Morphology and electronic alignment of the Poly(3-hexylthiophene)/ZnO interface

Photovoltaics
No catalysis

Switchable surface chemistry on ferroelectric surfaces

Catalysis
no photons

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Collaborators

Photovoltaics

← Dr. Jie Jiang
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Experimental collaborators:
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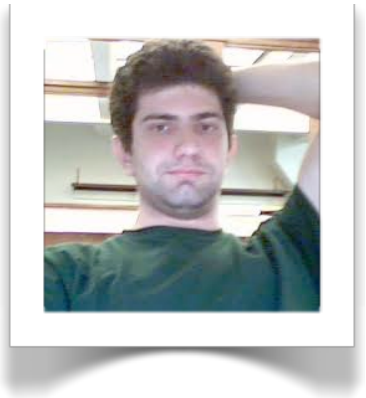
Chemical Engineering, Yale

Funding: NSF SOLAR program



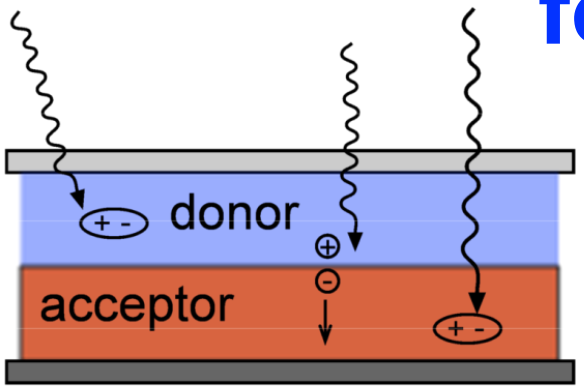
Catalysis

← Arvin Kakekhani
Physics, Yale

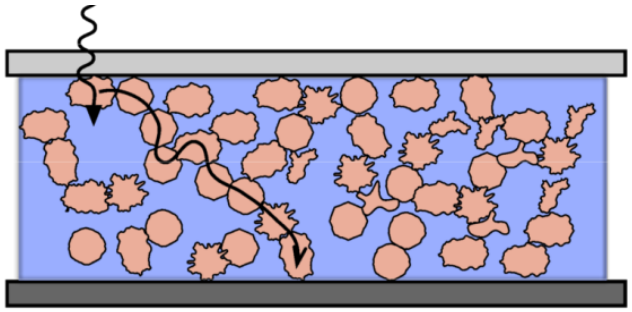
Experimental collaborators:
Matt Herdiech & Eric Altman
Chemical Engineering, Yale

Funding: Toyota Motor Engineering & Manufacturing North America, Inc.

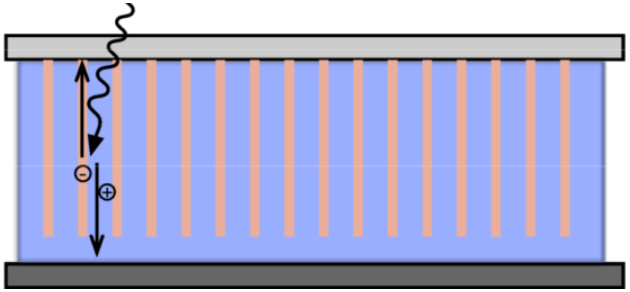
Some materials configurations for photovoltaics



Conventional planar
- High efficiency
- Expensive & fragile
- Limited active interface



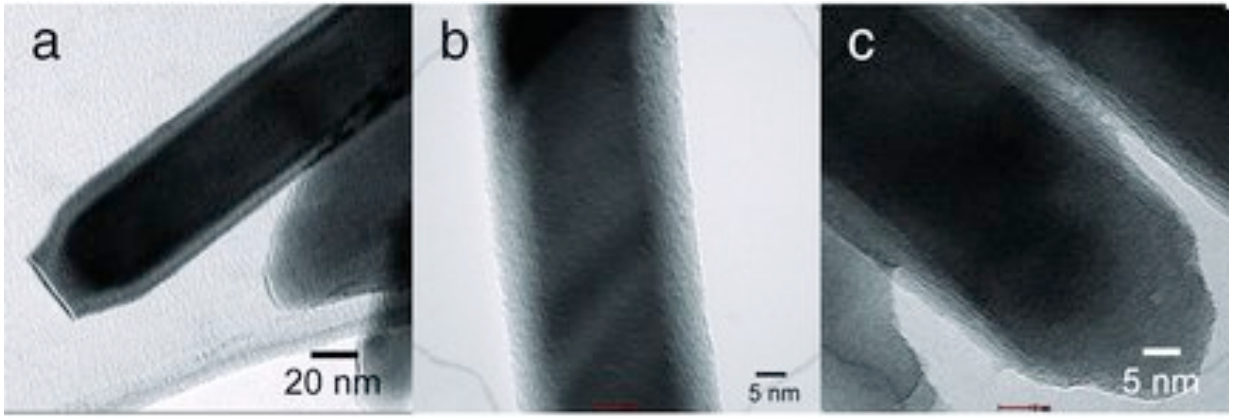
Bulk heterojunction
- Modest efficiency (~5 %)
- Cheap & easy to manufacture
- Carrier transport issues



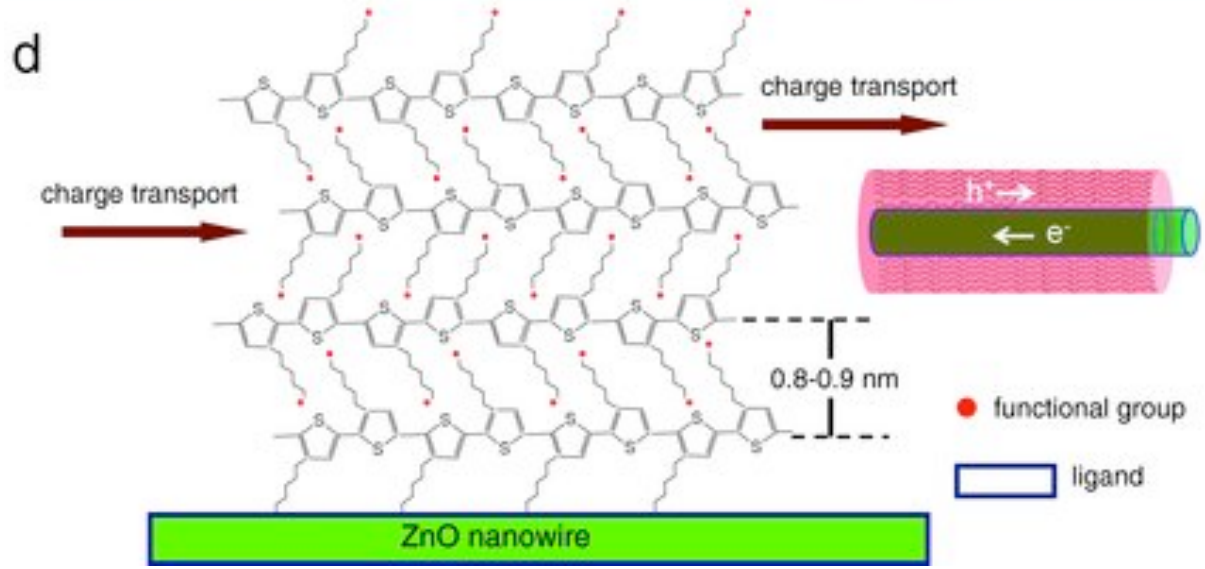
Ordered heterojunction
- Good efficiency
- Great carrier transport
- Difficult to realize: nm scale alignment

Self-assembly of polymer/nanowire

ZnO nanowires (NW): hexagonal facets, well-defined $(10\bar{1}0)$ surfaces
P3HT polymers

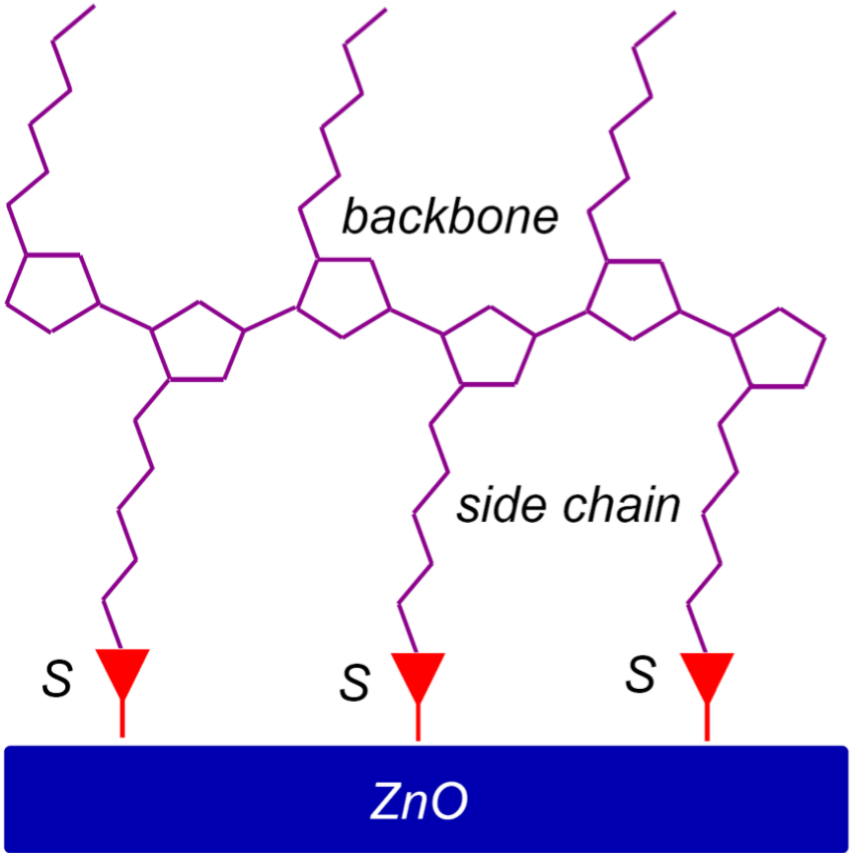


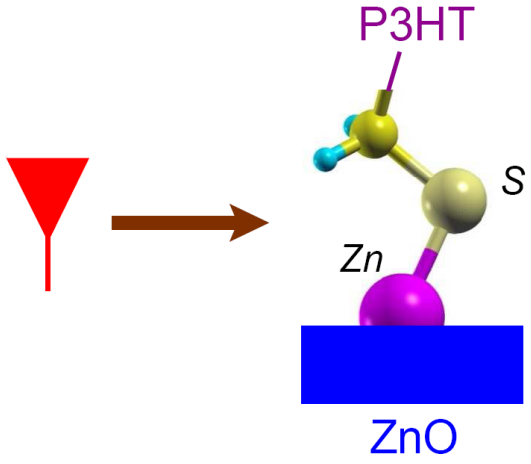
Small diameter NW:
- polymer well ordered
- coaxial with nanowire



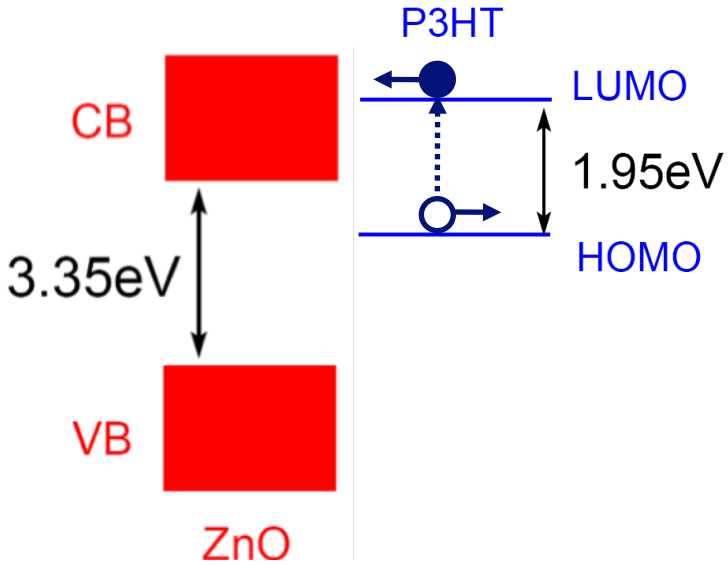
S. Zhang et al., *Advanced Materials* **24**, 82 (2012)

