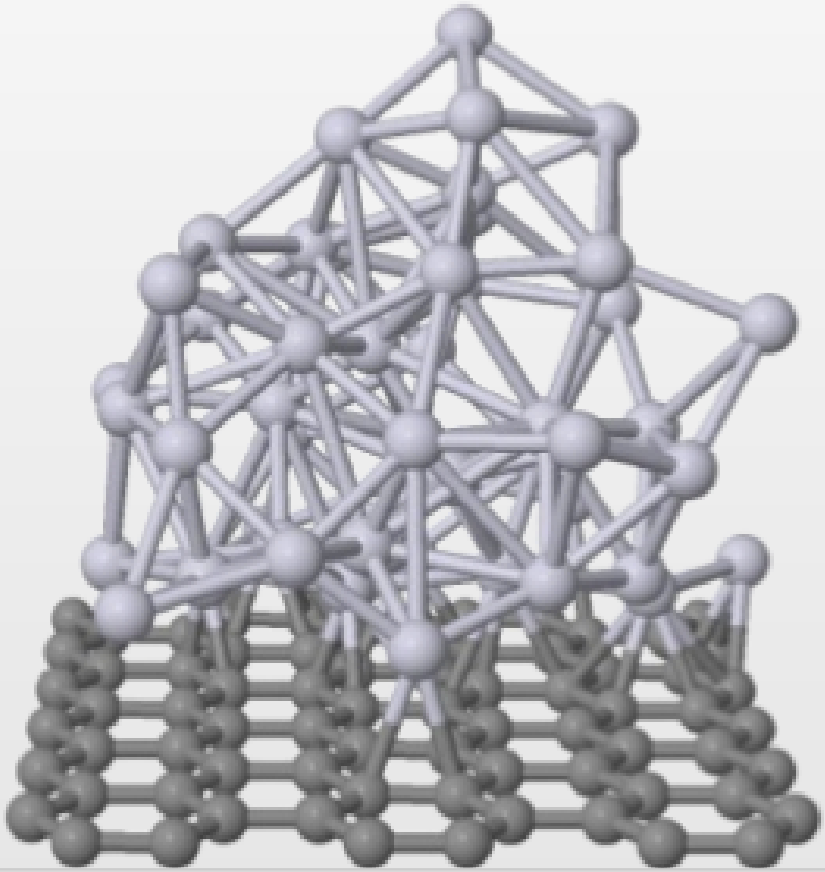

ANODE: Pt/C

What about Catalytic Activity?

First step in Hydrogen Oxidation

Reaction: $H_2 \longrightarrow 2\,H_{ad}$

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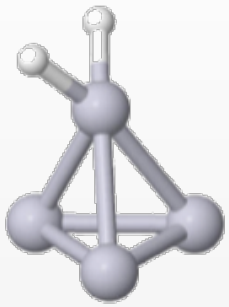

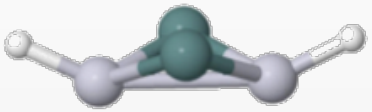

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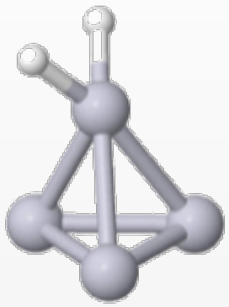

