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Workshop on Nanoscience for Solar Energy Conversion

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Charge Transport in Metal Oxides: Multi-scale Studies

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e^-/h^+ Transport and Reactivity in Metal Oxides: Multi-scale First Principles Characterization.

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Chemical & Materials Sciences Division

DOE Basic Energy Sciences/Chemical Transformations
EMSL and NERSC Computing Facilities

Pacific Northwest
NATIONAL LABORATORY

OUTLINE

- **e^-/h^+ Transport in TiO_2 electrodes**

- **electronic structure and reactivity on R(110)**
  - role of excess electrons from HO_b, O_{vac} ?
  - reactivity of oxygenated species

e^-/h^+ Transport and reactivity in Metal Oxide Photo-electrodes

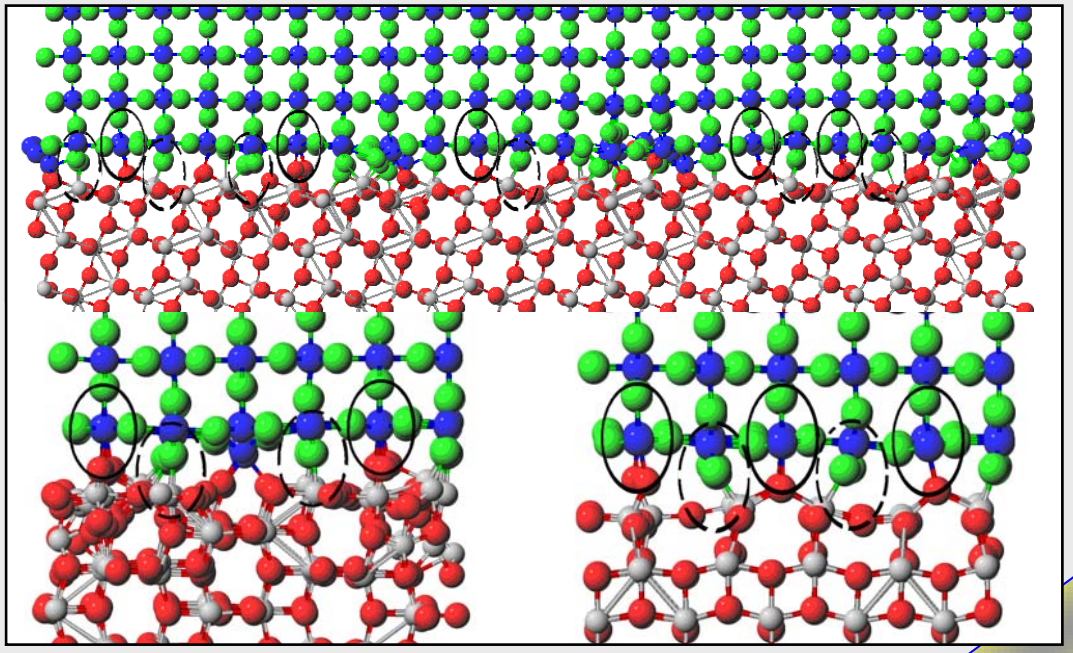
- Porous nanocrystalline transition metal oxide films have emerged as essential electrode materials for next-generation of photo-electro-chemical solar cells
  - photocatalysis
  - solar to fuel conversion
  - solar to electric conversion

- Breakthrough efficiency improvement in the diffusive e^-/h^+ transport in nanoparticulate metal oxides and across structurally complex metal oxide networks and interfaces are needed.

  priority research direction: "Fuels from water and sunlight: new photo-electrodes for efficient photo-electrolysis" and "Nanostructures for solar energy conversion: low cost and high efficiencies" in 2005 BES report on "***Basic Research Needs for Solar Energy Utilization***"

- Chemical physics characterization of photocatalysis on TiO_2

- **Goal** = multiscale simulation framework of the complex and collective charge carrier dynamics and reactivity toward the design of efficient photo-electrodes



Kinetic Monte Carlo
(complex;collective)

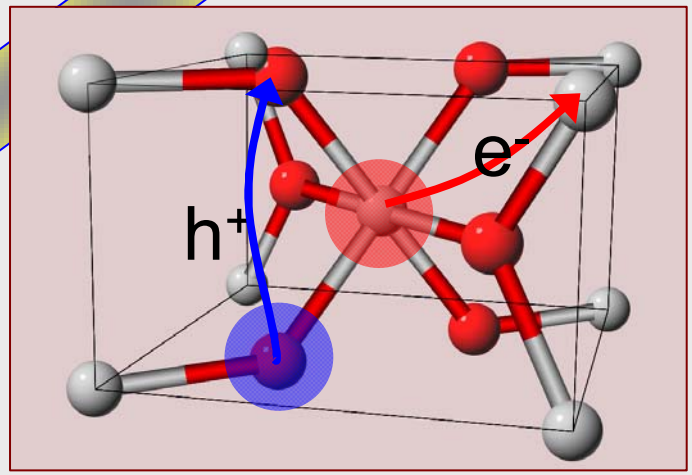
rates

MD; free energy
perturbation theory

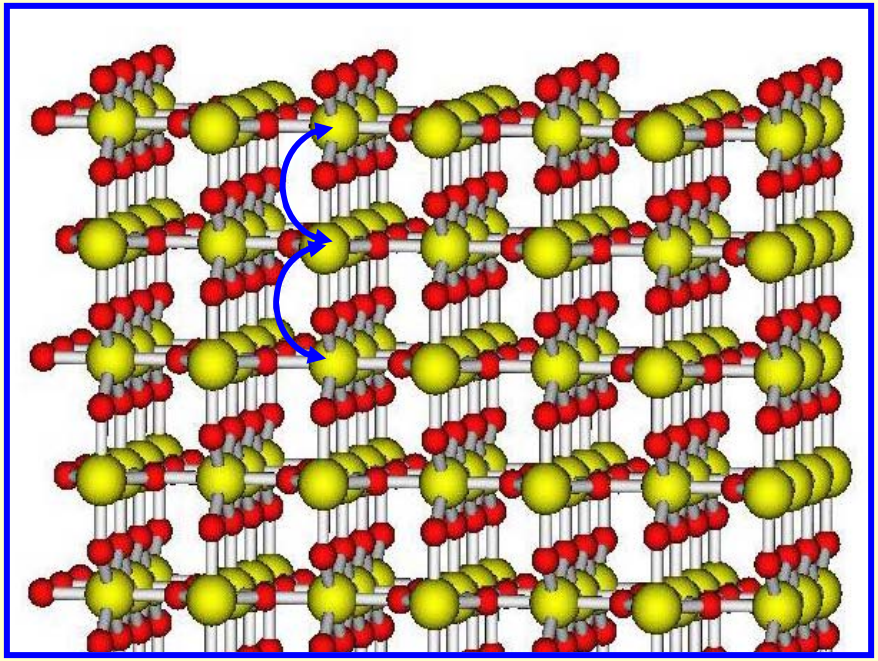
$$\Delta G = G_B - G_A = -RT \ln \left\langle e^{-\Delta H/RT} \right\rangle_A$$

parameters

QM(MO;DFT)



CHEMICAL PHYSICS of PHOTOCATALYSIS on TiO_2

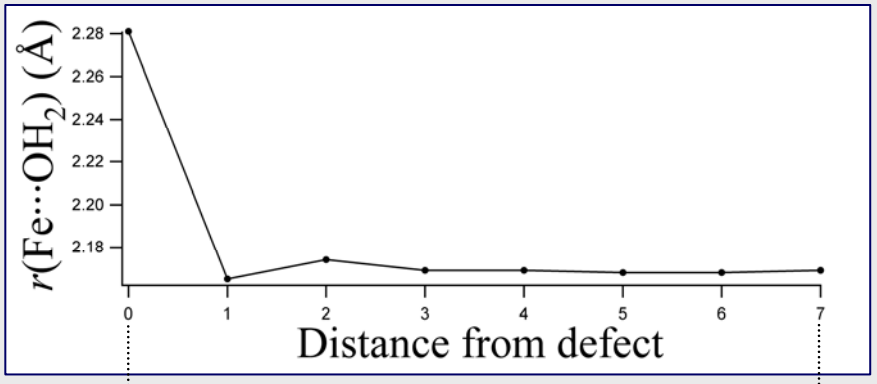


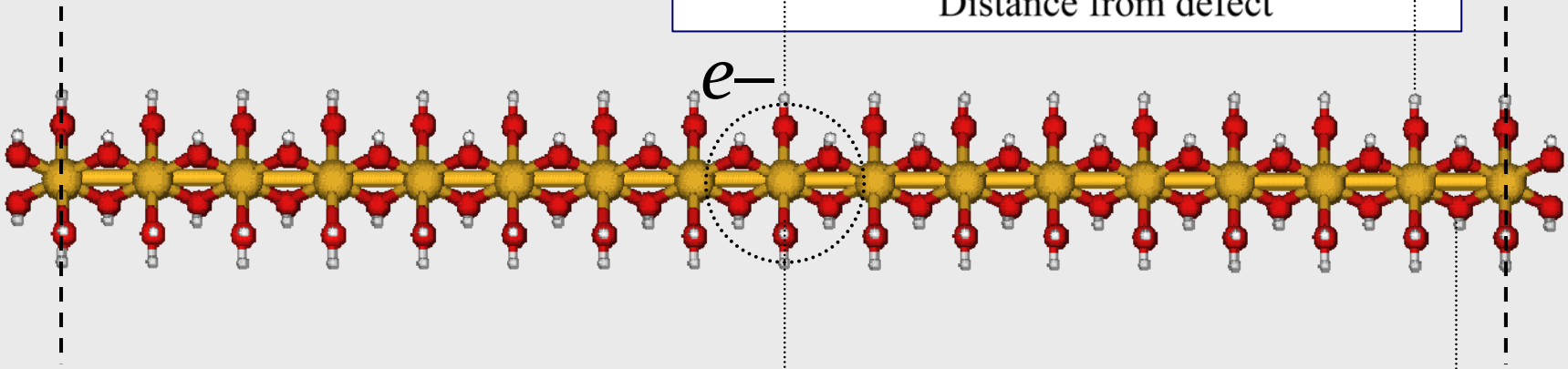
- **Charge carrier structure & dynamics**
  - rates of charge transport
  - trapping free energies
    - bulk
    - surface (terrace, steps, corners)
    - interface (rutile/anatase)
  - energy of activation for transport across interface (rutile/anatase)
  - interactions with adsorbates