P3HT/ZnO interface



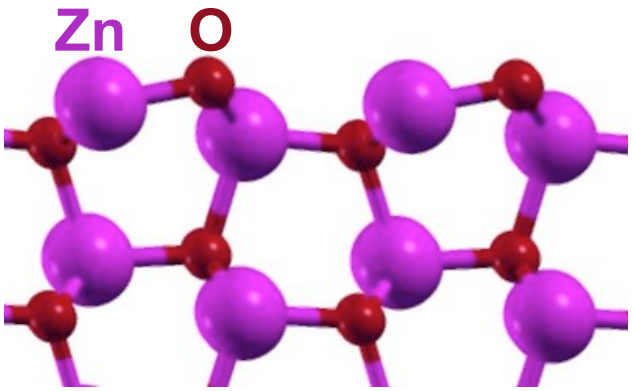


Energy alignment for
separated P3HT & ZnO



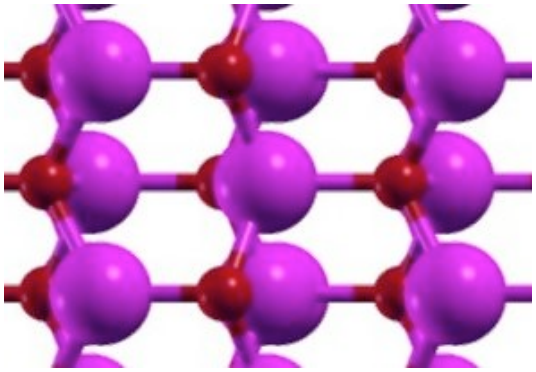
ZnO surface

ZnO nanowire surface: $(10\bar{1}0)$

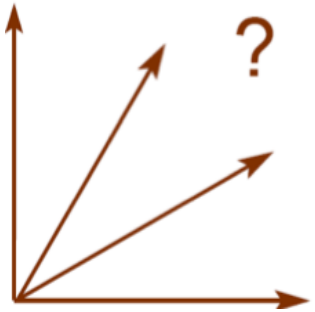


Side view

nanowire axis

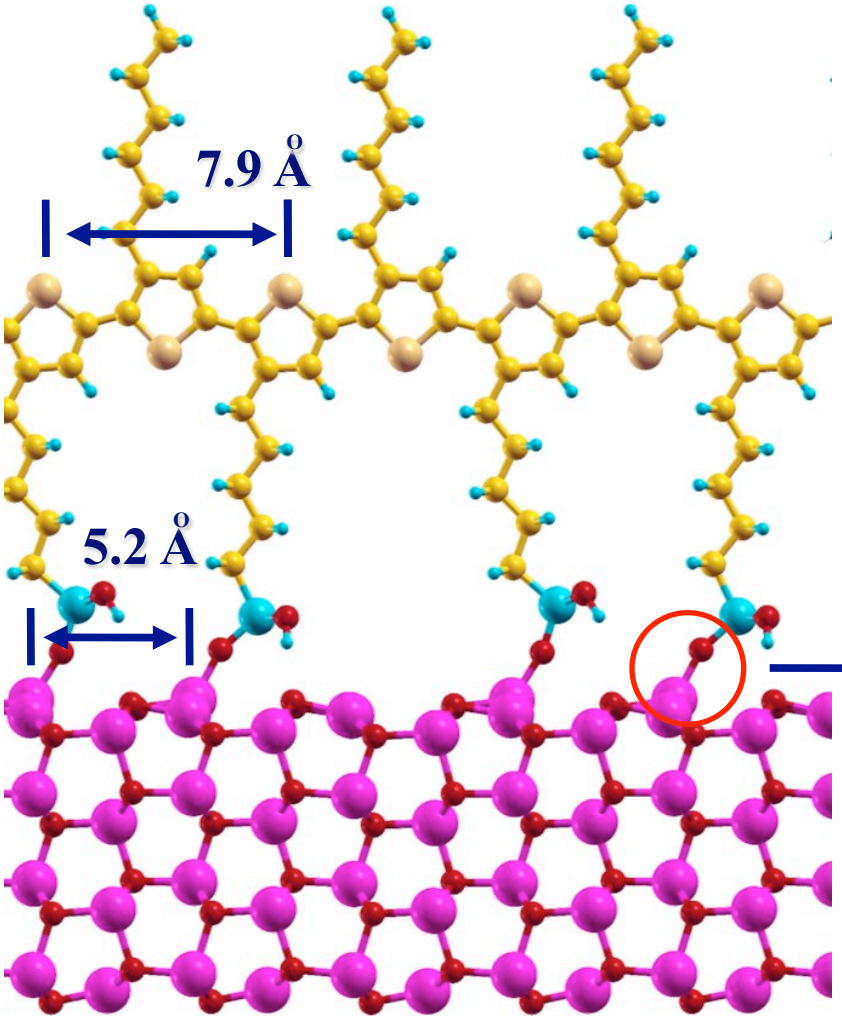


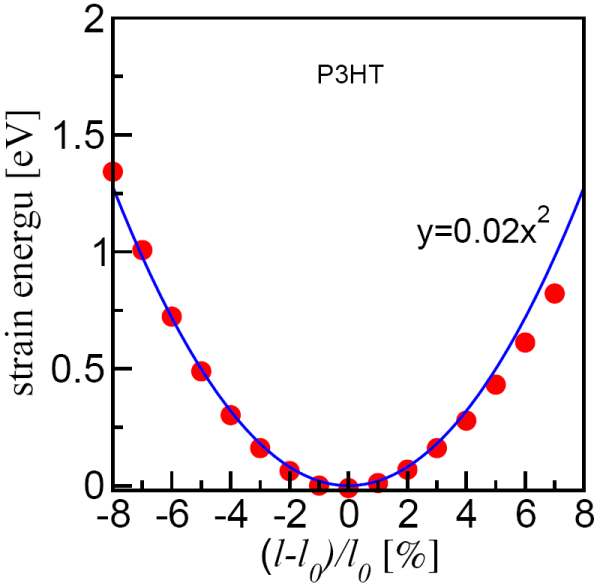
Top view



Which surface direction does P3HT prefer?

P3HT binding & strain energies

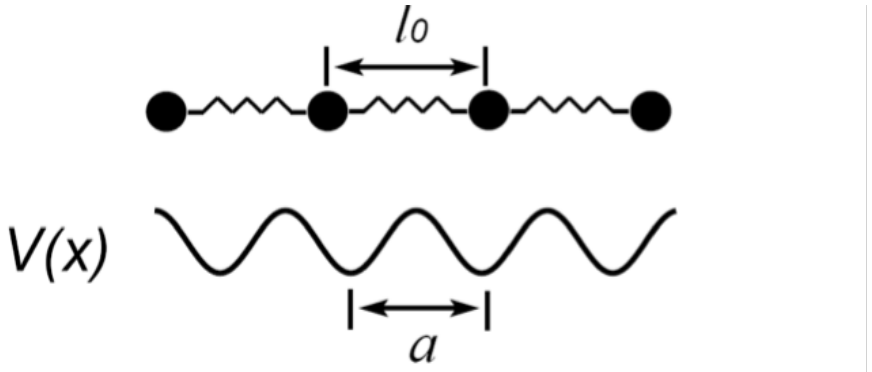




PWSCF (Quantum Espresso)
Plane wave basis
Ultrasoft pseudopotentials
PBE GGA functional

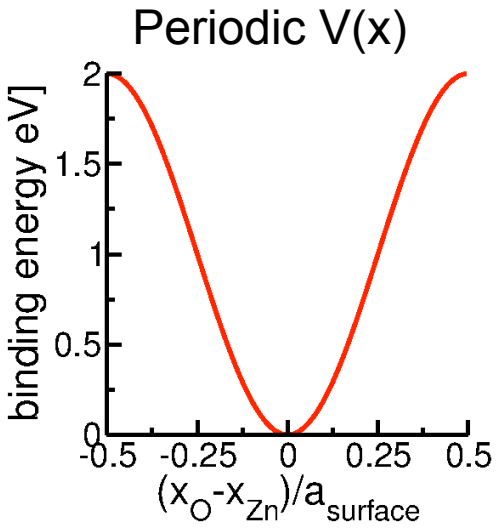
Frenkel-Kontorova model

1D competition of strain & periodic binding potential



$$E = \frac{1}{2}\sum_i k(x_{i-1} - x_i - l_0)^2 + \sum_i V(x_i)$$

Strain Binding

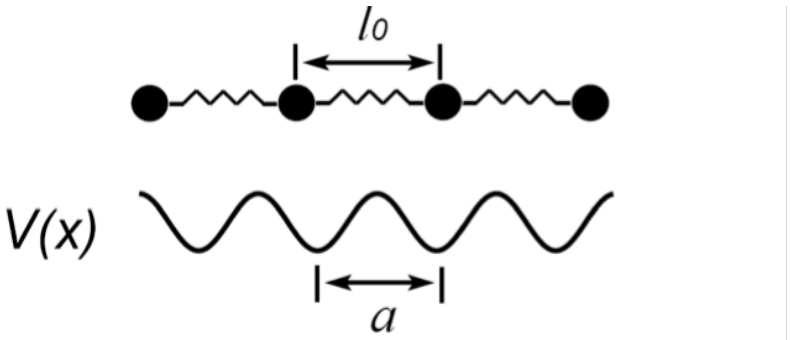


Dynamics of this model is very hard...

But (despite what I learned in grad school), the ground state of this model is solved with a simple efficient algorithm.

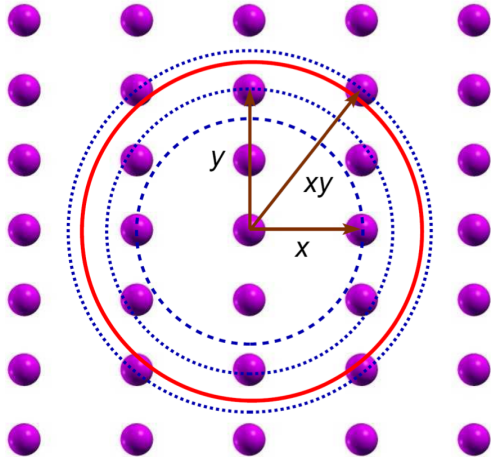
Chou & Griffiths, *Phys. Rev. B* (1986)