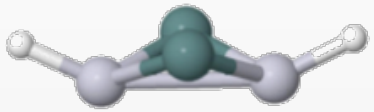

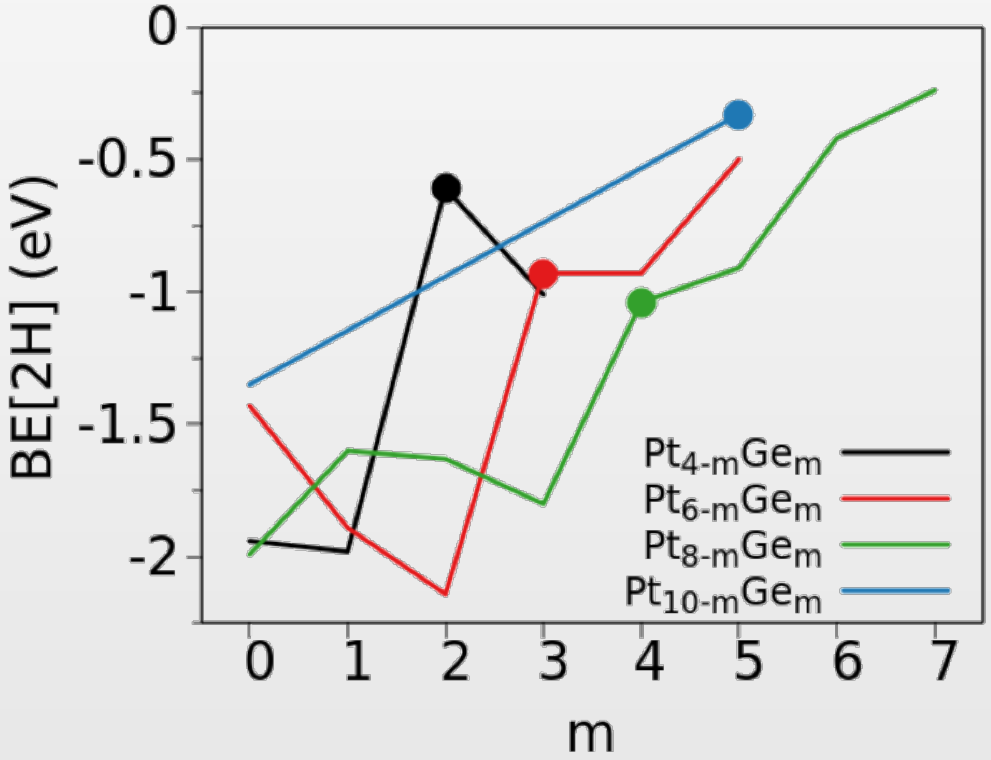

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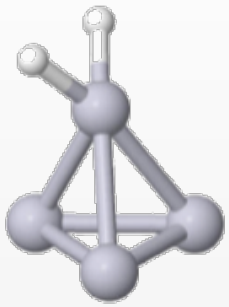
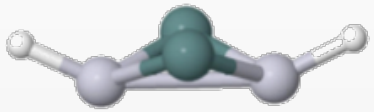
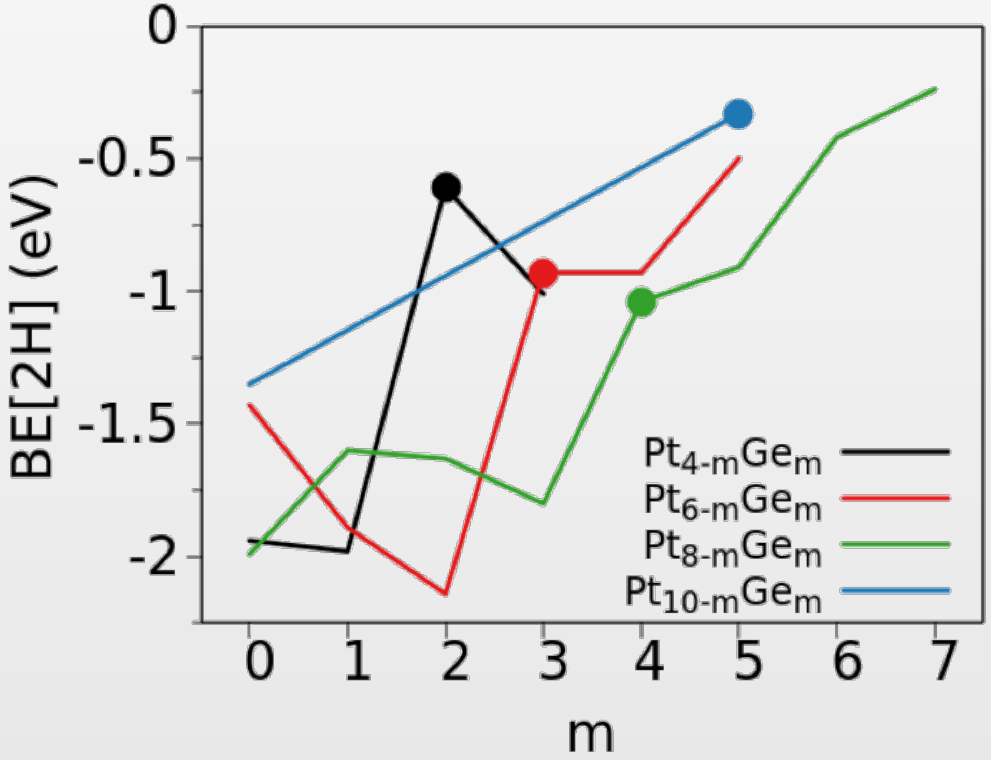