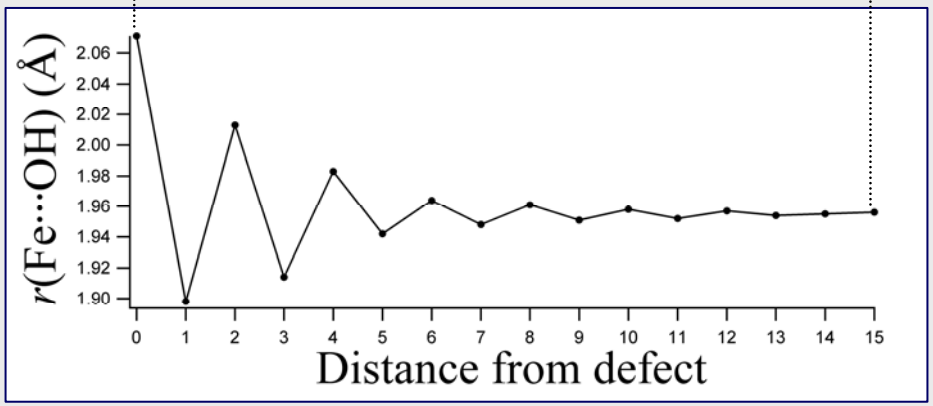
- **First principles characterization**
  - $\Rightarrow$ *ab initio* electronic structure & ET coupling
  - $\Rightarrow$ classical potentials for stochiometric TiO_2 and e^- / h^+ polarons
  - $\Rightarrow$ large scale MD & free energy calculations

  - Complex and collective dynamics at mesoscale (*kinetic Monte Carlo*)
    - spatial resolution
    - temporal resolution

Solid State ET – Polaron Distortion

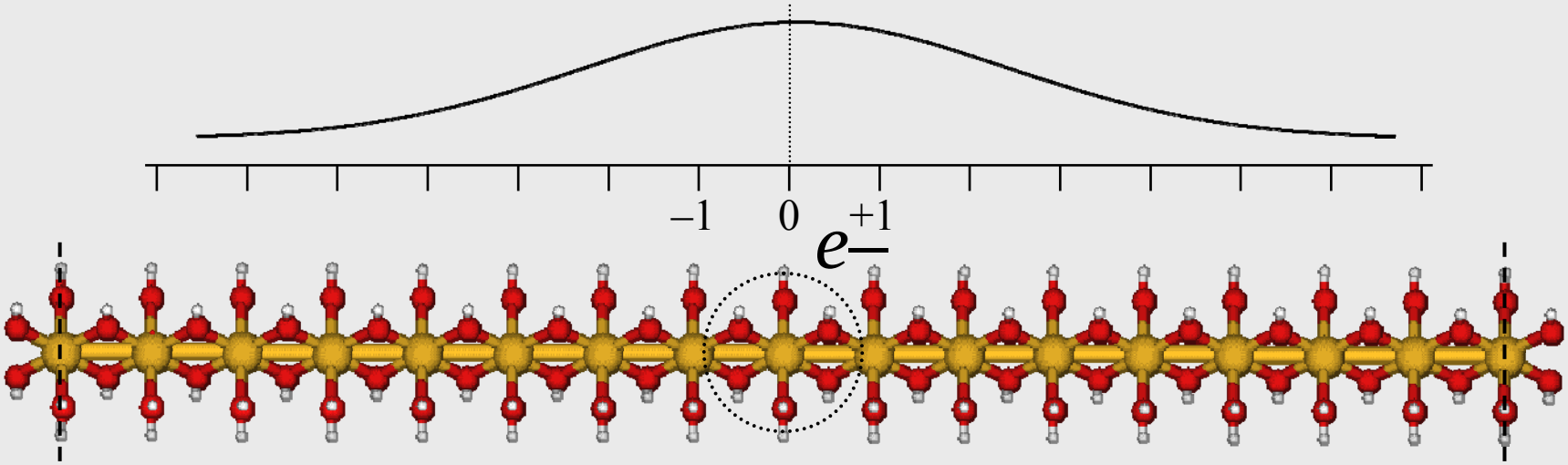


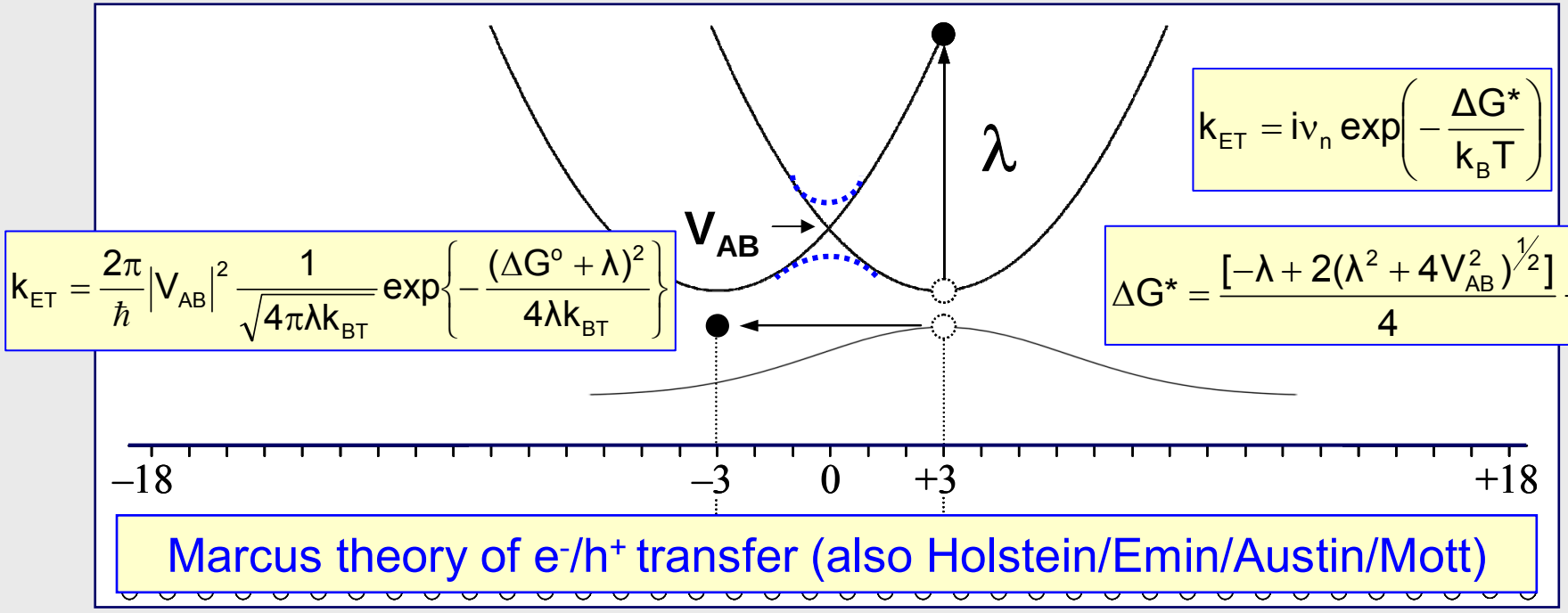




Crystal98 / LoptCG / UHF / Durand ECP

Solid State ET – Polaron Transfer





$$k_{ET} = i\nu_n \exp\left(-\frac{\Delta G^*}{k_B T}\right)$$

$$k_{ET} = \frac{2\pi}{\hbar}|V_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_{BT}}} \exp\left\{-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_{BT}}\right\}$$

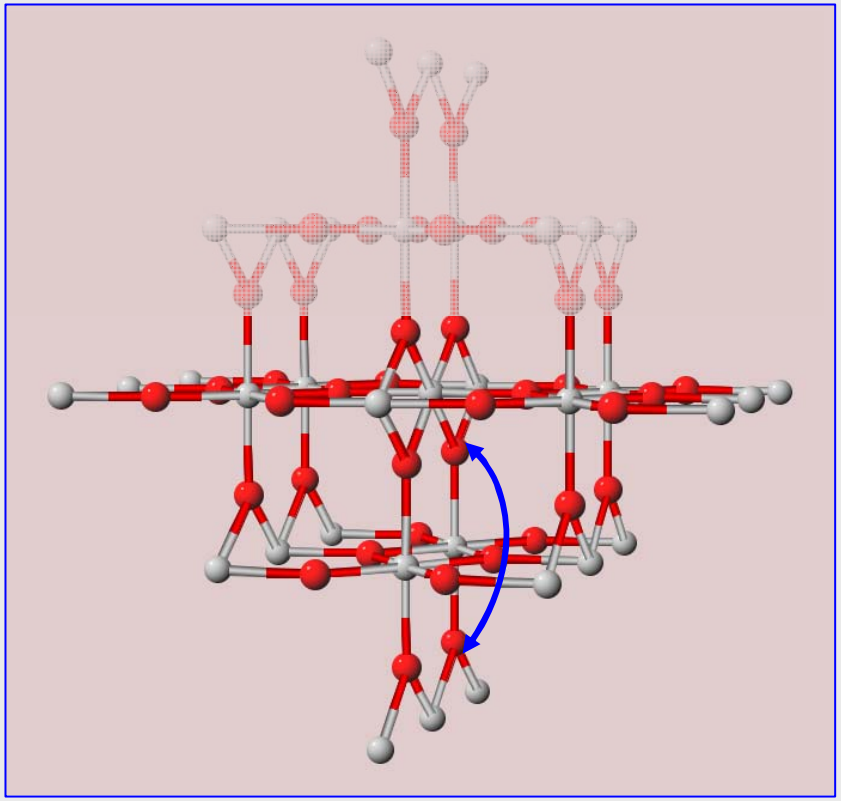
$$\Delta G^* = \frac{[-\lambda + 2(\lambda^2 + 4V_{AB}^2)^{1/2}]}{4} - V_{AB}$$