Frenkel-Kontorova model



$$E = \frac{1}{2}\sum_i k(x_{i-1} - x_i - l_0)^2 + \sum_i V(x_i)$$

Search possible directions

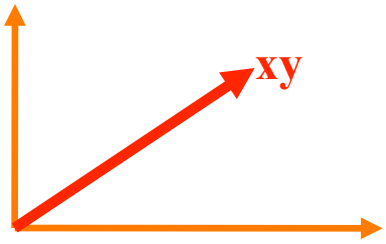


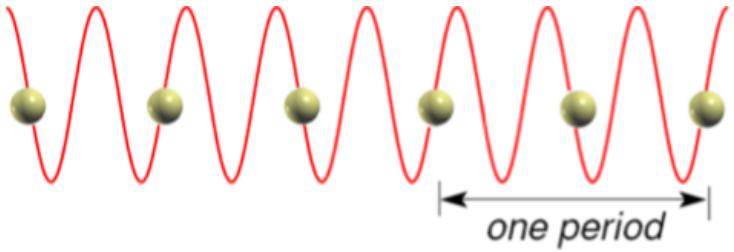
Red is optimum distance for P3HT

Within 25% strain:
only matches are x, y & xy directions

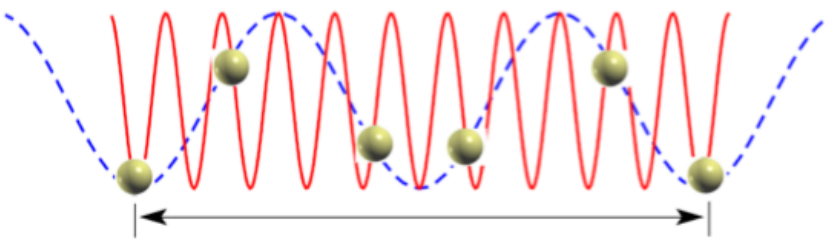
Alignments for flat ZnO surface

Ground states

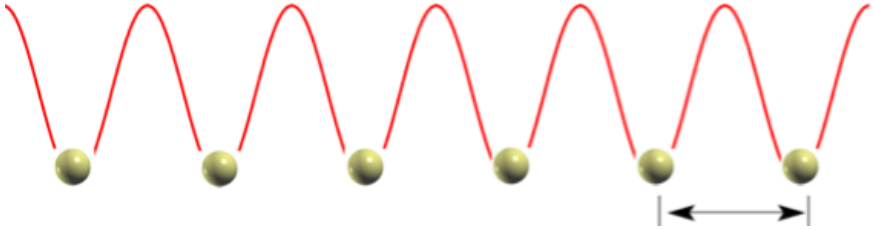




x
E=0.67 eV



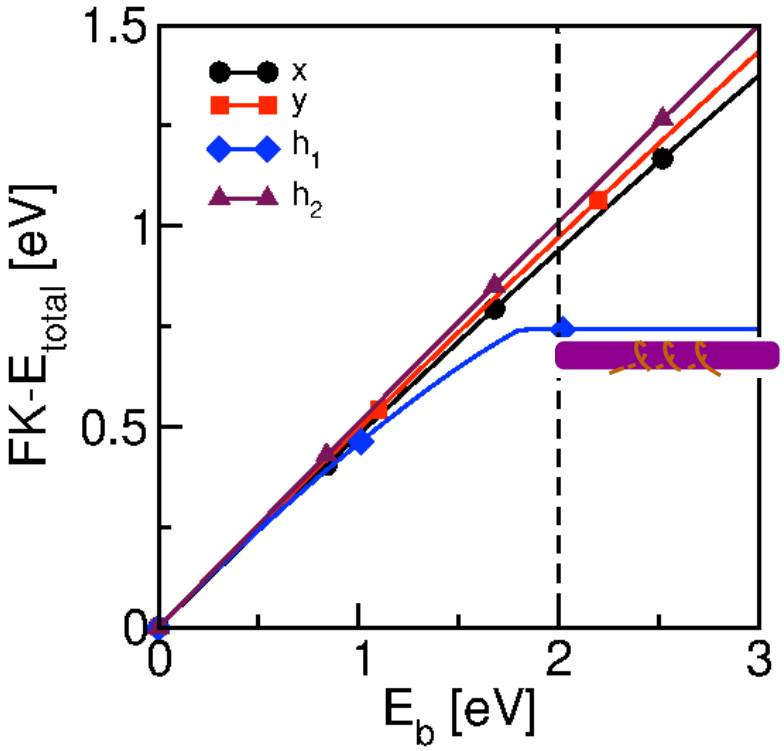
y
E=0.64 eV

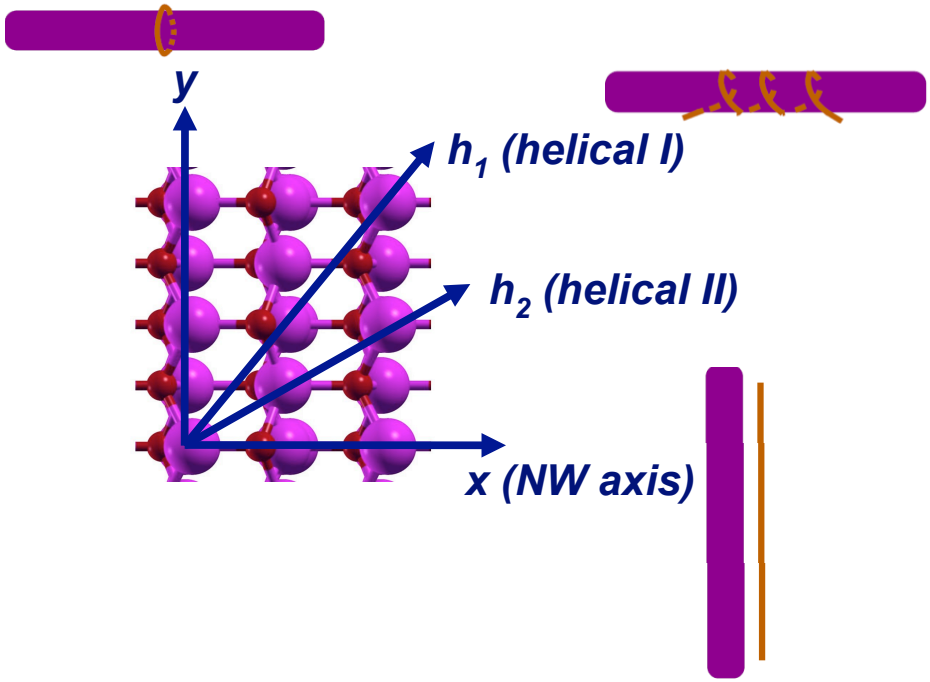


xy
E=0.23 eV

- Valid for surface or large diameter NW
- Smaller diameters:
  if curvature energy > 0.4 eV,
  can change alignment

Fixed morphology versus binding

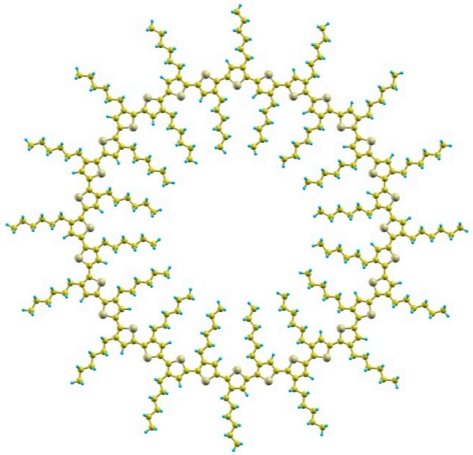


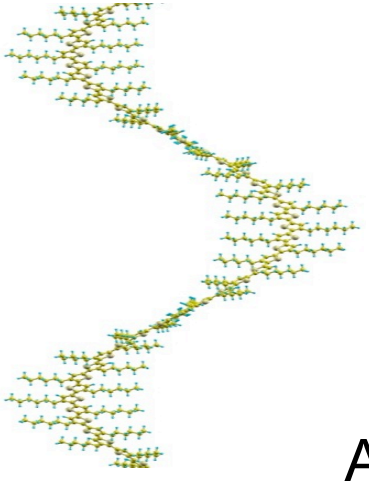


Helical wrapping preferred for almost any binding energy

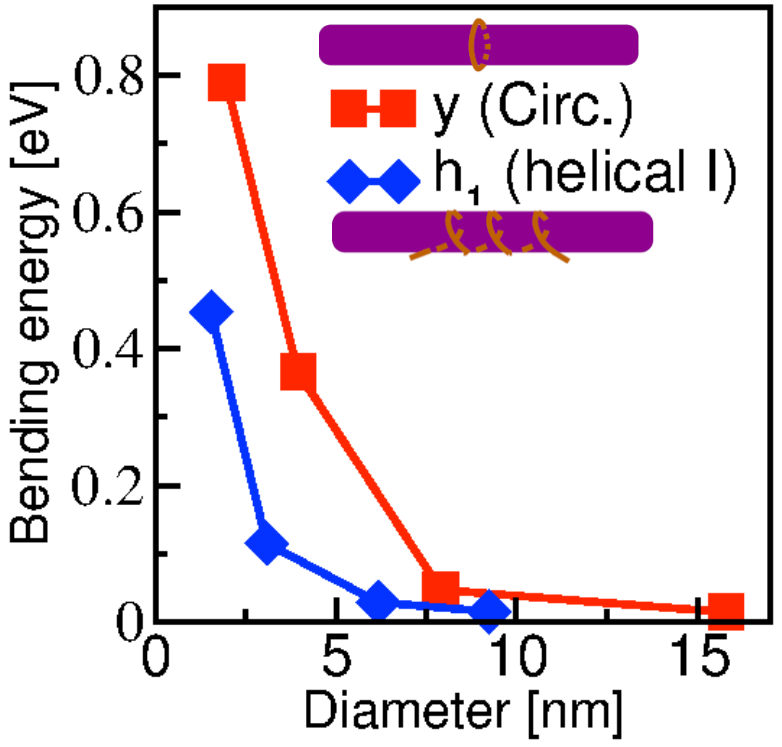
This is for very large nanowires
Can curvature make for coaxial?

Curvature effect 1





Elementary elastic effect:
curving polymer backbone costs energy



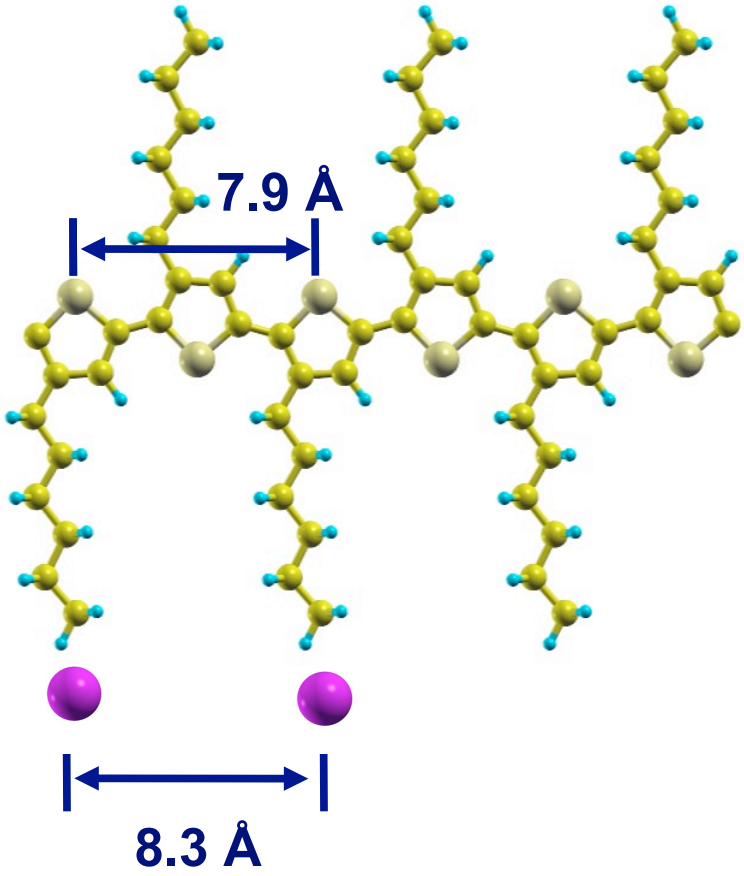
Actually <u>irrelevant</u>
for ~20 nm nanowires...

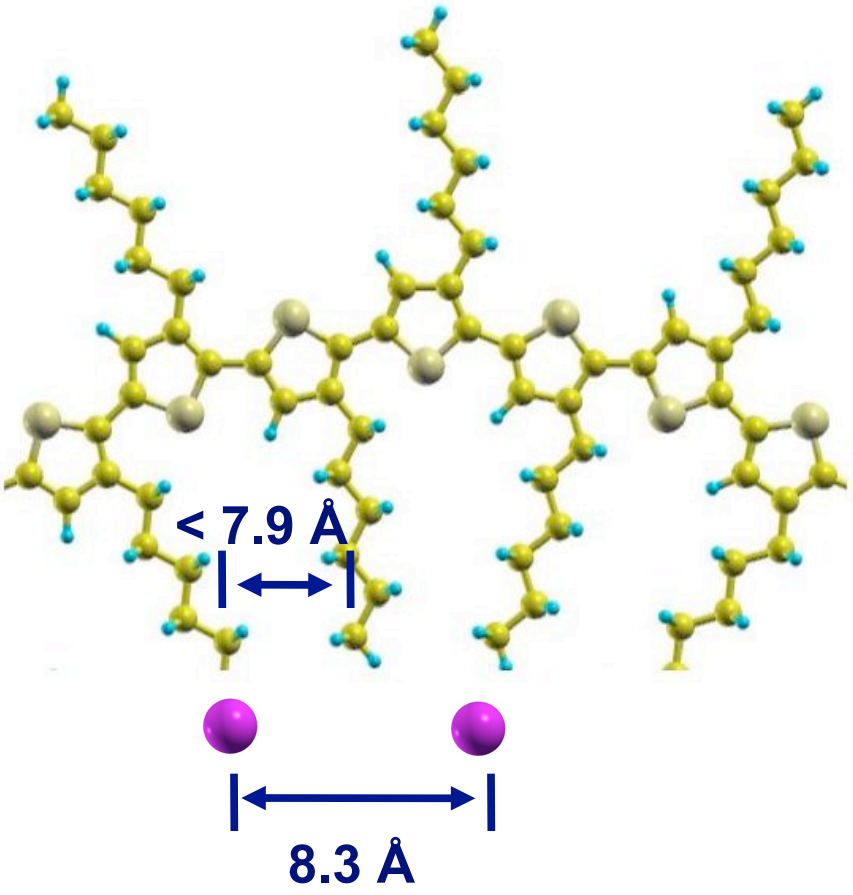
Curvature effect 2

Curved polymer makes binding ends closer :