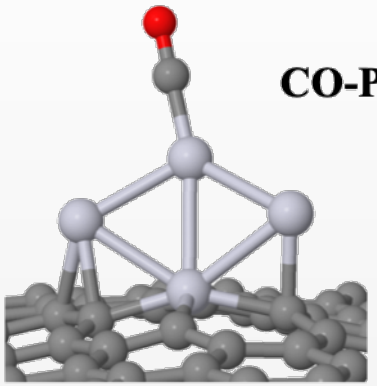


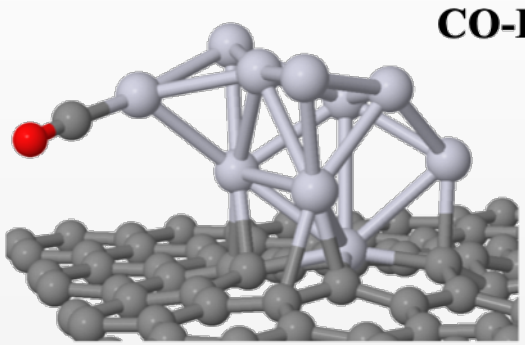


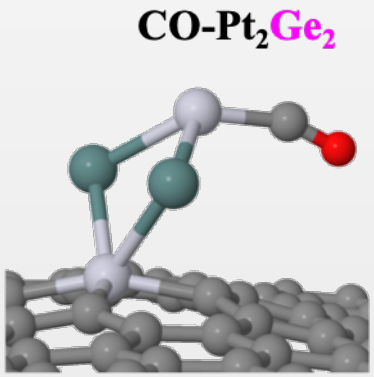
Larger Ge content $\rightarrow$ BE[2H] $\downarrow$