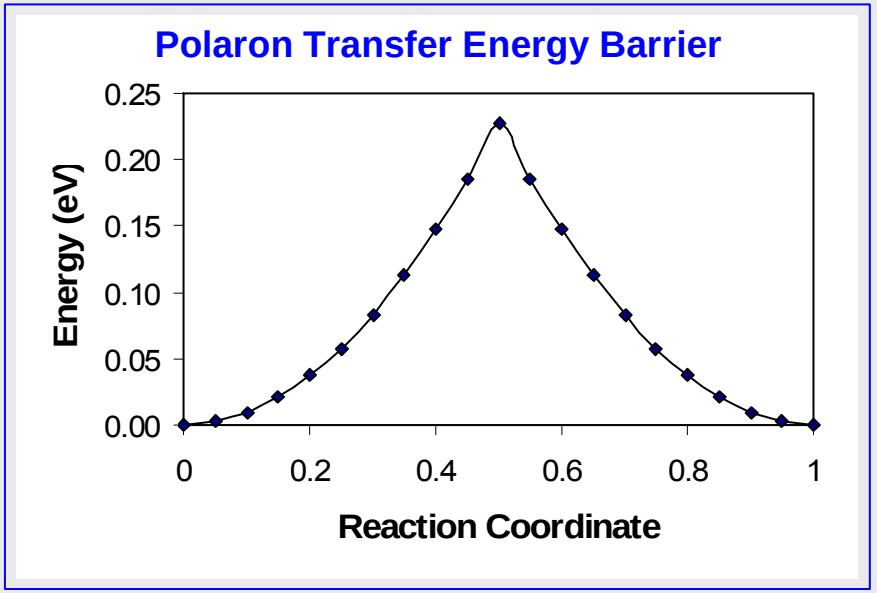
Marcus theory of e^-/h^+ transfer (also Holstein/Emin/Austin/Mott)

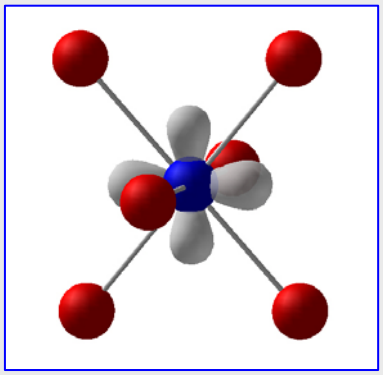
Bulk Rutile Polaron Transfer

- Marcus/Holstein theory for e^-/h^+ transfer

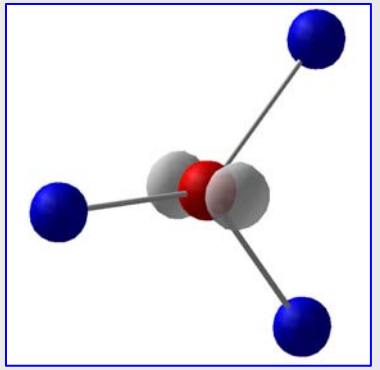
- DFT(GGA + U)
- U to match experimental band gap
- Linearized reaction coordinate







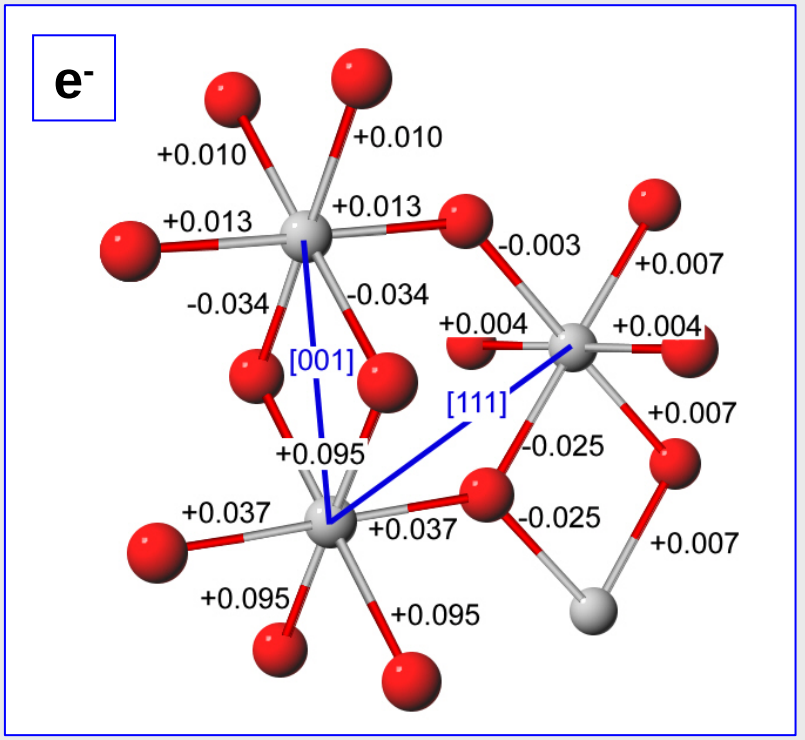
e^- polaron

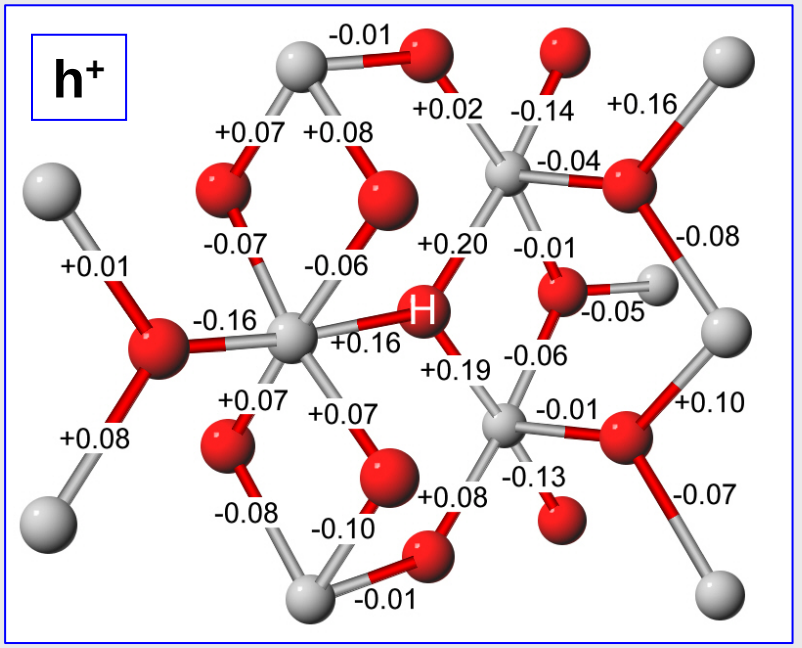


h^+ polaron

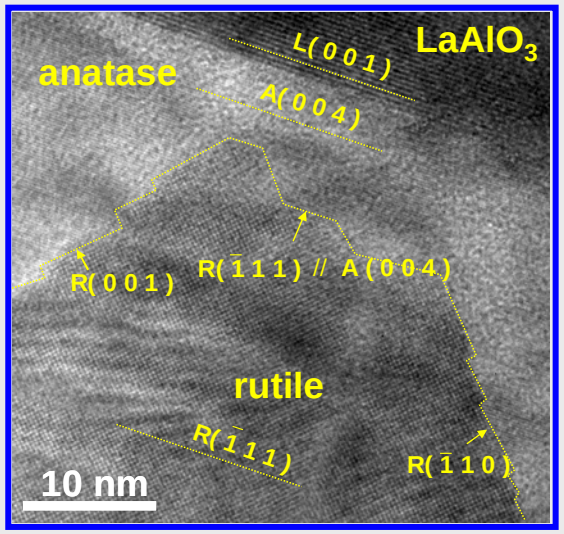
General Findings:

- **Lattice distortions smaller for e^- vs. h^+**
  - ~ 0.1 Å in e^- polaron vs. ~ 0.2 Å in h^+ polaron
  - increased Ti^{3+} – O^{2-} (increased elec. repul.)
  - increased O^{1-} – Ti^{4+} (decreased elec. attrac.)
- **Polaron size for h^+(O) larger than e^-(Ti)**
  - Distortions extend further in h^+ polaron
- **Thermal transport, phonon assisted**
  - $\Delta E_{act}(e^-)$ ~ 0.09 eV (expt. 0.07 eV)
  - $\Delta E_{act}(h^+)$ ~ 0.16 eV
  - in accord with experimental observation (Duzhko et al., PRB 64 (7) (2001)