→ effective change of periodicity of potential

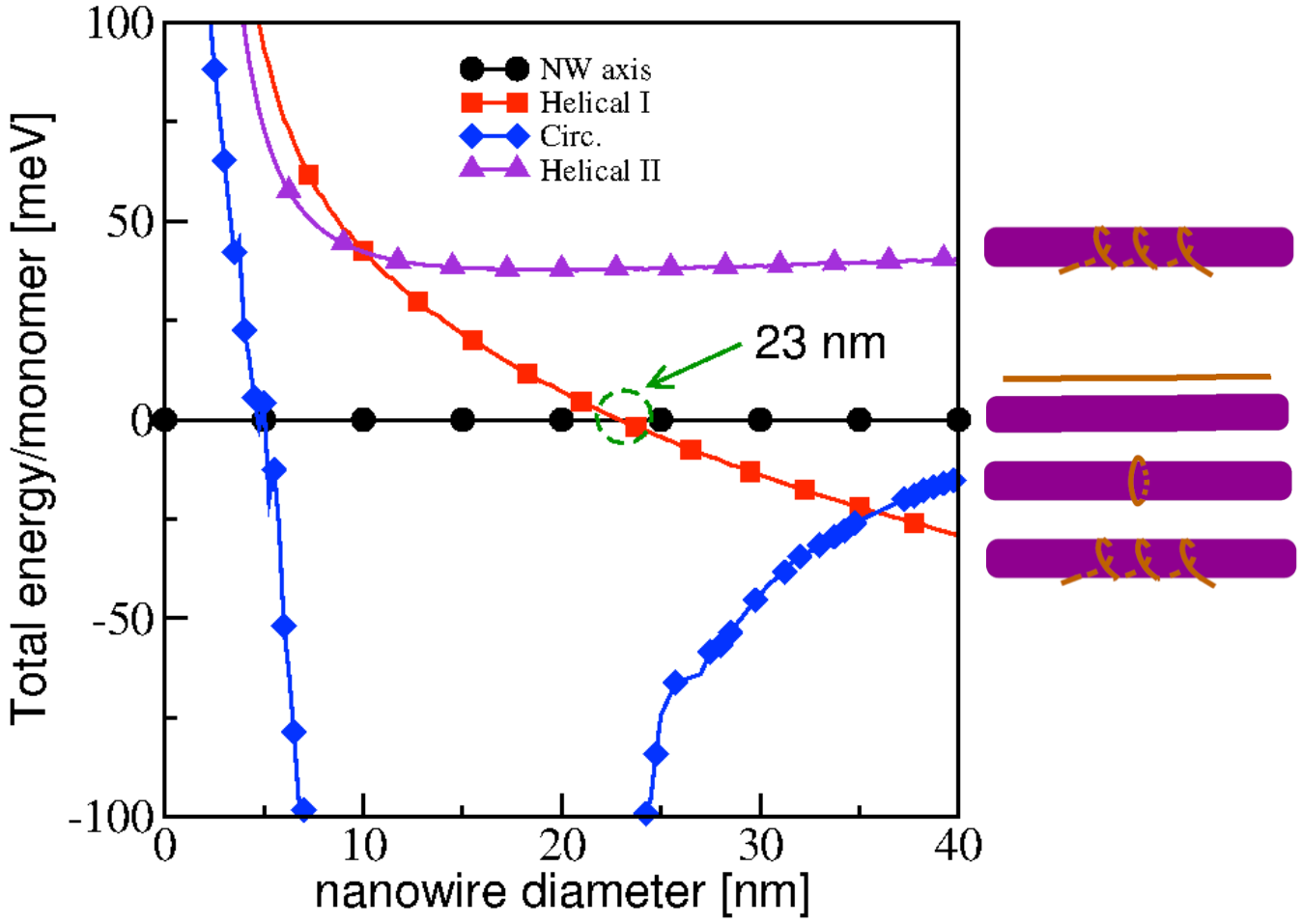
→ has significant energetic effect





Easy to model: change lattice constant in Frenkel-Kontorova

Final morphology prediction

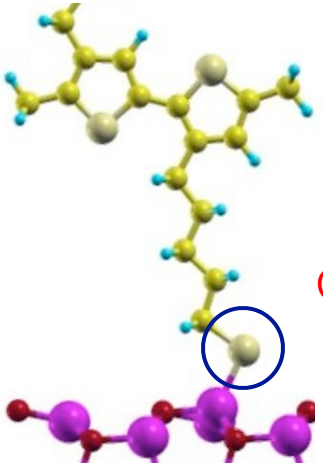


Helical → coaxial transition predicted

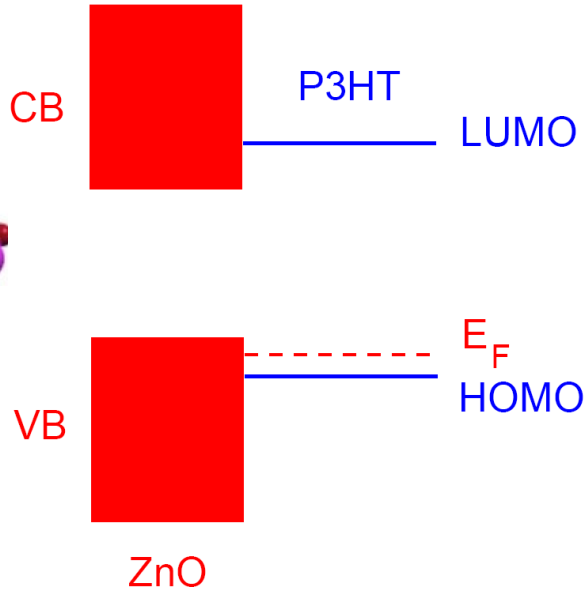
Seems to agree with experiment

Electronic structure (PBE0)

Clean ZnO, clean linker

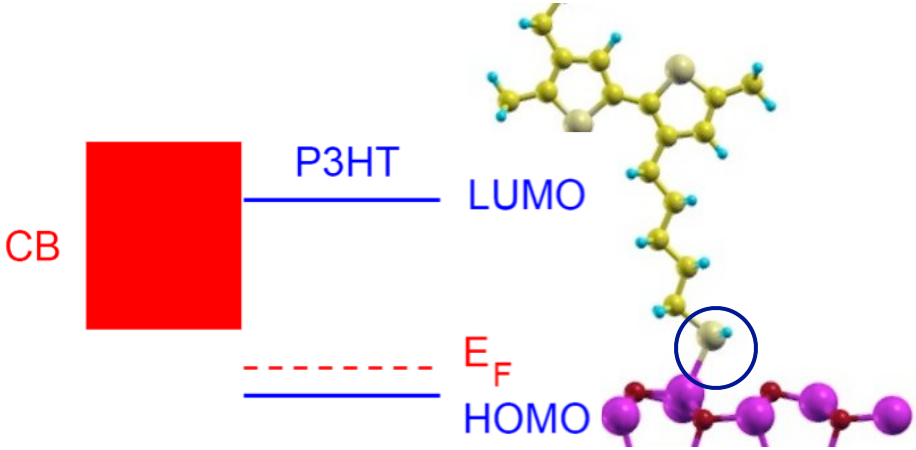


Bad alignment



S linker is open shell
Accepts electrons from ZnO
(hole dopes)

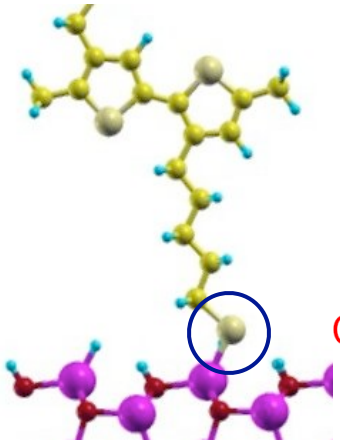
Clean ZnO, hydrogenated linker

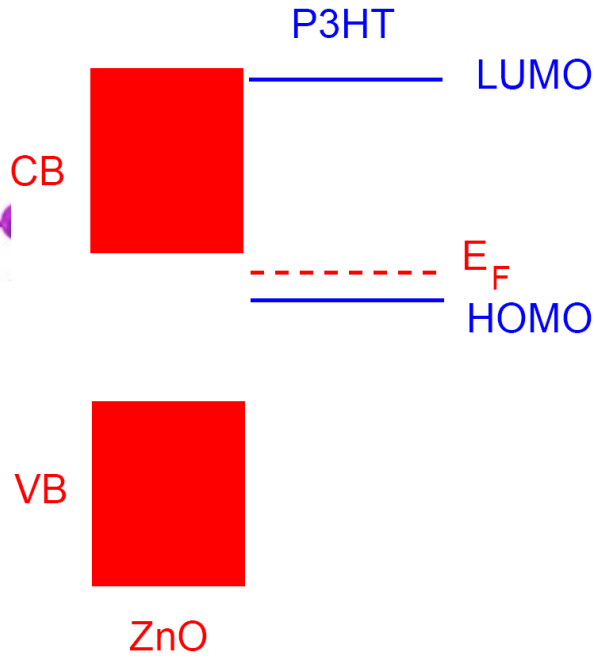


Good alignment

Electronic structure

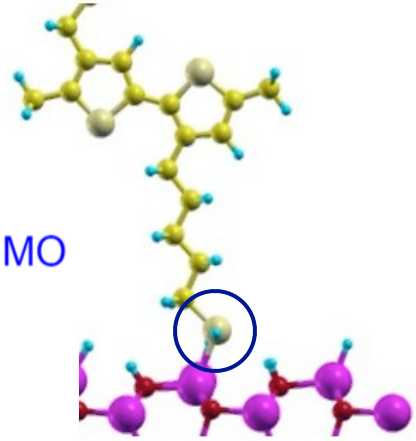
Hydrogenated ZnO, clean linker

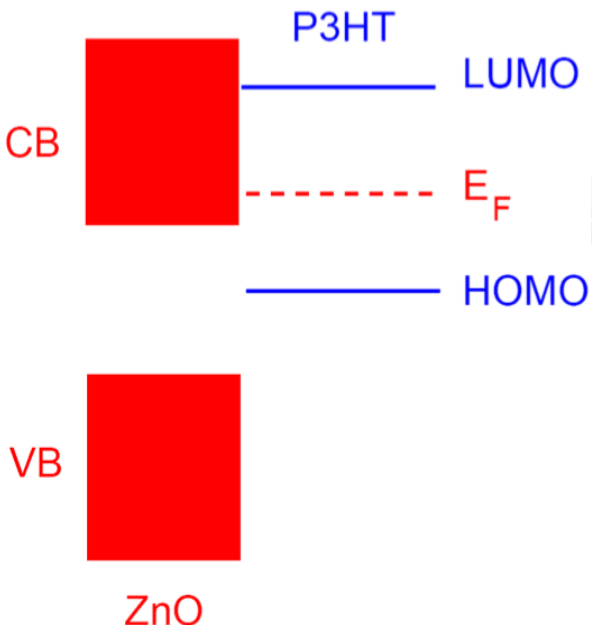




Good alignment

Hydrogenated ZnO and linker

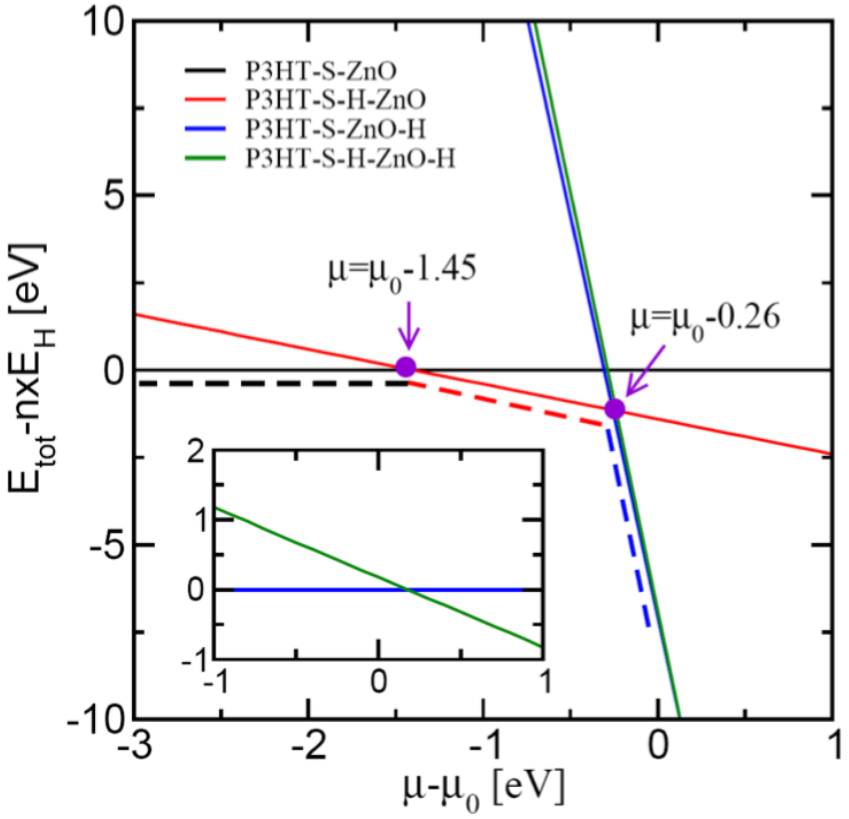




Bad alignment

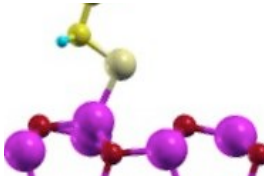
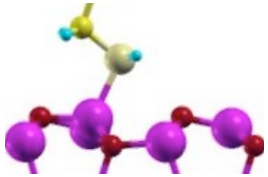
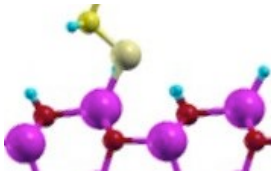
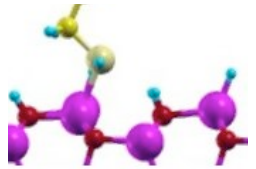
Structure, stability, and alignment