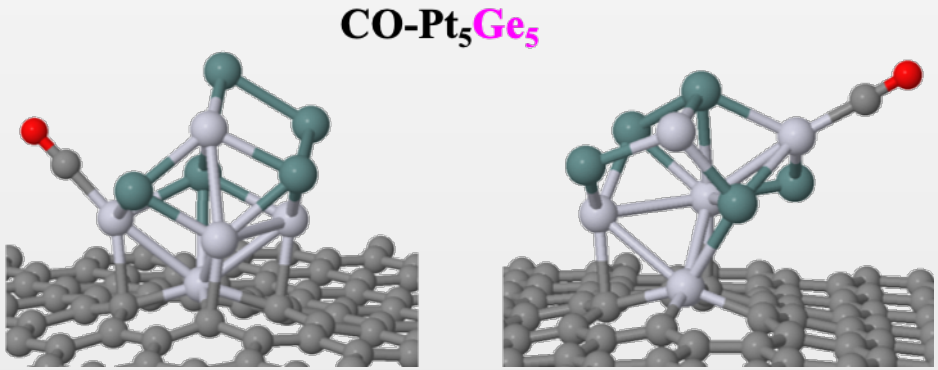
PtGe on defected graphene

PtGe on defected graphene

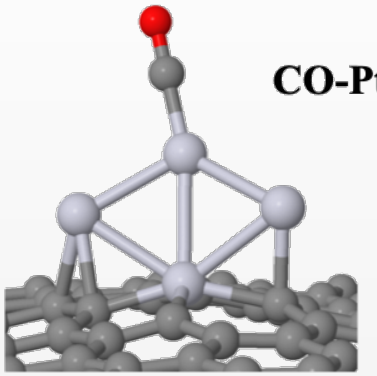


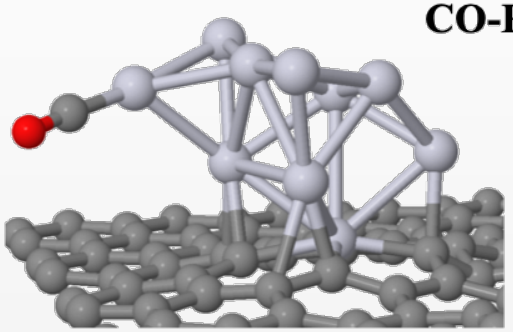






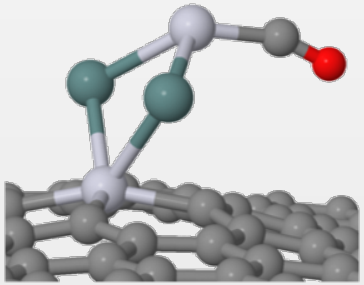
PtGe on defected graphene

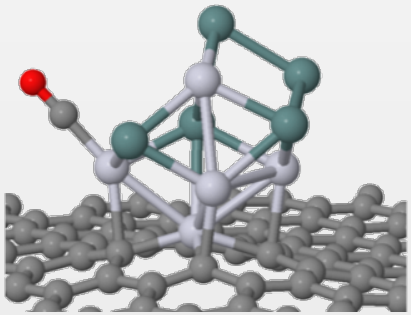


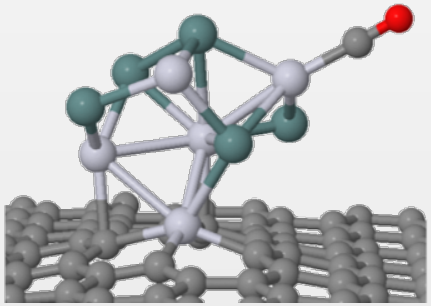


BE(CO) reduced by > 1.1 eV

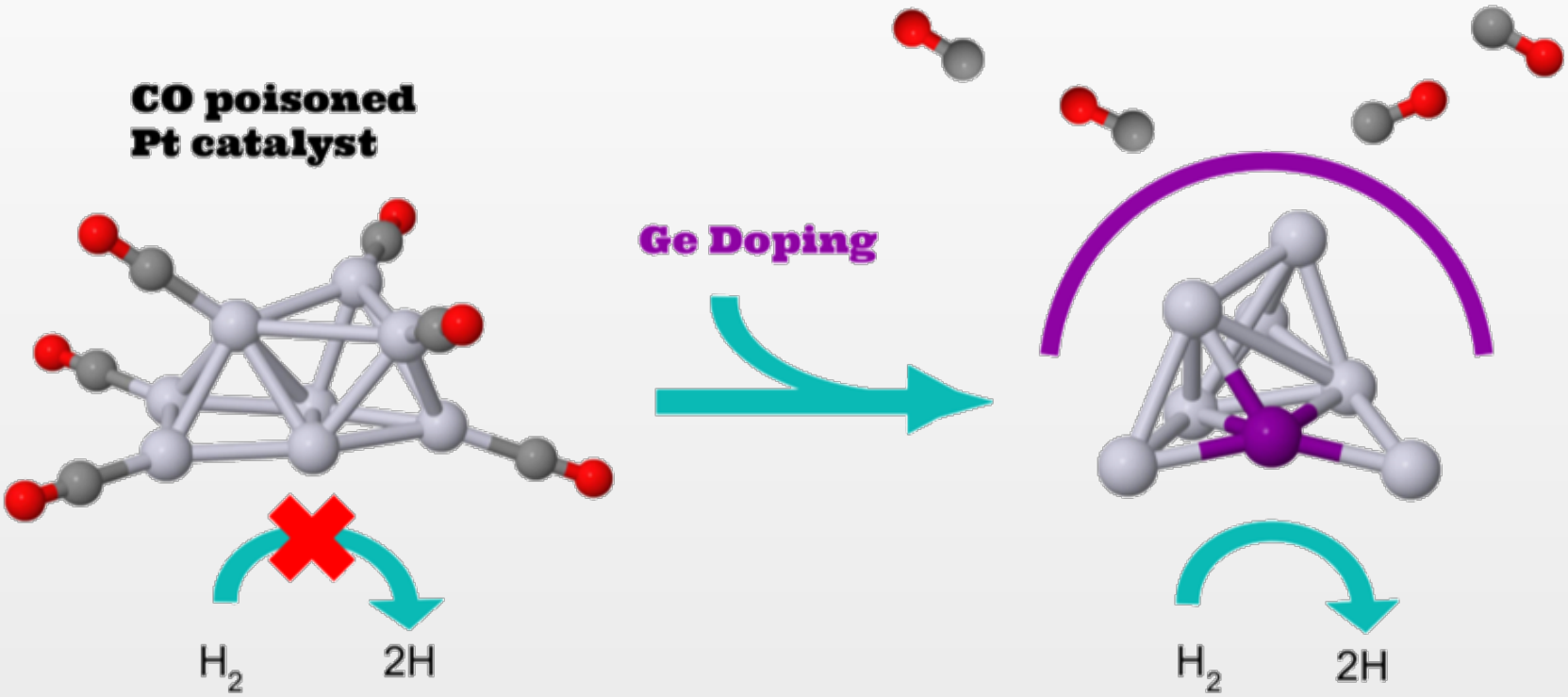
BE(CO) reduced by > 1.6 eV



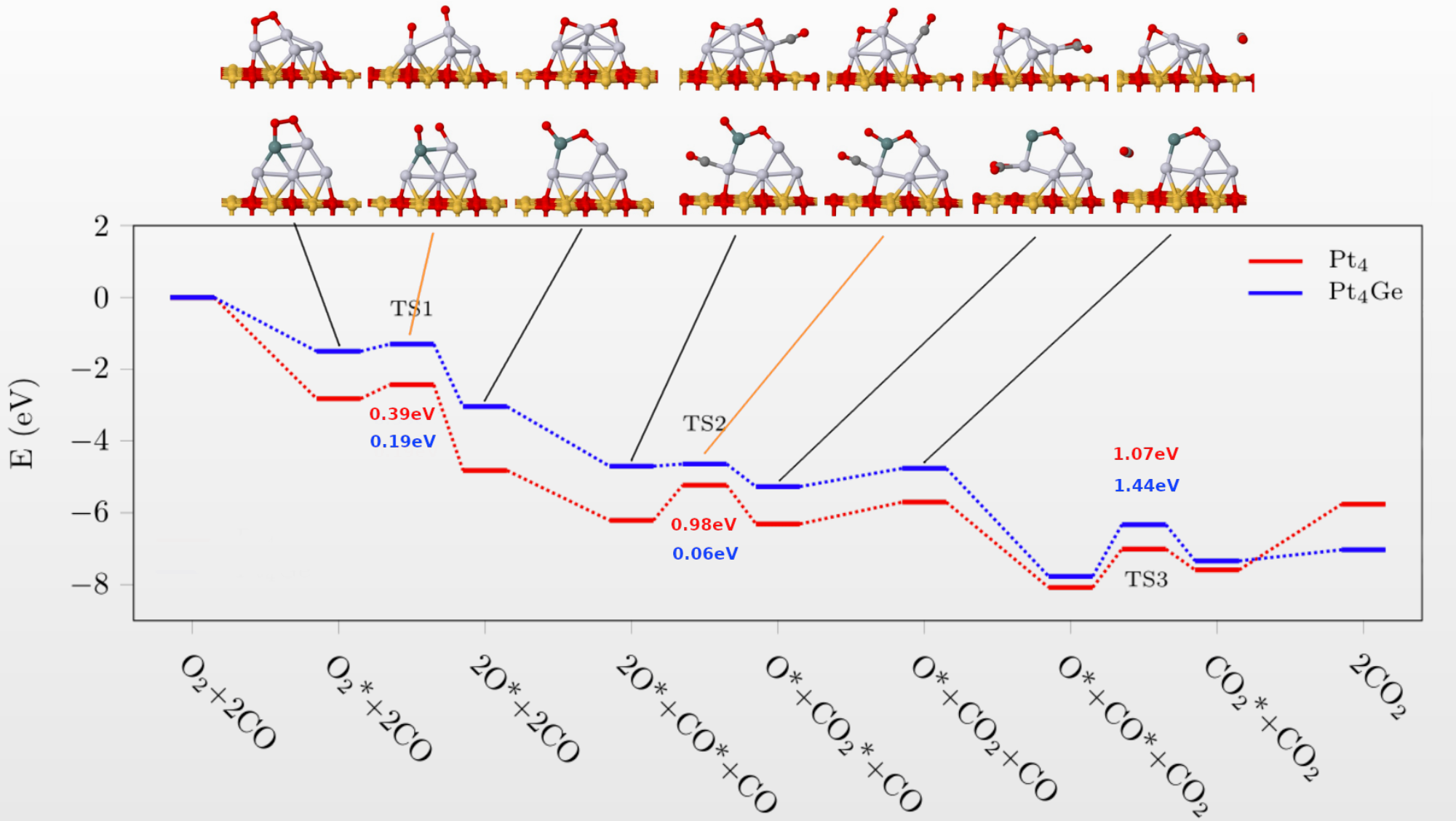




Conclusions



Further Work



Calculations Details