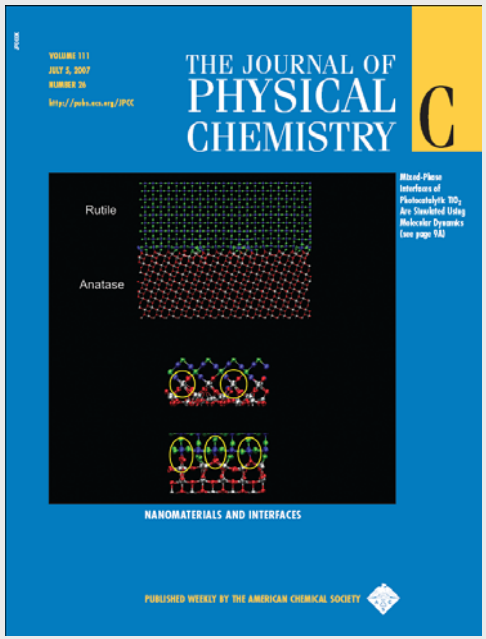


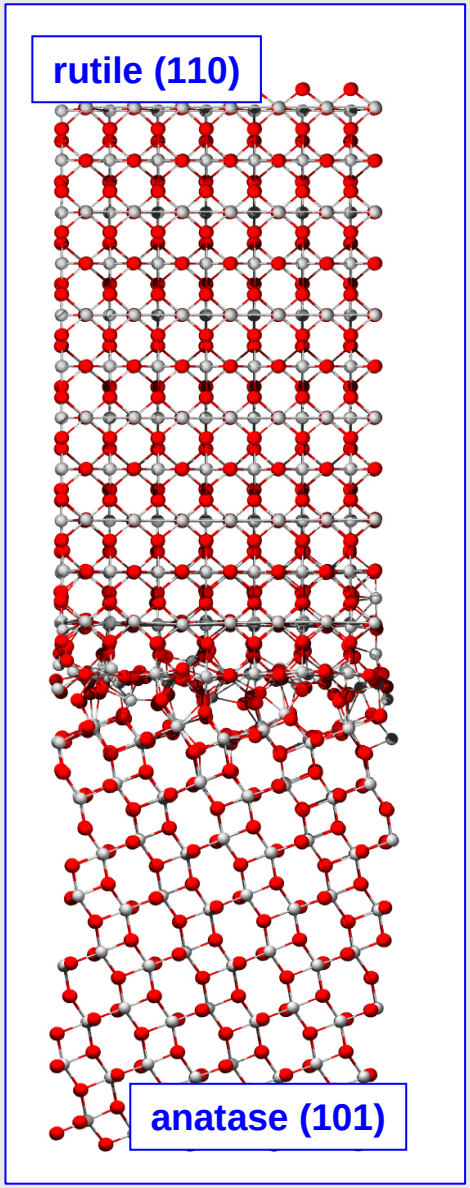


TiO_2-TiO_2 interface

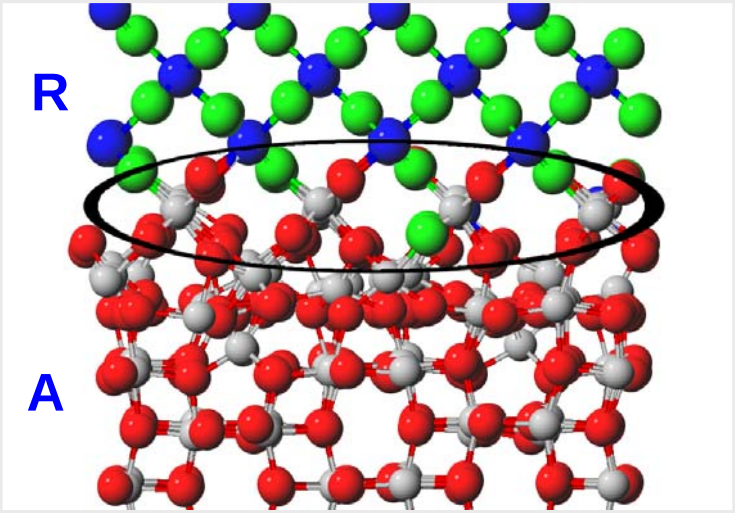


S.A.Chambers et al.,
Thin Solid Films 418 (2002) 197-210

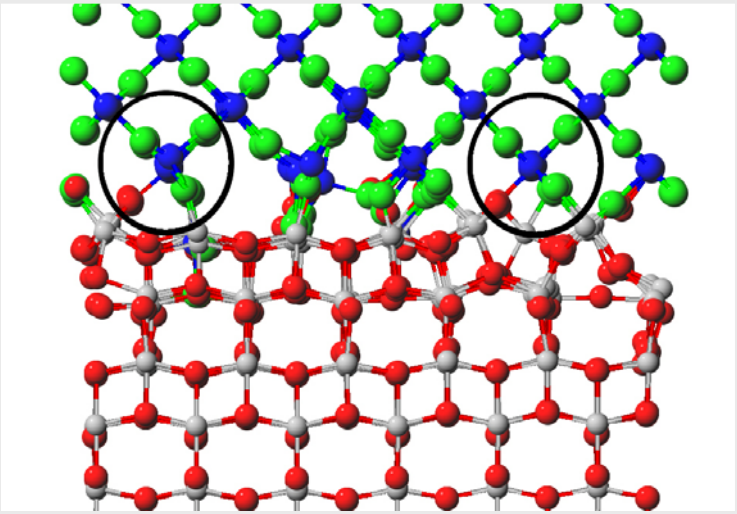




(110)r-(100)a Interface

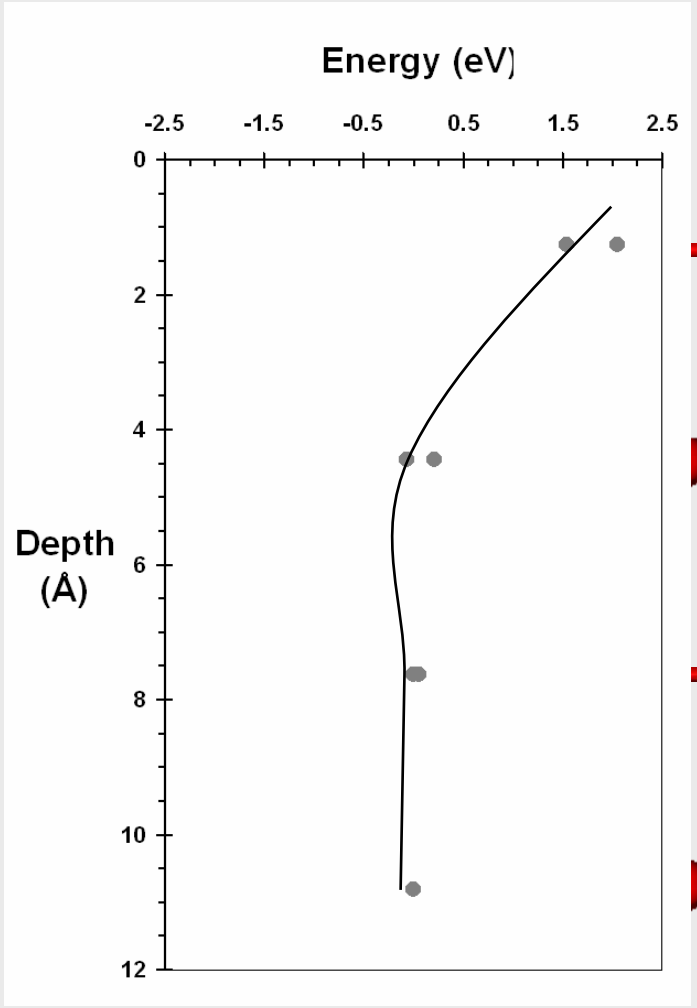


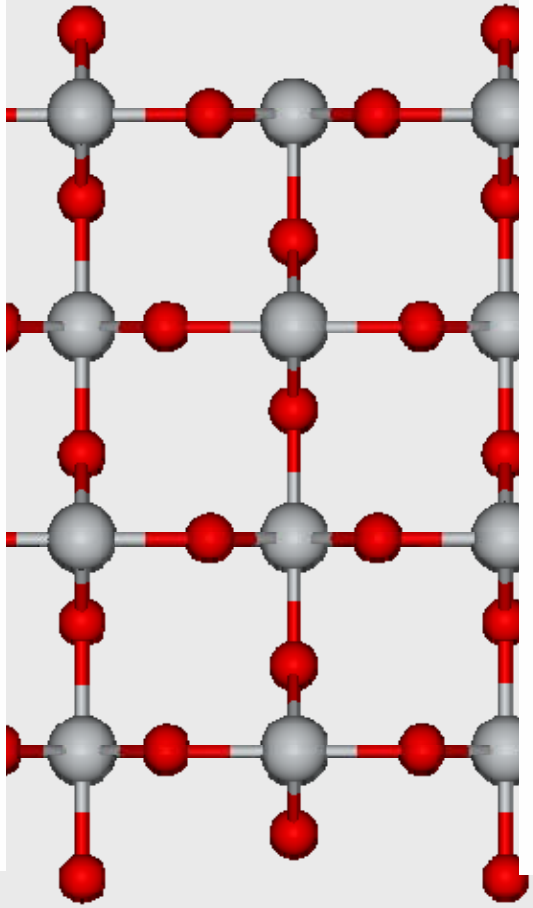
(100)r-(001)a Interface

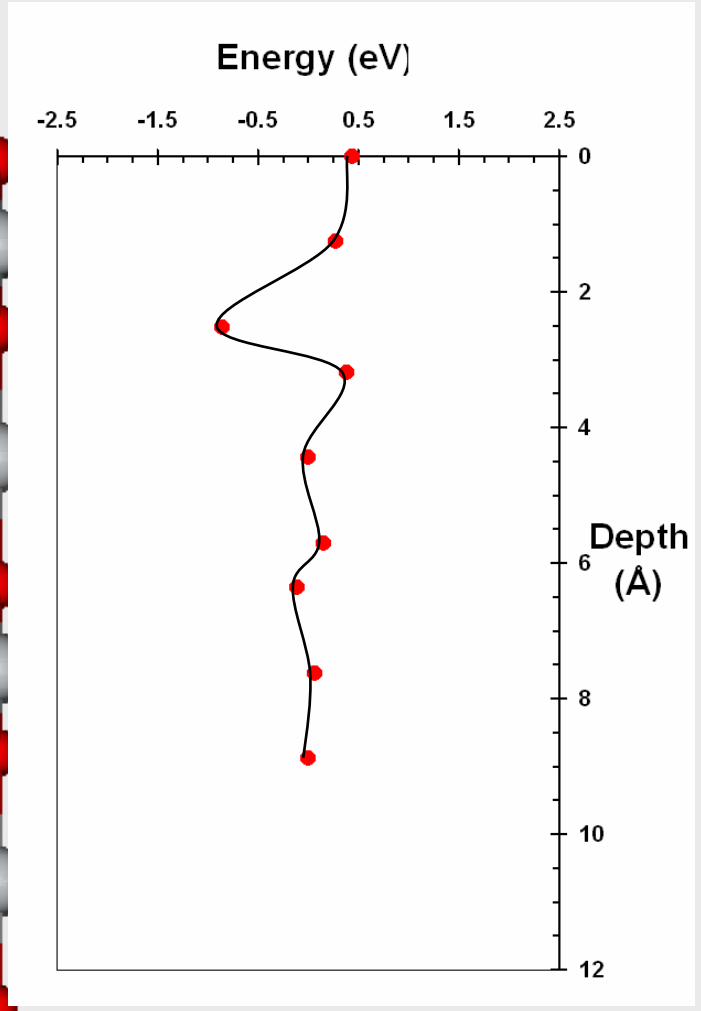


Formation of rutile octahedral structures

Rutile(110) Surface: free energy profile