Thermodynamic phase diagram



μ_0 : H chemical potential at T=0,P=0
μ_0 -0.26 eV: T=373K and P=1 atm
μ_0 -1.45 eV: T=1773K and P=1 atm

Structure, stability and band alignment

structure		
stability (μ- μ_0)	**< -1.45 eV**	**[-1.45, -0.26) eV**
alignment	**bad**	**good**
structure		
stability (μ- μ_0)	**[0, -0.26) eV**	**> 0**
alignment	**good**	**bad**

Summary 1

- Curvature effects can align polymer/nanowire coaxially
- FK model a cheap and useful model for these systems
- Covalent tethering of polymer makes interfacial chemistry and passivation critical --- difficult extra materials problem to deal with...
- Open circuit voltage for good alignments are ~ 1.0 eV which is as good or better than physisorbed P3HT (0.4-0.8 eV)

Catalysis on ferroelectrics: outline

- **Overview of precious metal catalysts & problems**
- Overview of ferroelectrics
- Theoretical approach: DFT, NEB
- Sampling of results
- Proposed NO_x reduction cycle
- Preliminary results on key energy barriers
- What's next

Current Methods for NO_x Reduction

(Primary focus is on automotive applications)

- Precious metals catalysts -- expensive
- Some key reactions
  - oxidize CO → CO_2
  - reduce NO_x → $N_2 + O_2$
- Current catalysts bind O too strongly
  - Air:fuel ratio must be ≈ stoichiometric (no excess O_2)
  - Some fuel/CO used to remove O from catalyst

Sabatier Principle

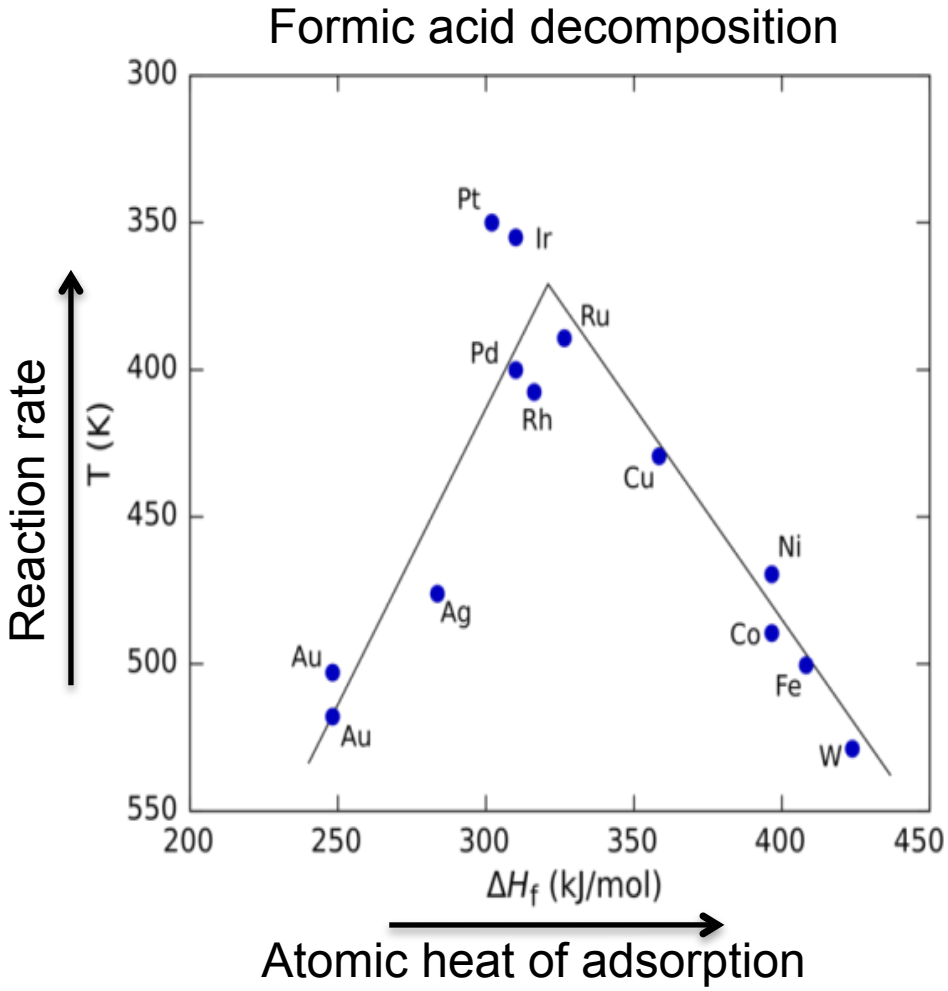
Catalyst-molecule interaction must be “just right”:
not too strong, not too weak

Standard volcano plot

Strong atomic adsorption:
→ Barrier low, fast dissociation
→ But atoms never come off!

Weak atomic adsorption:
→ Barrier high, very slow reaction

<u>Compromise</u> situation

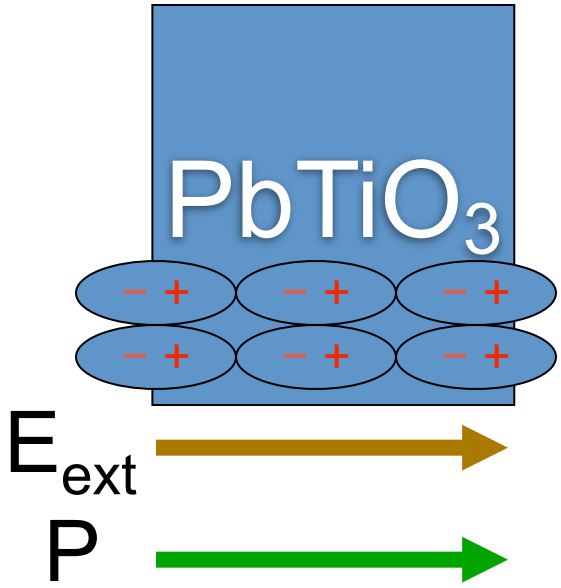


Outline

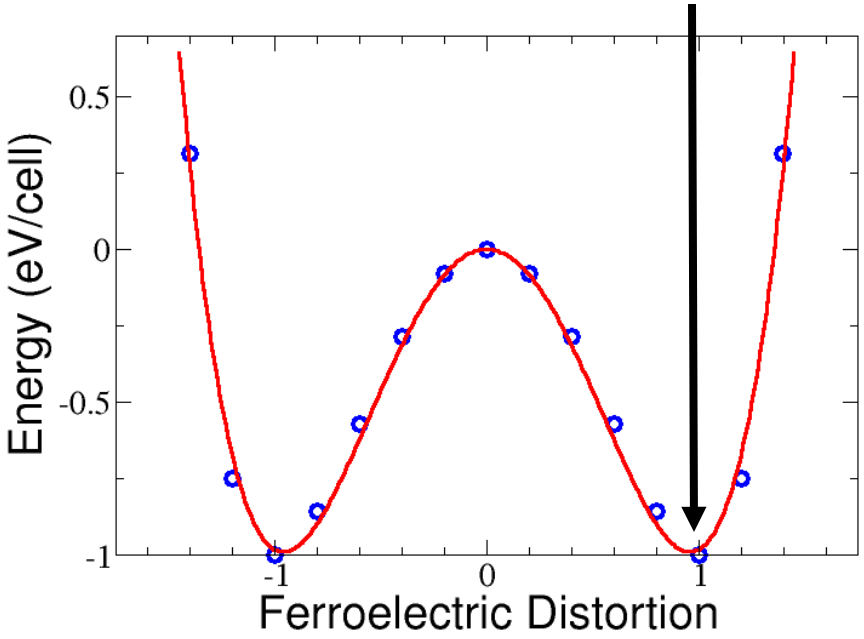
- Overview of precious metal catalysts & problems
- **Overview of ferroelectrics**
- Theoretical approach: DFT, NEB
- Sampling of results
- Proposed NO_x reduction cycle
- Preliminary results on key energy barriers
- What's next

What is a ferroelectric?

- Two stable polarization states.
- Switch with Electric field.



+X Polarization



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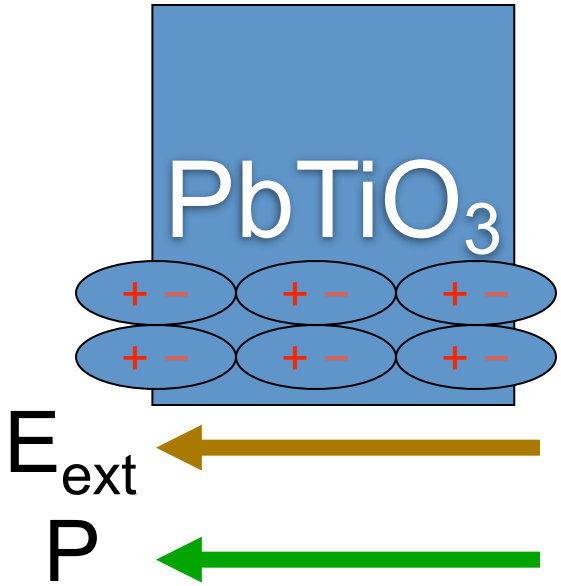
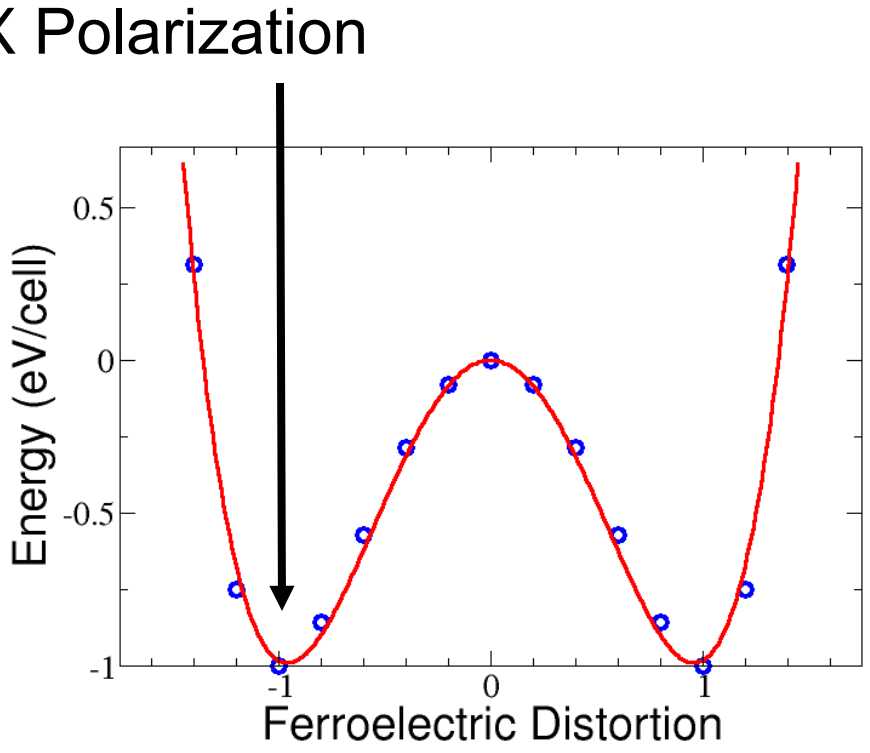
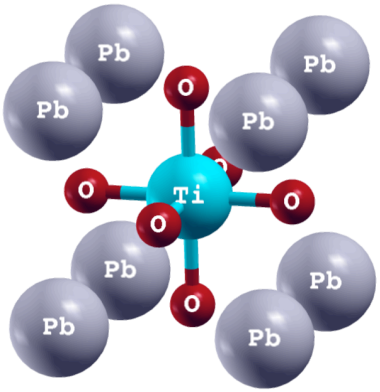
- Two stable polarization states.
- Switch with Electric field.