Global minima search of $CO-Pt_n^+$ / $CO-GePt_{n-1}^+$ (n = 5–9)

- Turbomole (DODO)
- TPSSH-D3/def2-TZVP

- PGOPT/VASP PBE-D3
- cutoff: 450 eV
- SCF convergence 10^{-6} eV.
- The unit cell 15×15×25Å

- Final Energies and all analysis with LC- PBEh/def2-TZVP using GAUSSIAN.

Calculations run on local computers

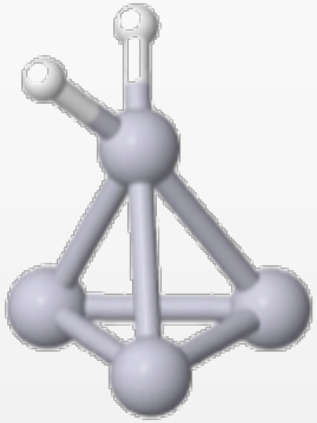
Calculations Details

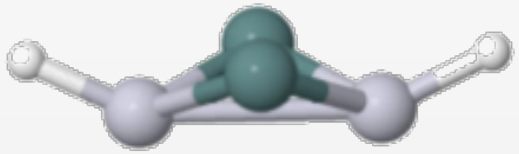
- PGOPT/VASP PBE-D3
- cutoff: 450 eV
- (SCF) convergence 10^{-6} eV.
- The unit cell 15×15×25Å

Largest clusters (around 10x800 structures) in BSC (48 cores 24 hours)

