Photocatalysis on TiO_2: insights from simulations

- TiO_2 as a prototypical material in photocalysis: surfaces, defects, reactivity
- Excess and photoexcited electrons at TiO_2 surfaces and aqueous interfaces
- Formation and structure of "black TiO_2"

Princeton University

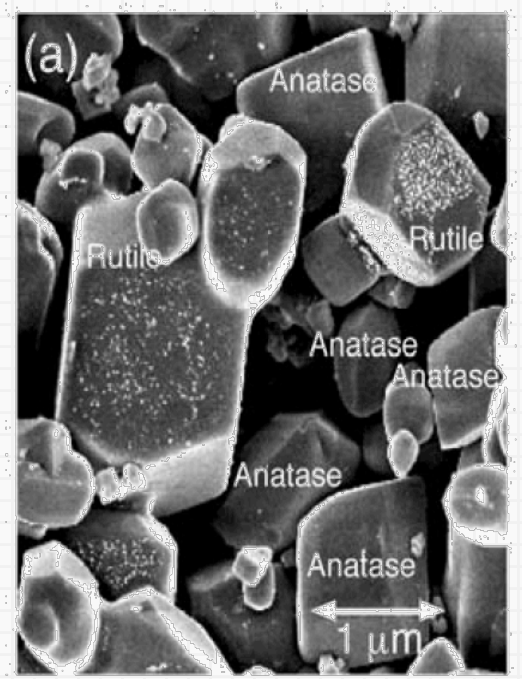
Photocatalysis on TiO_2: insights from simulations

Annabella Selloni
Department of Chemistry, Princeton University

Work with: Ulrich Aschauer, Jia Chen, Hongzhi Cheng, Cristiana Di Valentin, Ye-Fei Li, **Sencer Selcuk**, Patrick Sit, Antonio Tilocca, Andrea Vittadini, **Xunhua Zhao**

Expt: U. Diebold & M Setvin, TU-Wien

Titanium dioxide is among the most popular metal oxides



Ohno, New J. Chem, 2002

- Abundant & inexpensive
- Non-toxic, biocompatible, photostable

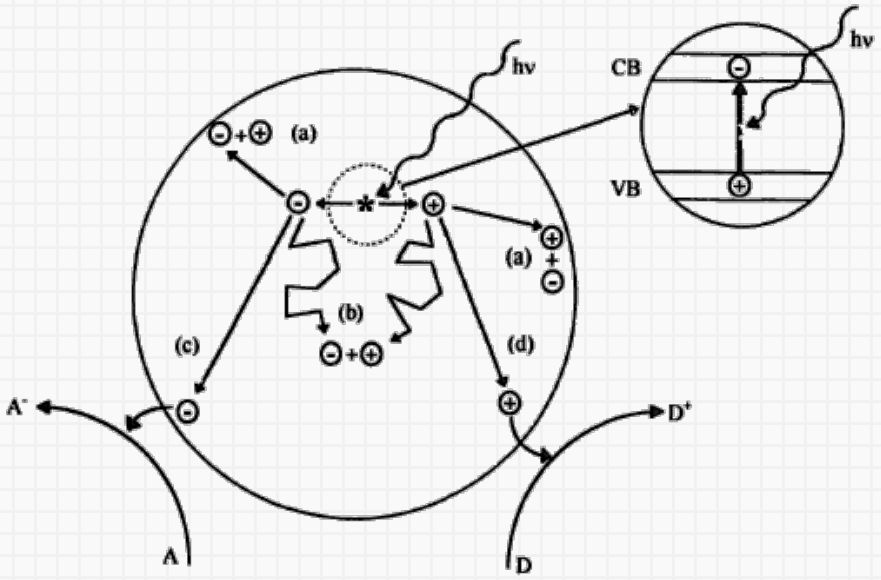
- Photocatalysis — Honda & Fujishima, Nature, 1972
- Dye sensitized solar cells — O'Brian & Grätzel, Nature, 1991
- Memristors — Williams et al Nature 2008