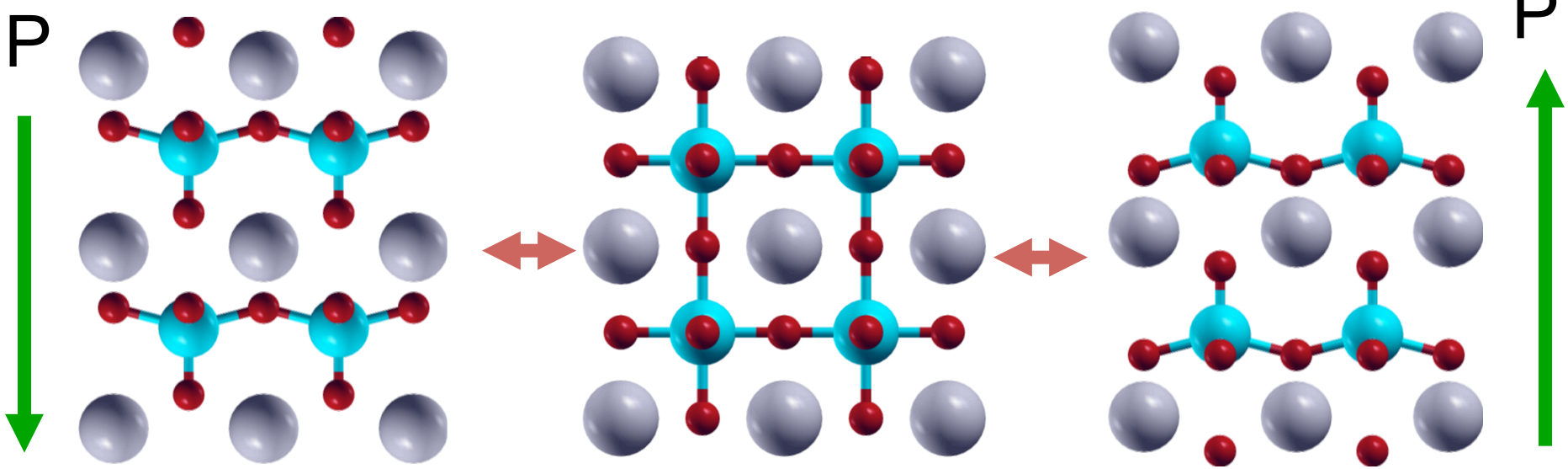




A ferroelectric: $PbTiO_3$

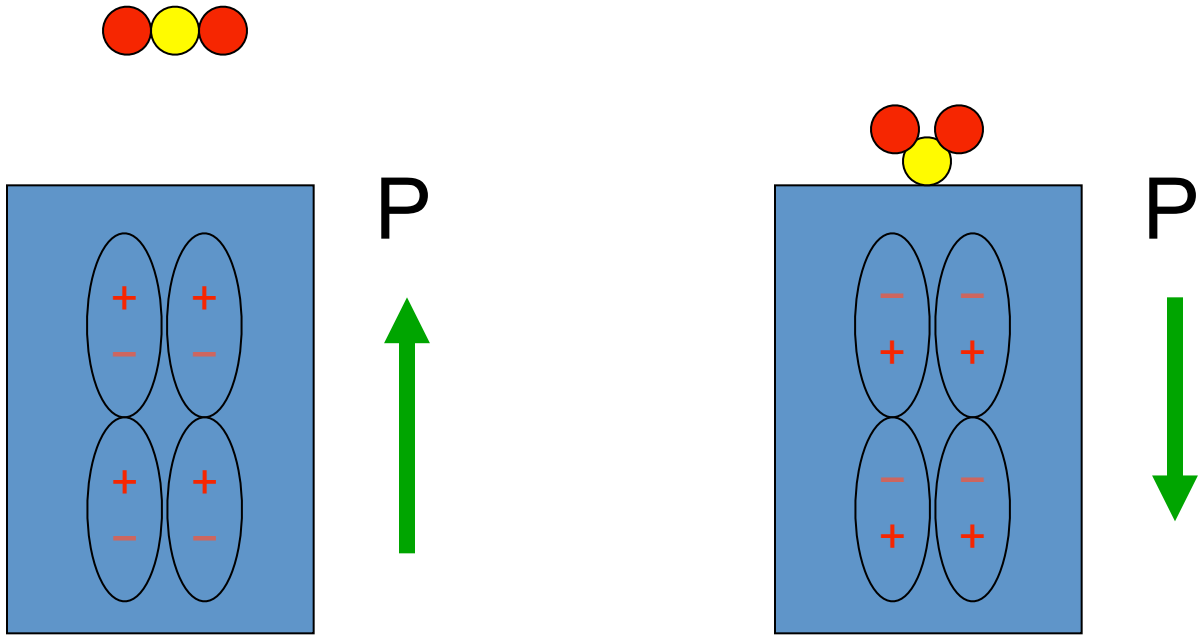
- Perovskite Structure
- Ferroelectric
- Strong Polarization





Ferroelectrics & surface chemistry

- 2 polarizations → 2 surfaces (for the price of 1)
- Control with **E** field
- Possible Uses:
  - Bind/Release Molecule
  - Change surface electronic states ➔ affect catalysis
  - Chemical Sensing



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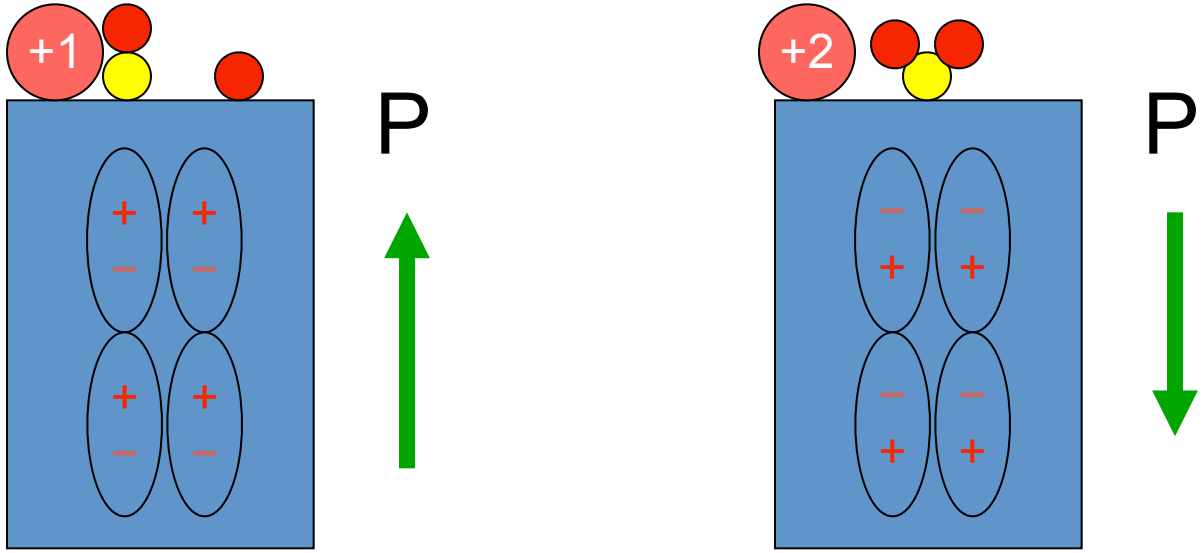

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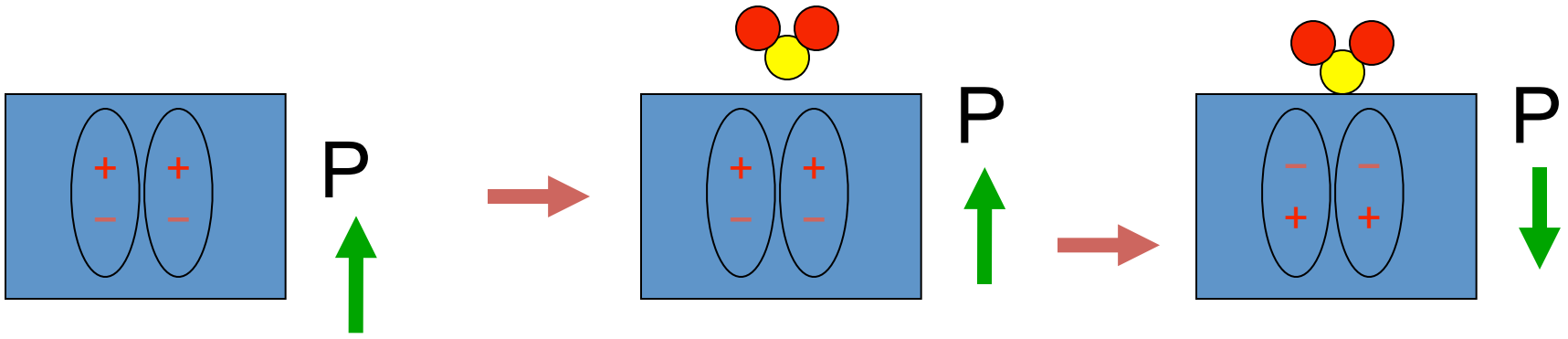

Outline

- Overview of precious metal catalysts & problems
- Overview of ferroelectrics
- **Theoretical approach: DFT, NEB**
- Sampling of results
- Proposed NO_x reduction cycle
- Preliminary results on key energy barriers
- What's next

DFT modeling

- Plane wave basis
- Ultrasoft (Vanderbilt) pseudopotentials
- 15 Å vacuum
- Dipole Correction

→ Converge binding energies to ~ 0.01 eV

PWSCF (Quantum Espresso)
Cold smearing
8x8 k-point sampling per 1x1 cell
PW91 GGA
30 Ryd cutoff

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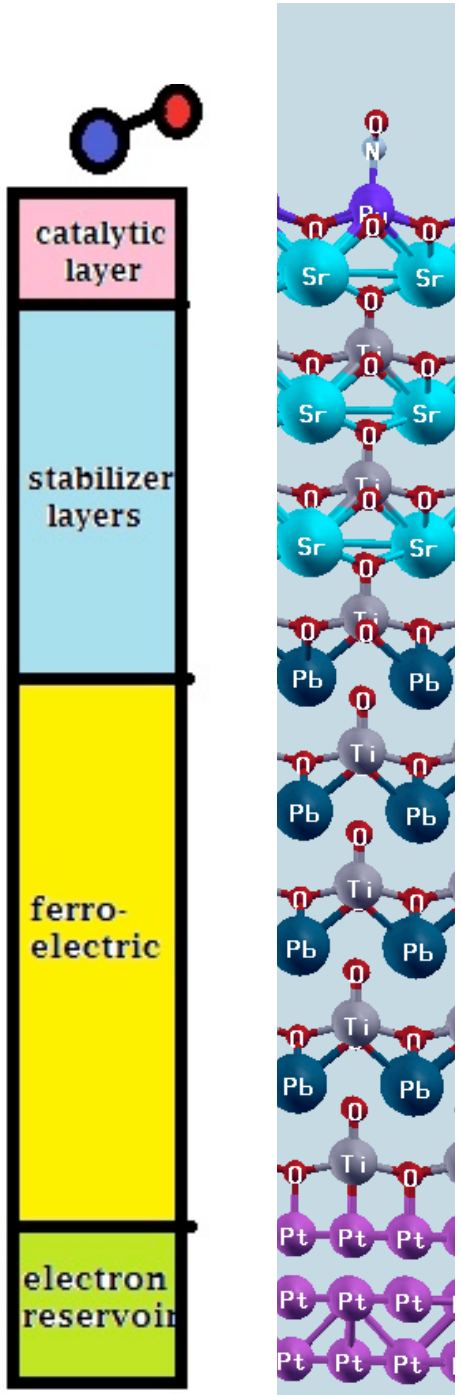

Outline

- Overview of precious metal catalysts & problems
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- Theoretical approach: DFT, NEB
- **Sampling of results**
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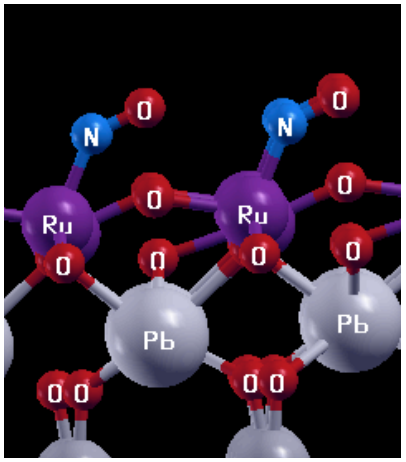
What we calculated (so far)

	NO	NO dis.	O_2	O_2 dis.	N_2	N_2 dis.	N	O
$PbTiO_3$ (PbO term.)								
$PbTiO_3$ (TiO_2 term.)								
$PbTiO_3$ (Stable)								
RuO_2 / $PbTiO_3$								
$RuO_2/(SrTiO_3)_1/ PbTiO_3$								
$RuO_2/(SrTiO_3)_2/PbTiO_3$								
$RuO_2/(SrTiO_3)_3/PbTiO_3$								
$SrTiO_3$ (SrO term)								
$SrTiO_3$ (TiO_2 term.)								
$SrRuO_3$ (SrO term.)								
$SrRuO_3$ (RuO_2 term.)								