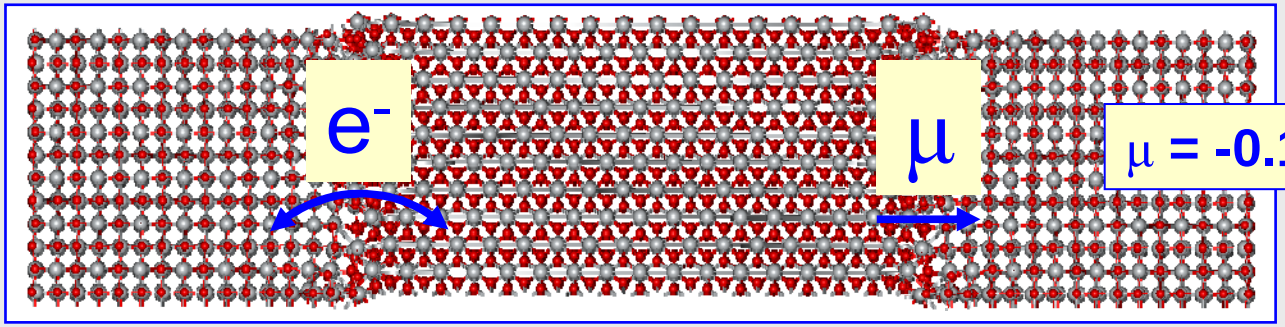




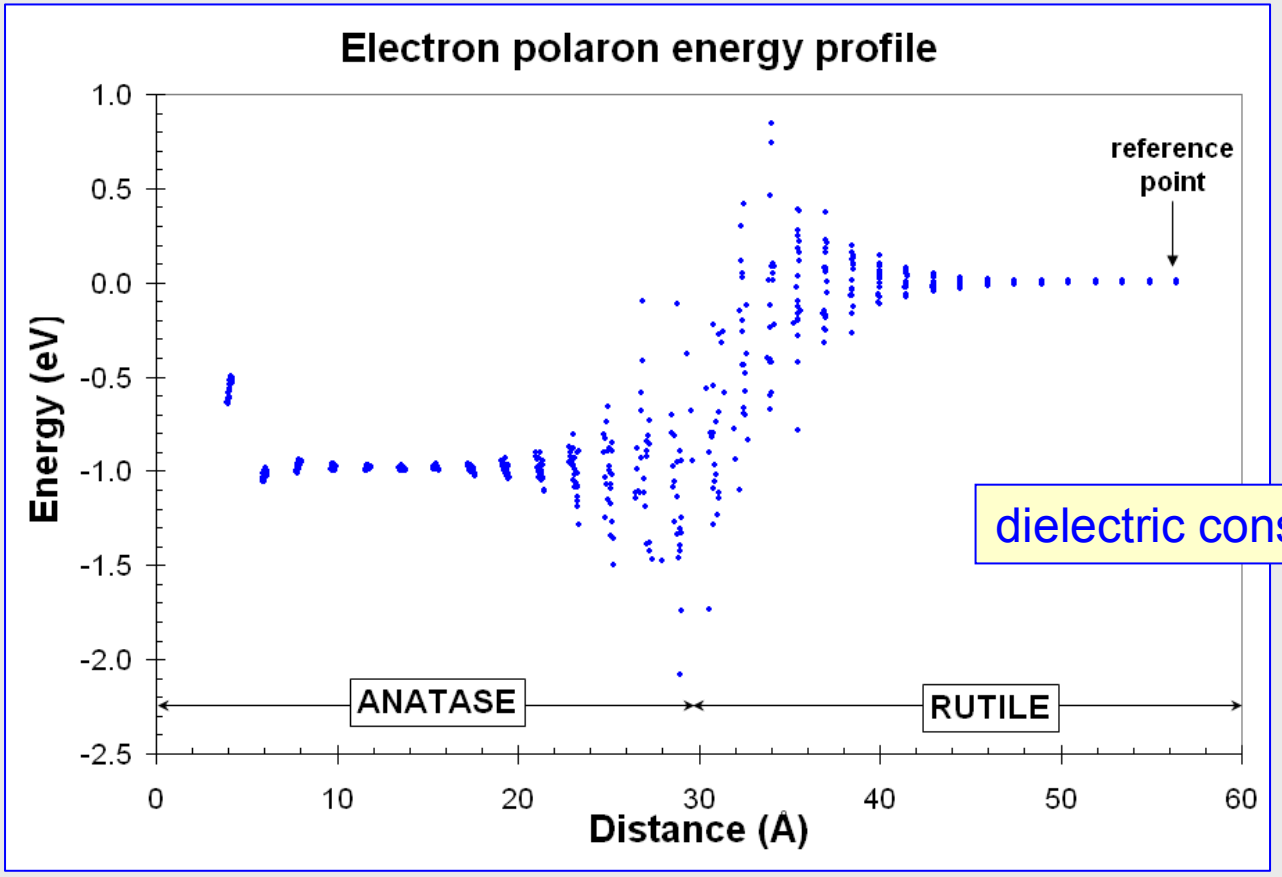
e^- polaron

h^+ polaron

e^- polaron across interface: energy profile

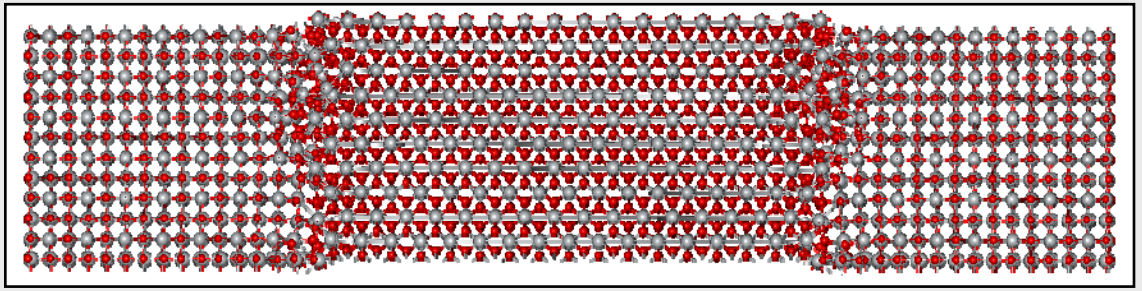


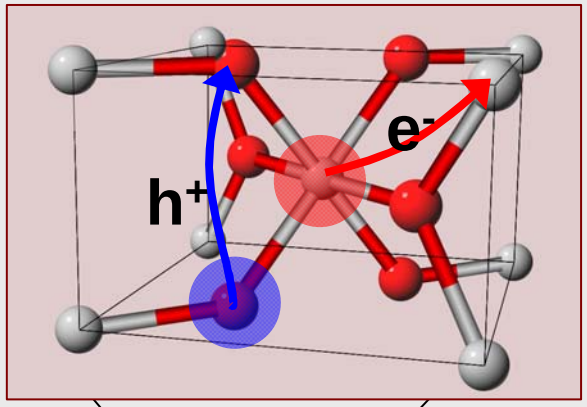
μ = -0.18 e.Å

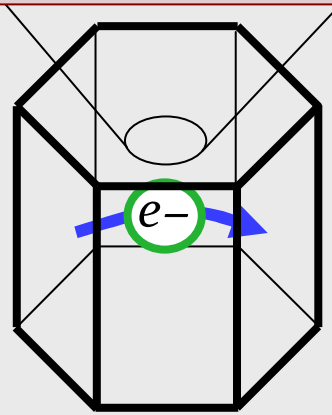


dielectric constant ?

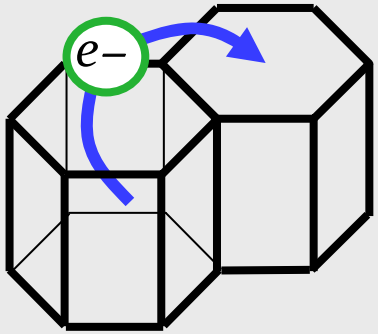
Multi-scale Approach



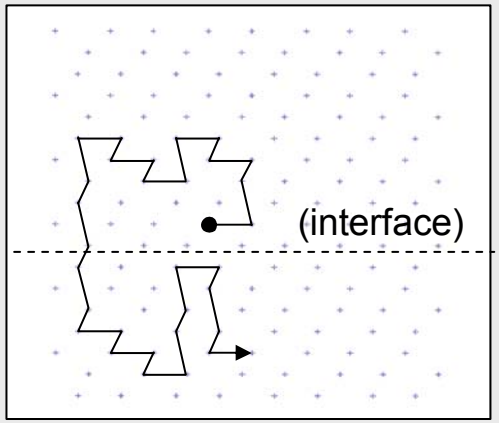




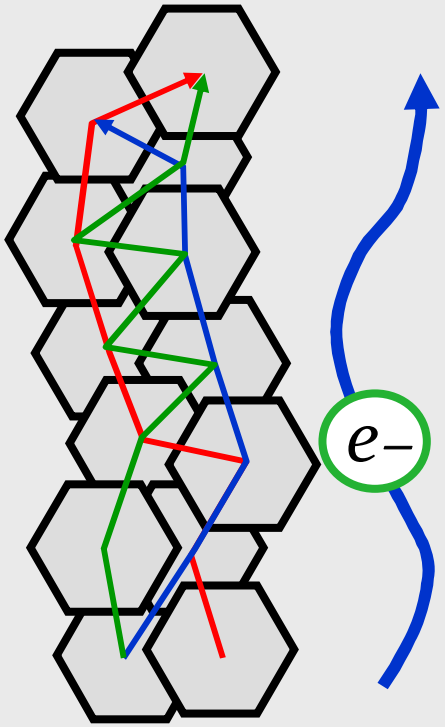
Intragrain (QM/meta-dynamics and MD)