Calculations Details

First step in Hydrogen Oxidation Reaction: $H_2 \longrightarrow 2\,H_{ad}$

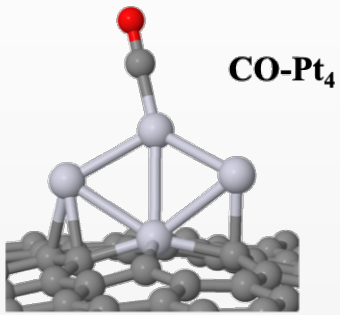


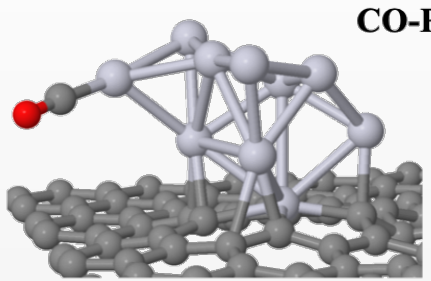


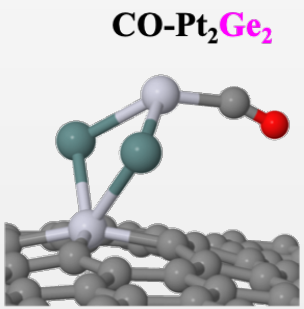
- PGOPT/VASP PBE-D3
- cutoff: 450 eV
- (SCF) convergence 10^{-6} eV.
- The unit cell :15×15×25Å
- Climbing image nudged elastic band (CI-NEB)

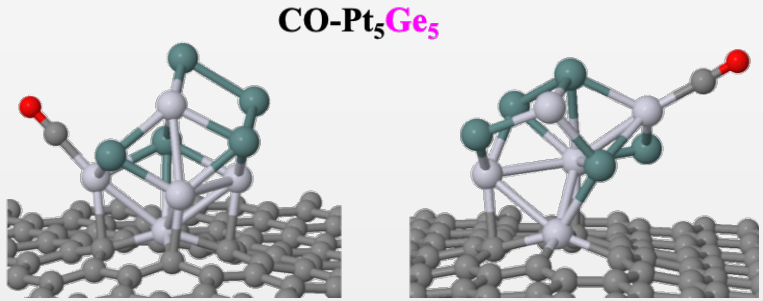
Largest clusters (around 10x800 structures) in BSC (48 cores 24 hours)

Calculations Details







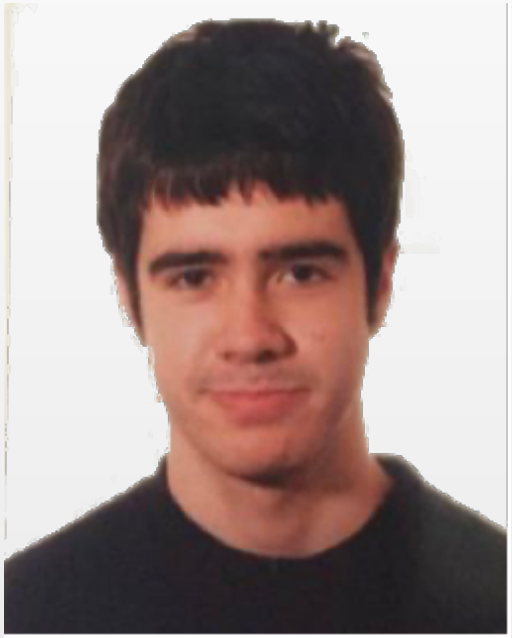


- Pt_4 and Pt_2Ge_2 on 5-8-5-DV 14.81 × 17.10 × 20.0 Å supercell (94 C atoms) + CO
- Pt_{10} and Pt_5Ge_5 + CO 17.28 × 21.38 × 20.0 Å supercell (138 C atoms) was required

Largest clusters (around 10x800 structures) in BSC (96 cores 24 hours)