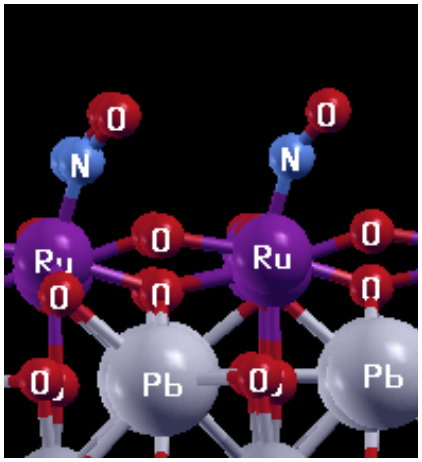
NO on RuO_2 / $PbTiO_3$

Positive



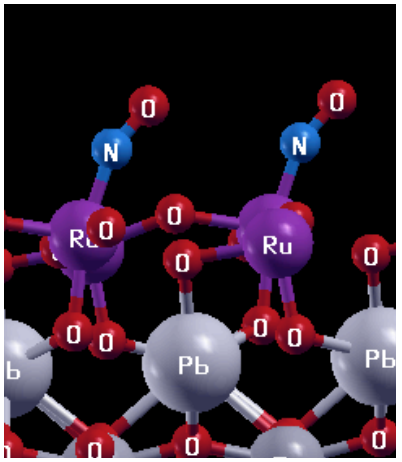
1.2 eV

Paraelectric

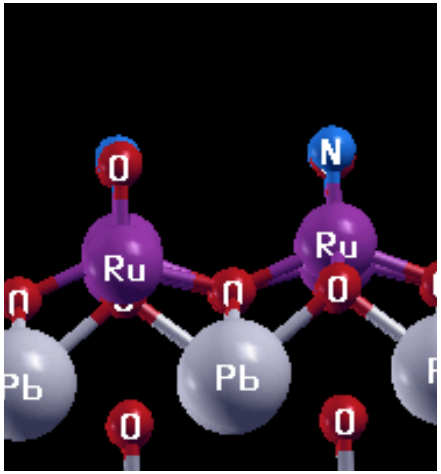


0.3 eV

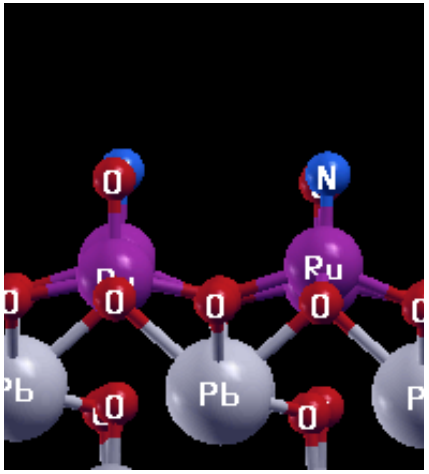
Negative



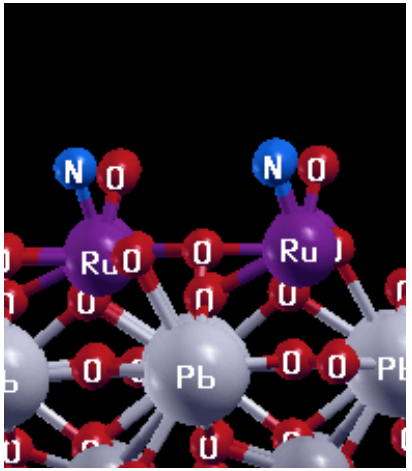
-1.4 eV



2.0 eV



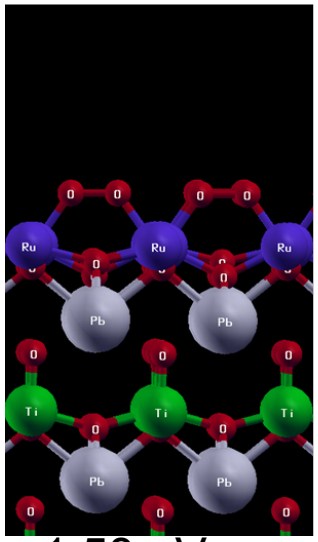
1.8 eV



1.4 eV

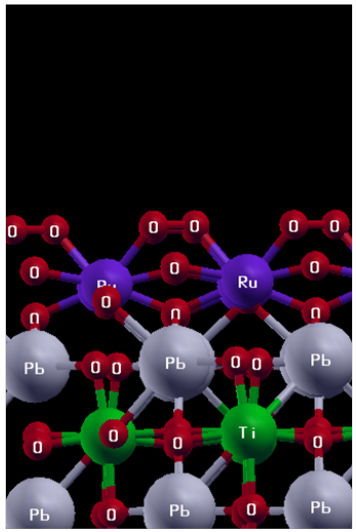
O_2 on RuO_2 / $PbTiO_3$

Positive

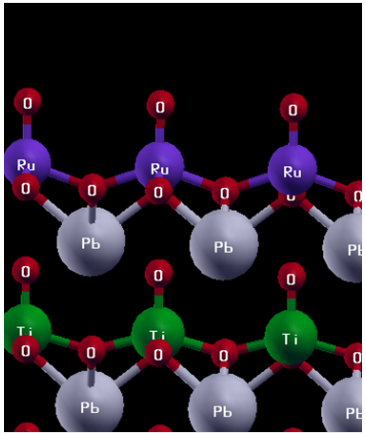


1.58 eV

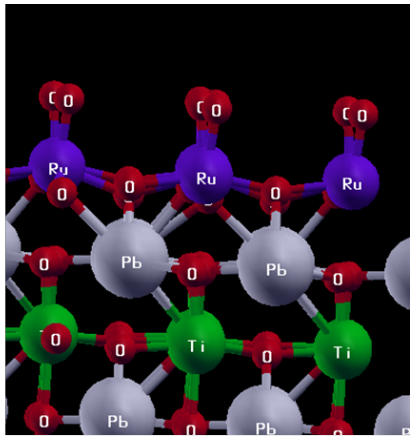
Paraelectric



0.88 eV



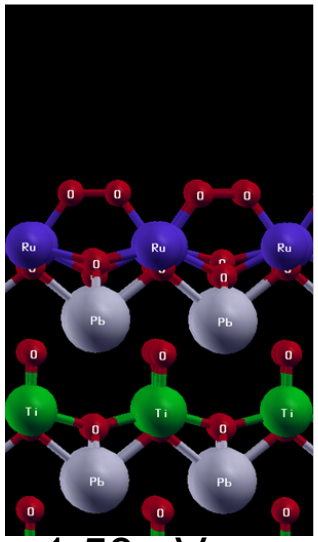
1.98 eV



1.14 eV

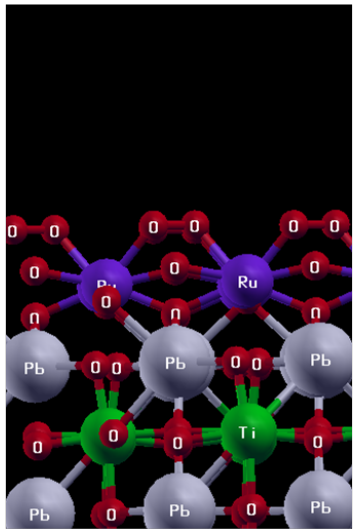
O_2 on RuO_2 / $PbTiO_3$

Positive



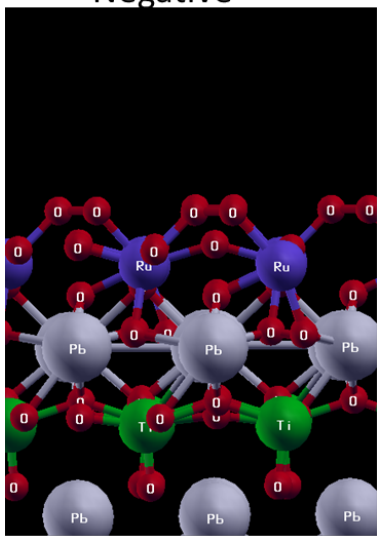
1.58 eV

Paraelectric

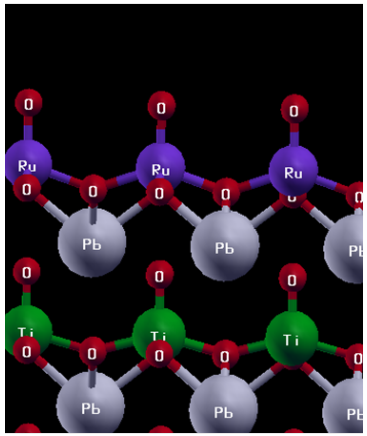


0.88 eV

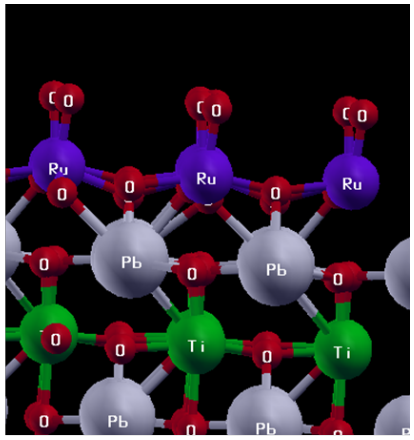
Negative



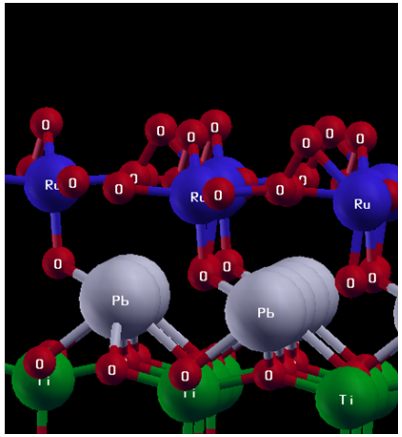
0.18 eV



1.98 eV



1.14 eV



-0.73 eV

Neg. polarization:

- weak interactions
- O + O → O_2 favored
- O_2 weakly physisorbed

2 N or N_2?

Surface	N_2 binding	N + N binding	N+N→N_2 ?
Positive	0.14	-2.02	Yes
Paraelectric	0.62	-3.13	Yes
Negative	0.26	-4.38	Yes