Single interfaces (MM/MD and KMC)



Knowledge transfer



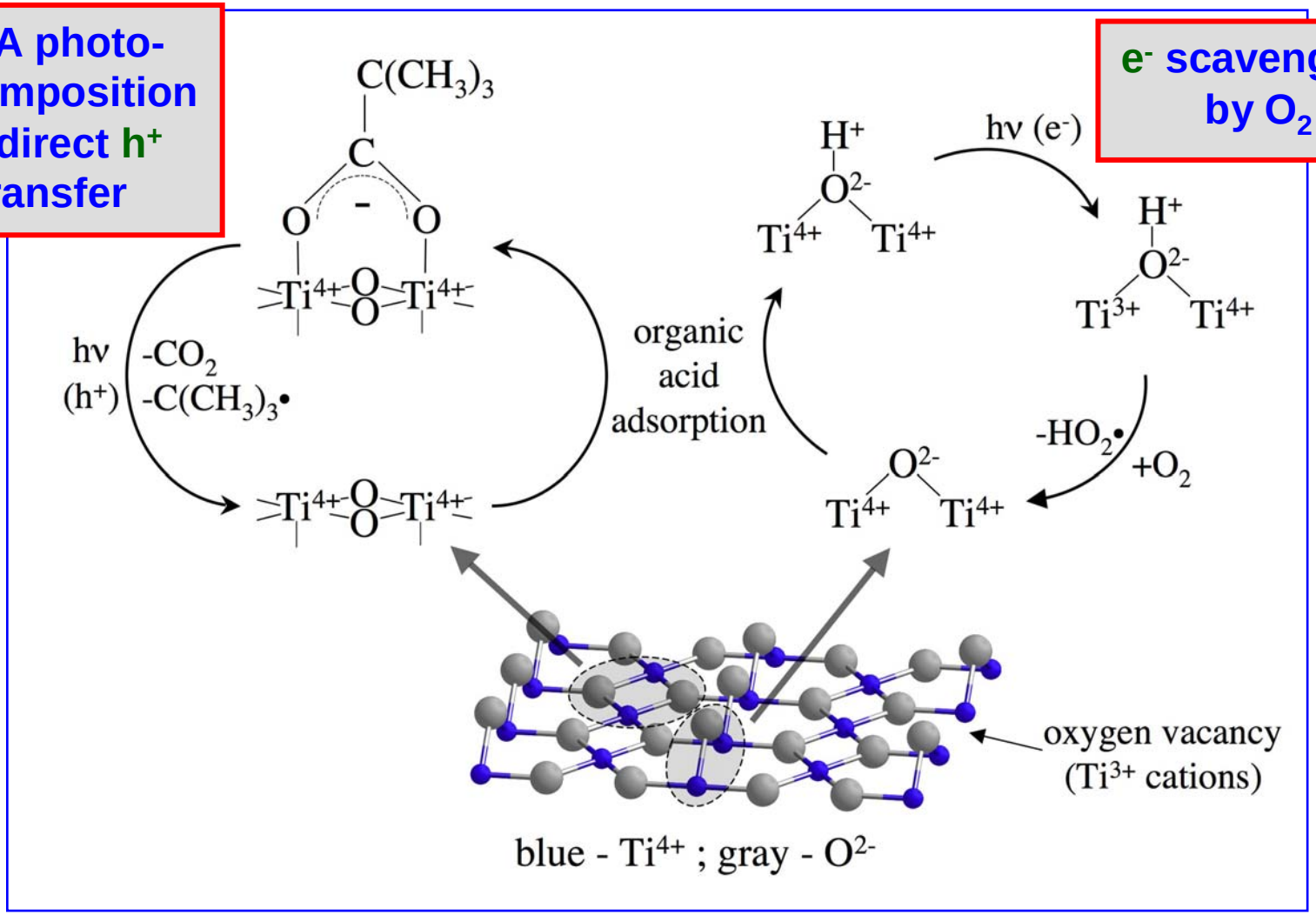
Polycrystalline networks (coarse-grained KMC)

CHEMICAL PHYSICS of PHOTOCATALYSIS on TiO_2:

M. Henderson, S. Chambers, W. Hess, Z. Dohnalek, and M. Dupuis

TMA photo-decomposition by direct h^+ transfer

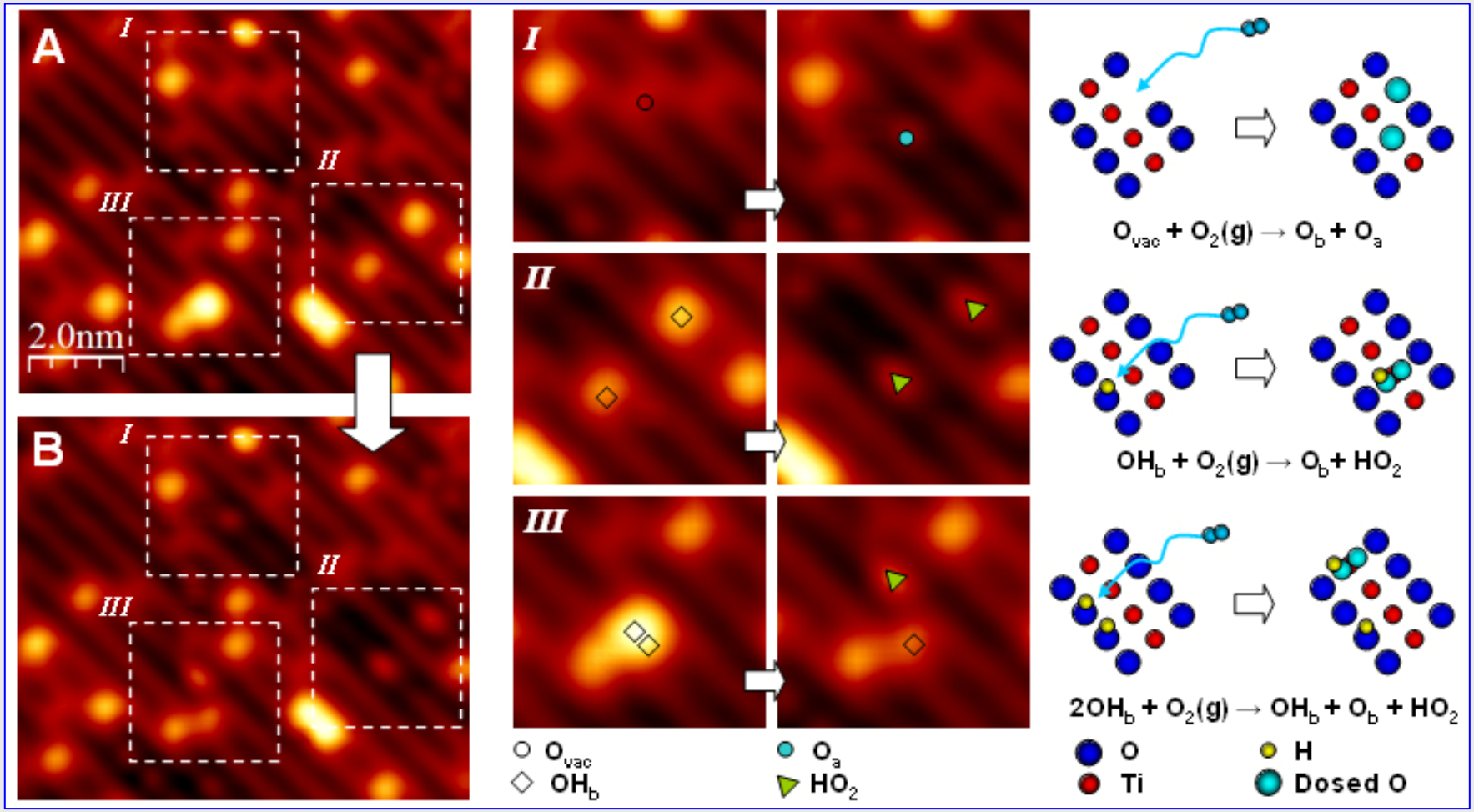
e^- scavenging by O_2



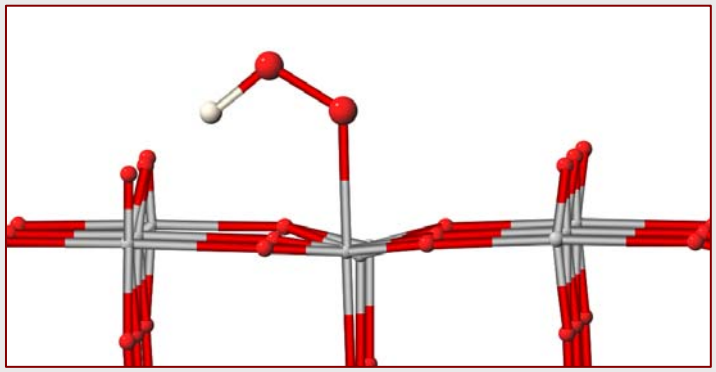
Coupled redox processes associated with photo-decomposition of organics on TiO_2(110).