Acknowledgements

Project Team Members and Funding



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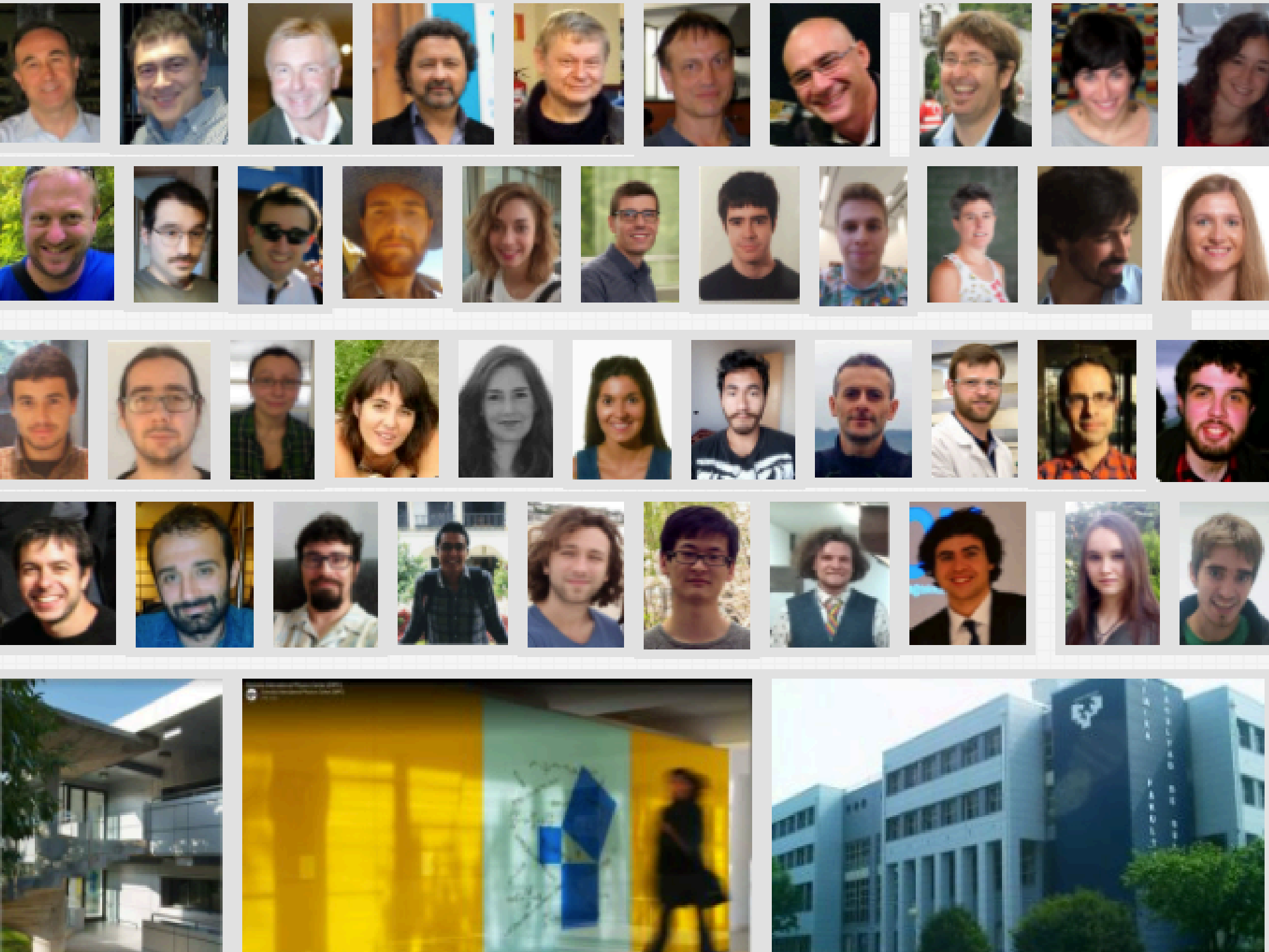
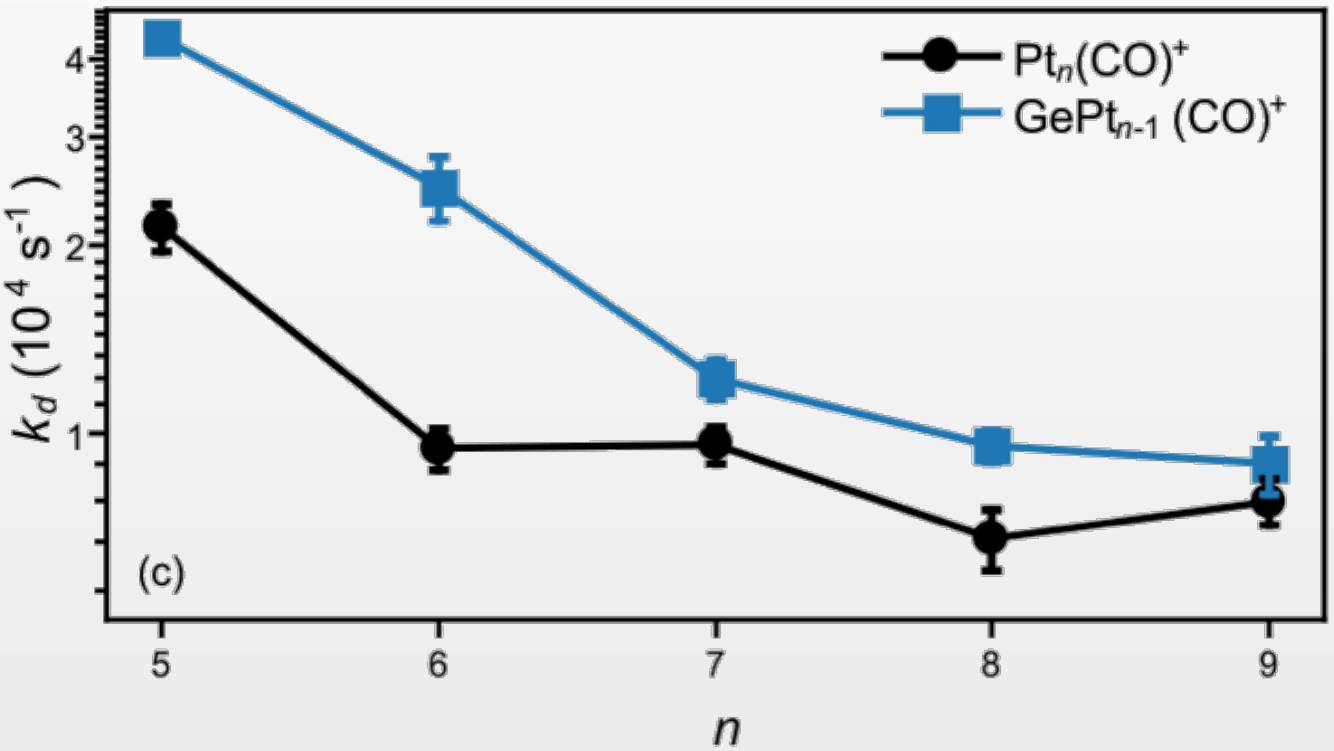