Rutile stable in bulk – **Anatase** in Nanomaterials

Anatase photocatalytically more active than rutile

Photocatalysis, DSSC & carrier diffusion

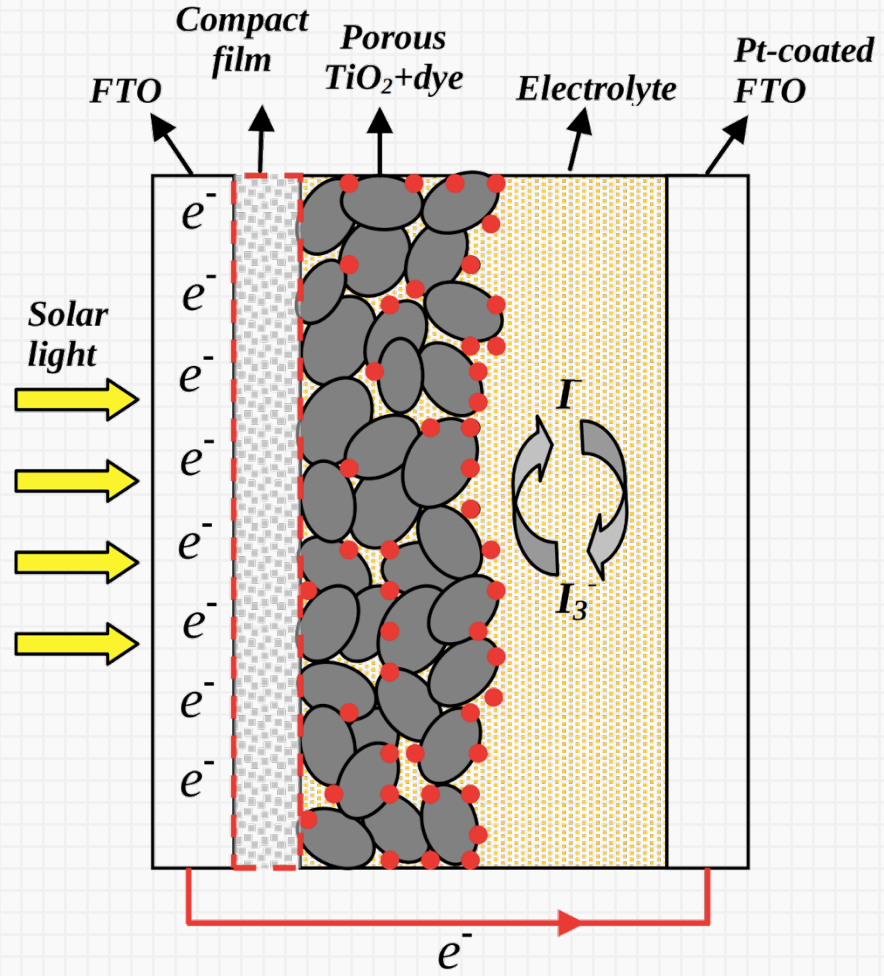
Photocatalysis



Yates, Chem. Rev. 1995

- Absorption & generation of e-h
- Carrier diffusion to the surface
- Charge transfer to adsorbed species

DSSC



- Transport of photoinjected electron through nanostructured film

Excess and photoexcited electrons show similar behavior

- As a reducible oxide, TiO_2 unavoidably contains oxygen vacancies and Ti interstitials
  - 1 O-vacancy = 2 excess electrons
  - 1 Ti interstit. = 4 excess electrons
- Other donors include metal and non-metal impurities, e.g. Nb (substituting Ti), F (replacing O), adsorbed and interstitial atomic H, etc