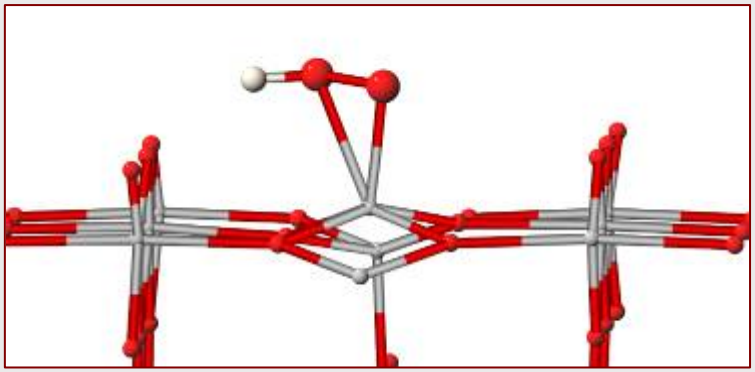
Reaction of O_2 with Hydroxylated rutile (110) Surfaces

Yingge Du, Zhenrong Zhang, Zdenek Dohnálek, Igor Lyubinetsky (PNNL)
JPC 00, 0000 (2008)



HOO on rutile(110)

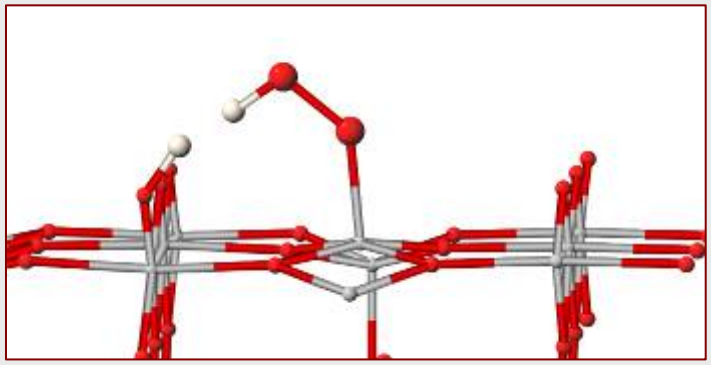


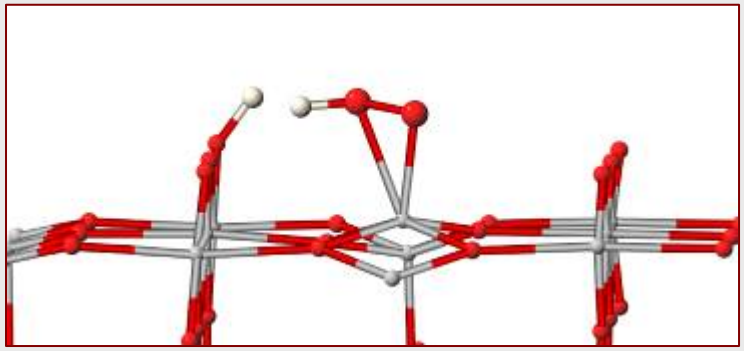


ΔE = -0.66 eV

$O_2(g) + HO_b \rightarrow HOO(ads)$

ΔE = +0.08 eV



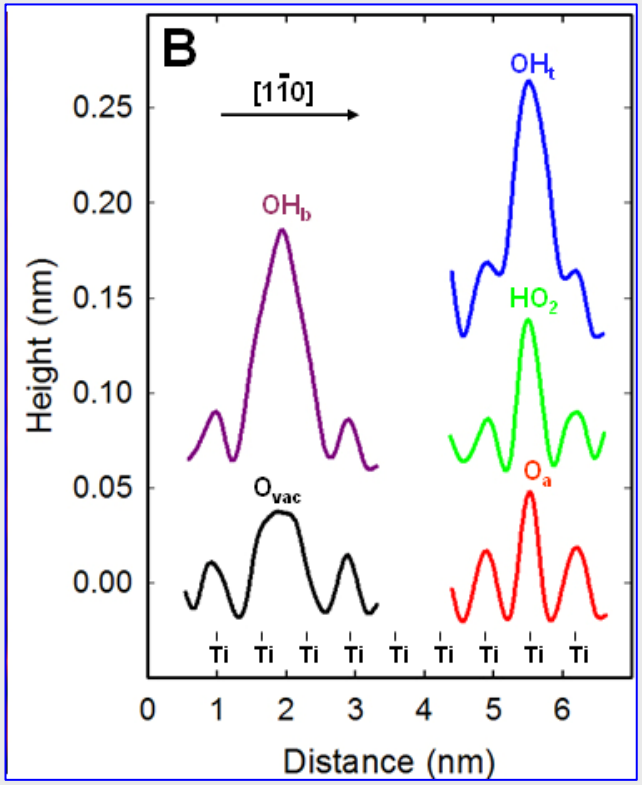


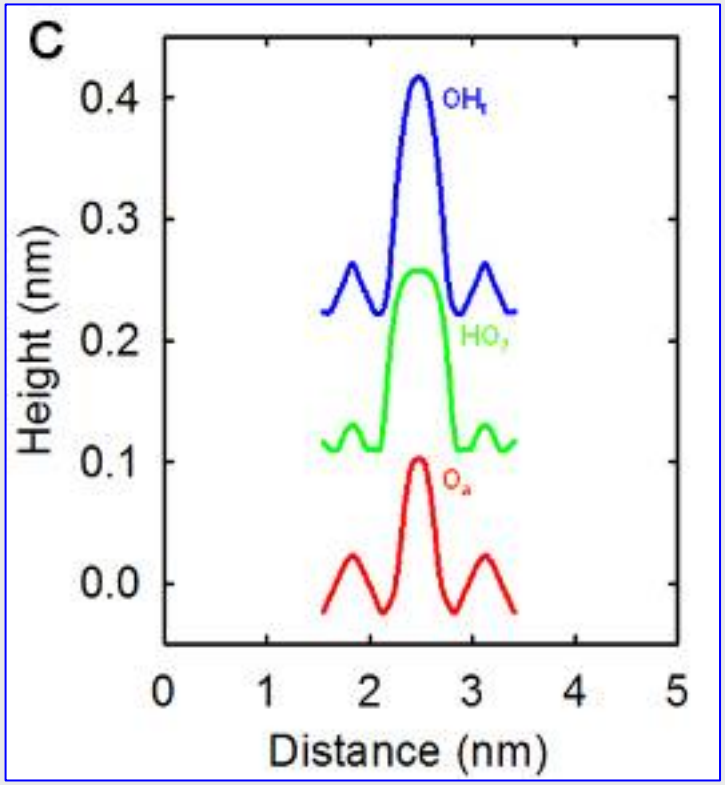
ΔE = -1.91 eV

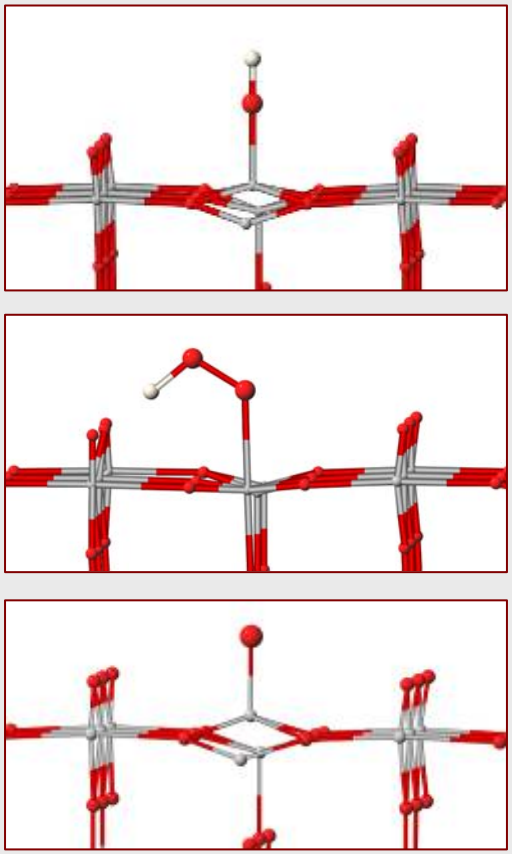
$O_2(g) + 2HO_b \rightarrow HOO(ads) + HO_b$