Pt_n^+ and $GePt_n^+$ clusters

Desorption rates of CO (Prof. Ewald Janssens (KU Leuven))



A. Ugartemendia, et al. *ChemPhysChem* 22, 1603 (2021)

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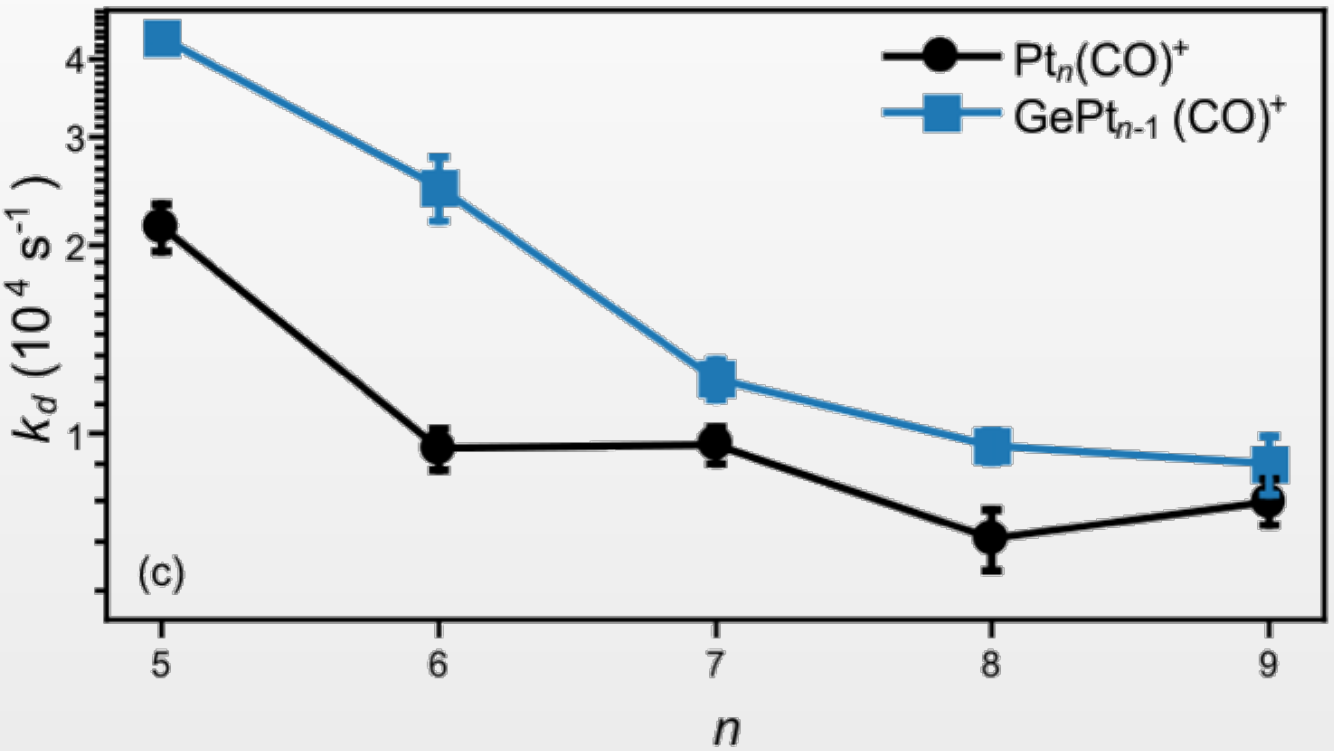

- Ge doping weakens Pt-CO interaction, reduces the tendency to CO poisoning.

A. Ugartemendia, et al. *ChemPhysChem* 22, 1603 (2021)