- N+N → N_2 always favored
- N_2 is weakly physisorbed

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- Overview of precious metal catalysts & problems
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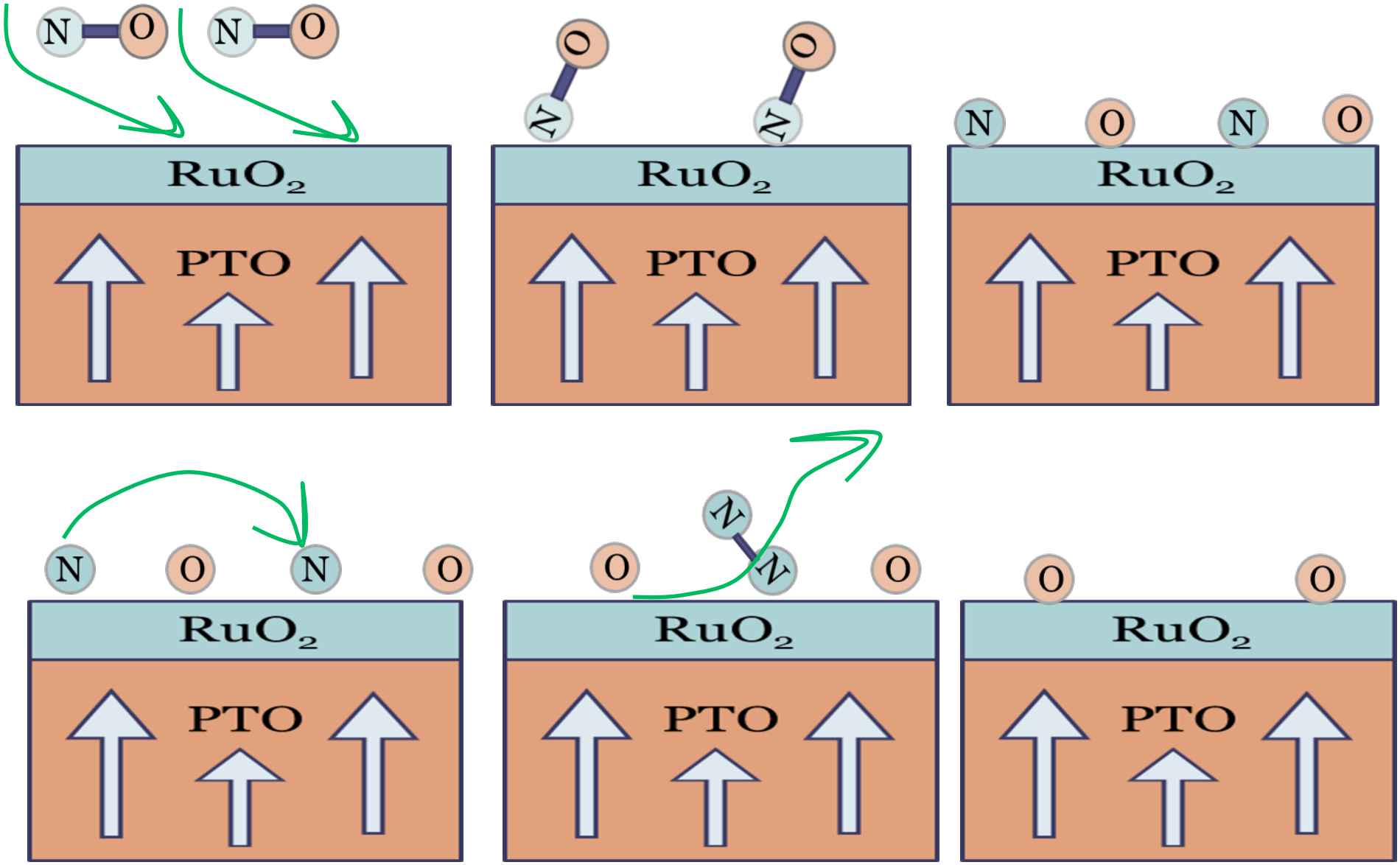
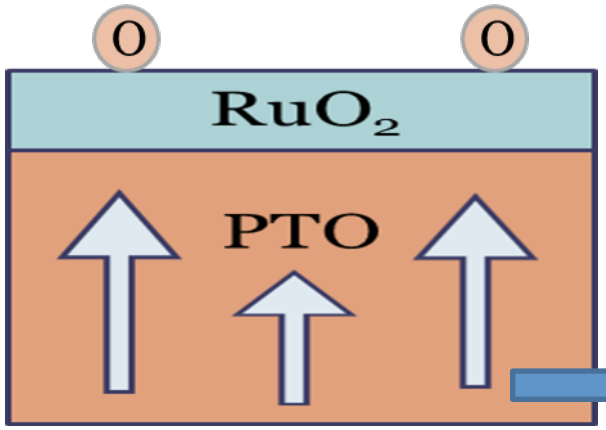
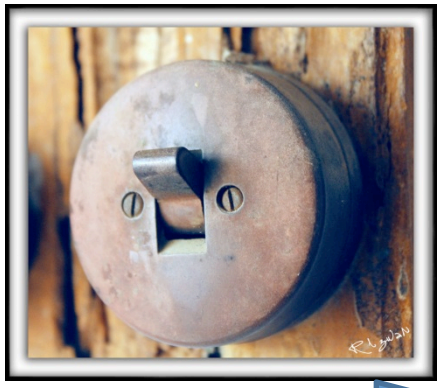
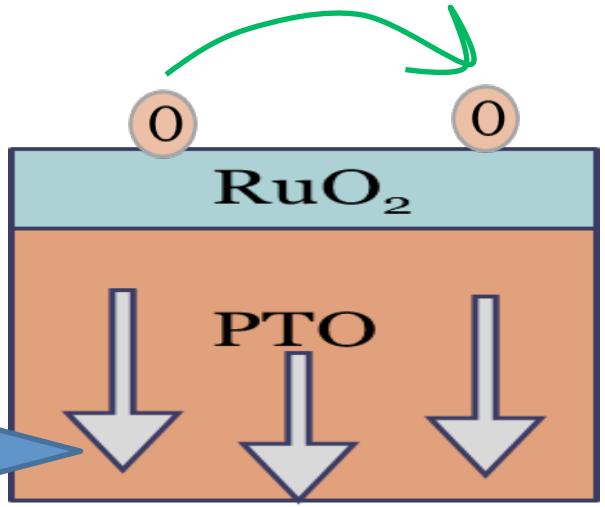
- Preliminary results on key energy barriers
- What's next


N
O
N
O
RuO2
PTO
O
N
O
N
RuO2
PTO
N
O
N
O
RuO2
PTO
N
O
N
O
RuO2
PTO
O
N
N
O
O
RuO2
PTO
O
O
RuO2
PTO

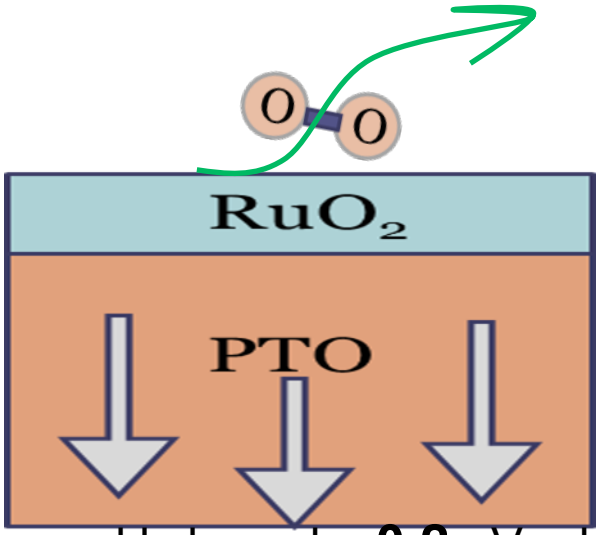


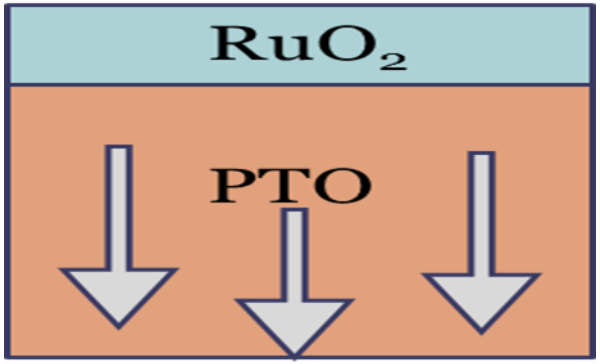




O+O strongly bound ~ **2** eV **:**
hard to release

O+O unstable ~ **- 0.7** eV
relative to gas phase





O_2 weakly bound ~ **0.2** eV relative to
gas phase: **easy to release**

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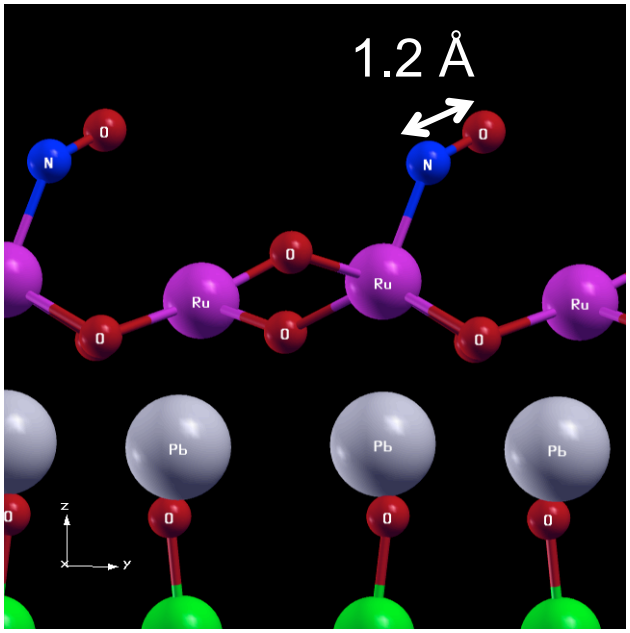
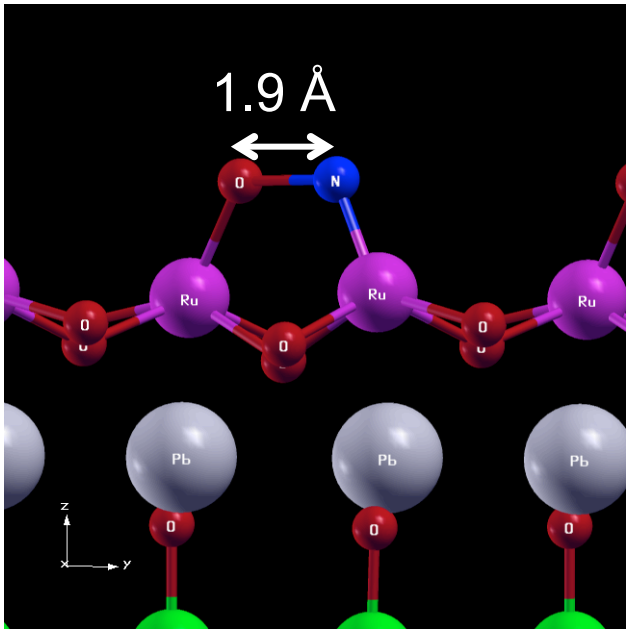
- **Some key energy barriers**
- What's next

NO dissociation: positive $RuO_2/PbTiO_3$

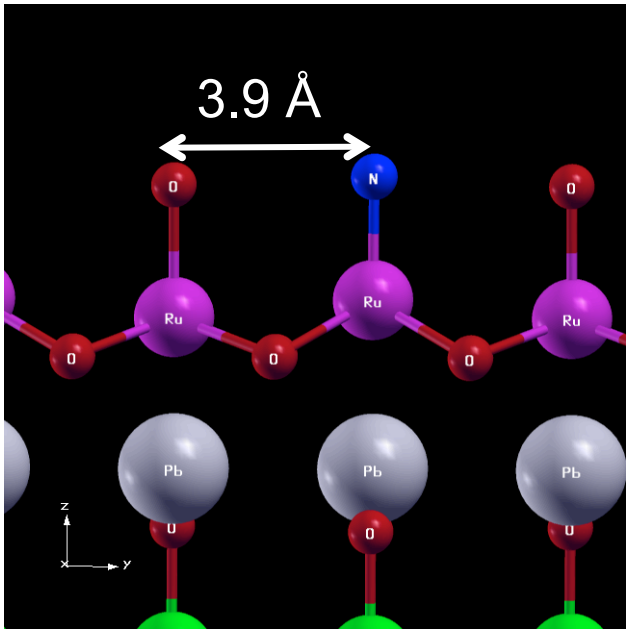
Initial



Transition state



Final



- Barrier = 1.3 eV
- Like transition metals: transition state is ≈ 2 separate atoms

Is 1.3 eV big or small?
Ru (0001) is active for NO dissociation and has barrier of 1.2-1.3 eV

Polarization dependent barriers

NO dissociation process on RuO_2 / $PbTiO_3$

	Pos.	Para.	Neg.
NO → N + O barrier	1.31	2.25	3.04
Adsorption energy of N + O	-1.2	-0.3	1.4

N + N → N_2 process

	Pos.	Para.	Neg.
Barrier	0.51	---	---

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What's next

1. Obviously calculate more barriers → kinetic Monte Carlo

2. Thermodynamics of monolayer RuO_2 on $PbTiO_3$

   Stays catalytic?
   Diffuses into bulk?
   What is its stoichiometry?

3. Poisoning effects of other gases (CO, CO_2 , H_2O, …)

4. Other ideas and broader point:

   can remove "Sabatier compromise" with ferroelectric….

Why Ru? Other metals?

- Chose RuO_2 because
  bulk RuO_2 is known “regular” NO catalyst

- Regular catalyst: has a “just right” interaction with NO

- Not stuck to “just right” interactions!

- Can choose different metals which may be more optimal on a ferroelectric surface