ΔE = -1.91 eV

STM Peak Identification





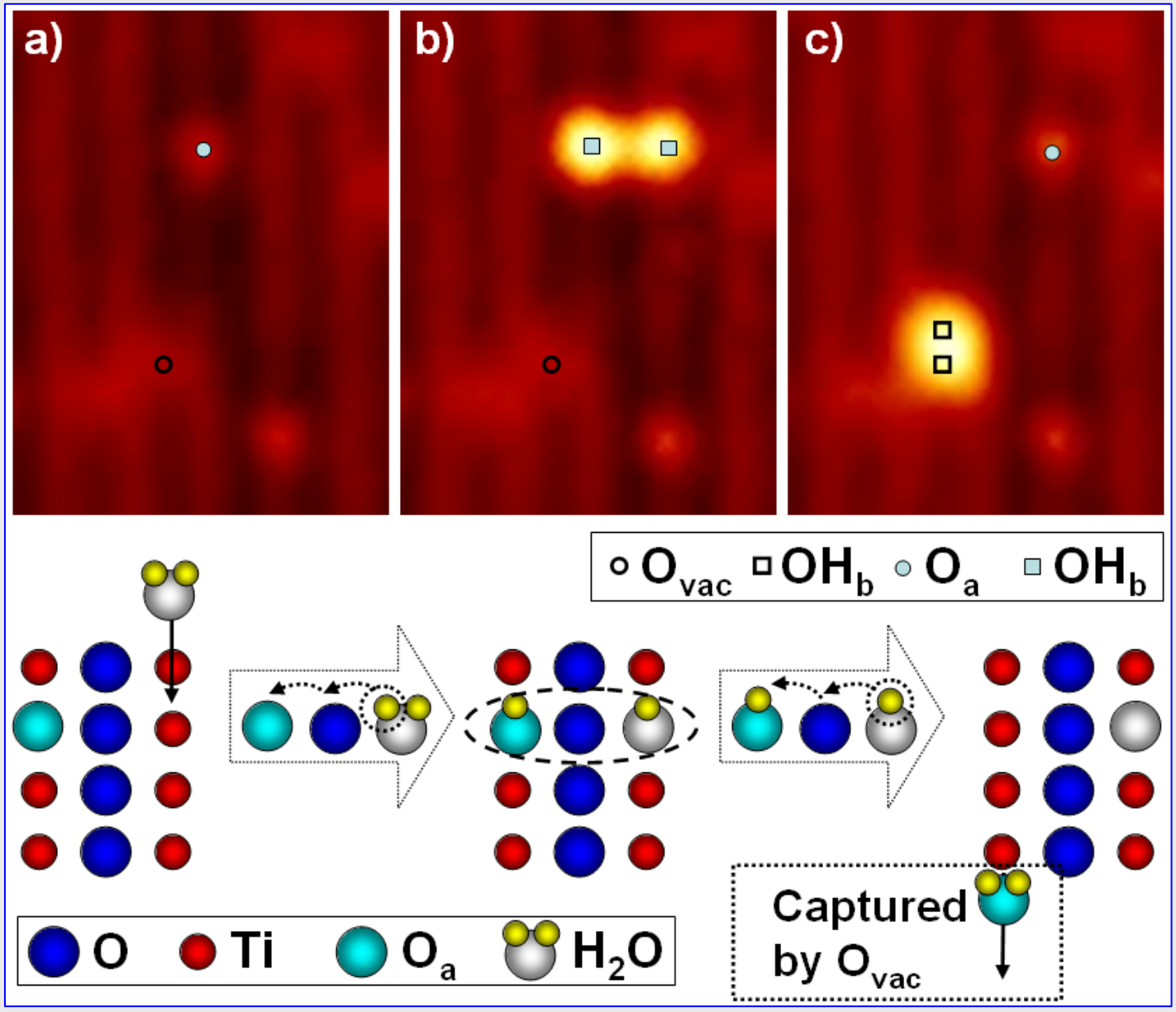


STM (experiment)

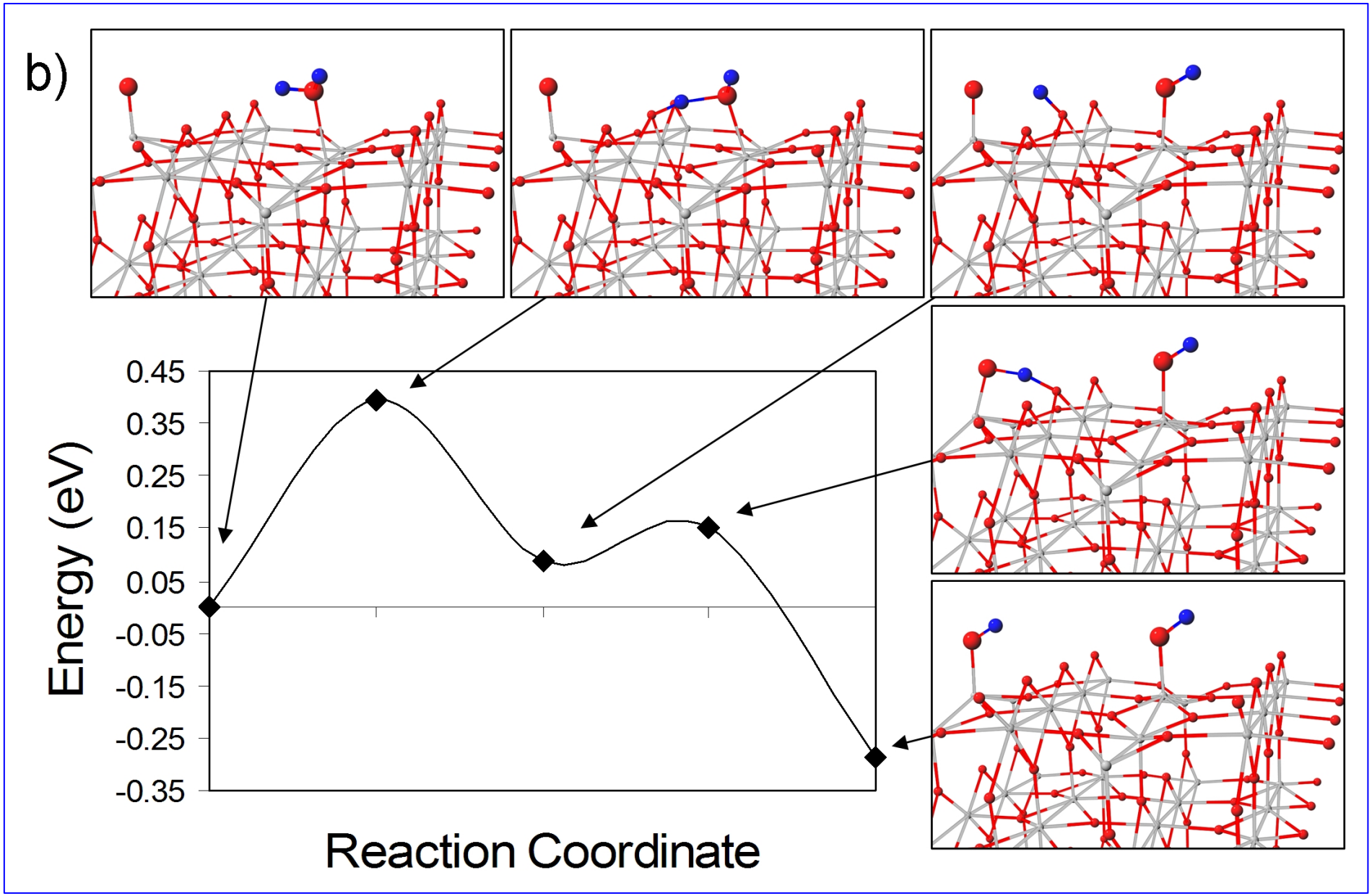
STM (theory)

$$h_{HO\text{-}Ti5c} > h_{HOO\text{-}Ti5c} > h_{O\text{-}Ti5c}$$

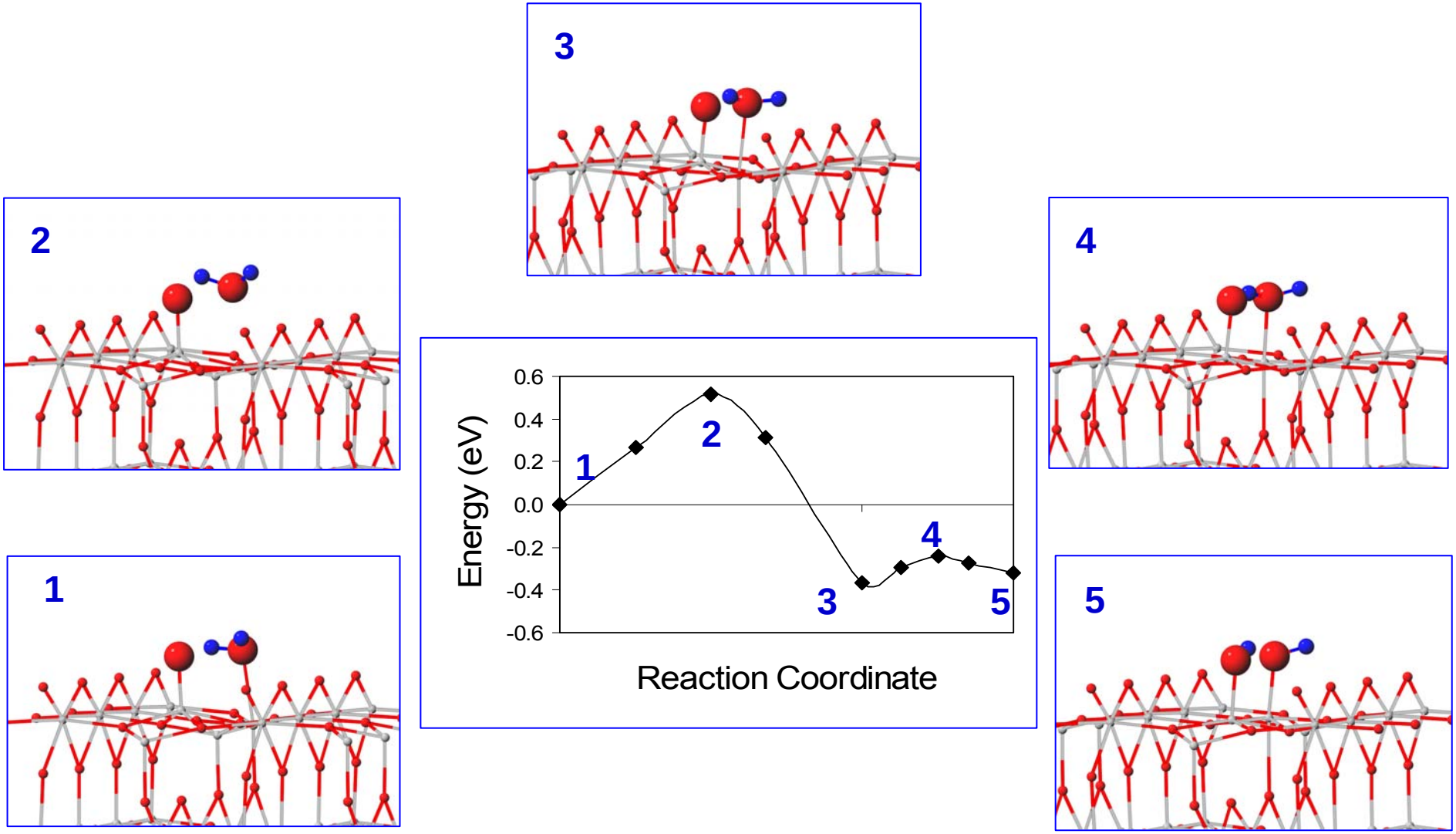
O Scrambling from {H_2O:O_{ad}} : O_{ad} hopping across rows



O Scrambling from {H_2O:O_{ad}} : O_{ad} hopping across rows



O Scrambling from $\{H_2O{:}O_{ad}\}$: O_{ad} hopping along rows



OUTLINE

- **e^-/h^+ Transport in TiO_2 electrodes**

- **electronic structure and reactivity on R(110)**
  - structure of excess electrons from HO_b, O_{vac}
  - reactivity of oxygenated species