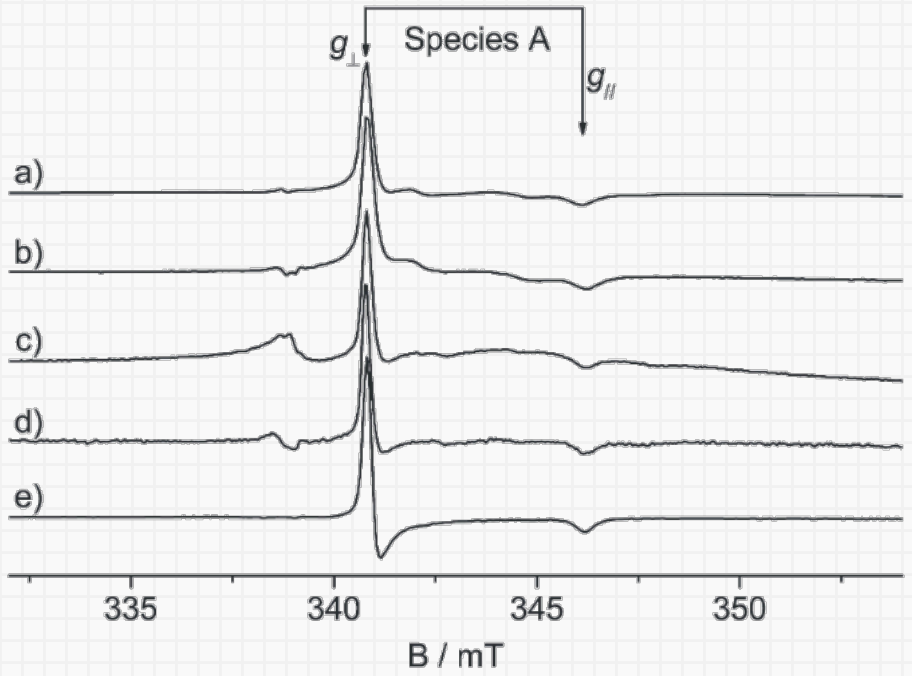
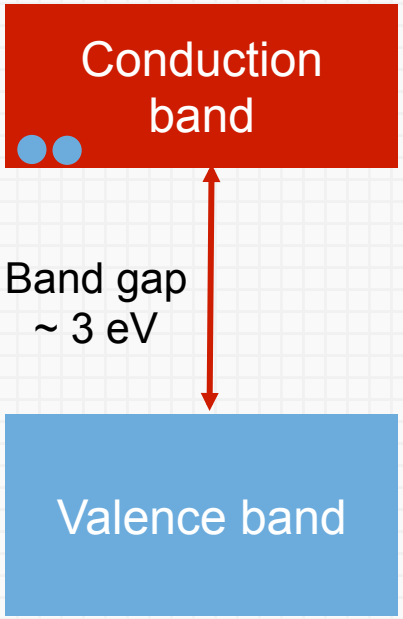
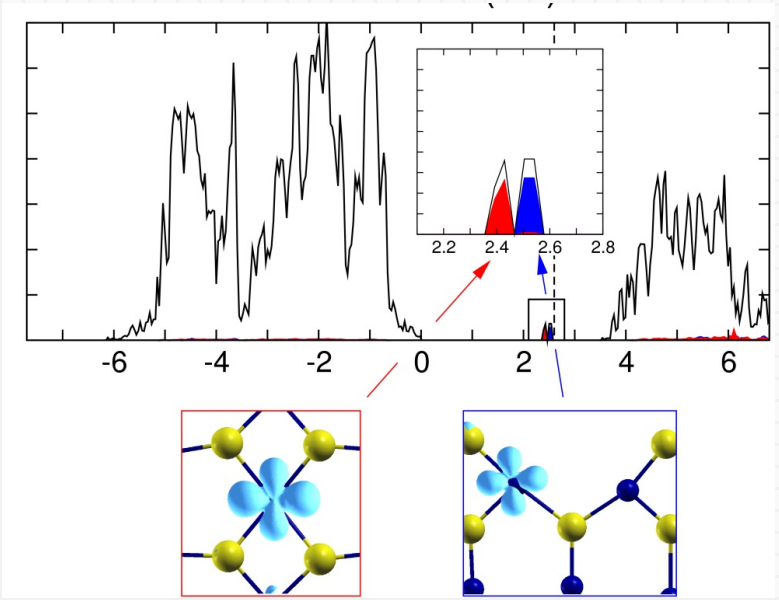


Figure 2. CW-EPR spectra in X band of (a) UV-irradiated anatase in a hydrogen atmosphere, (b) anatase contacted with atomic hydrogen, (c) anatase treated with Na vapors, (d) anatase annealed in vacuo at 570 K, and (e) Nb-TiO_2 (for comparison).

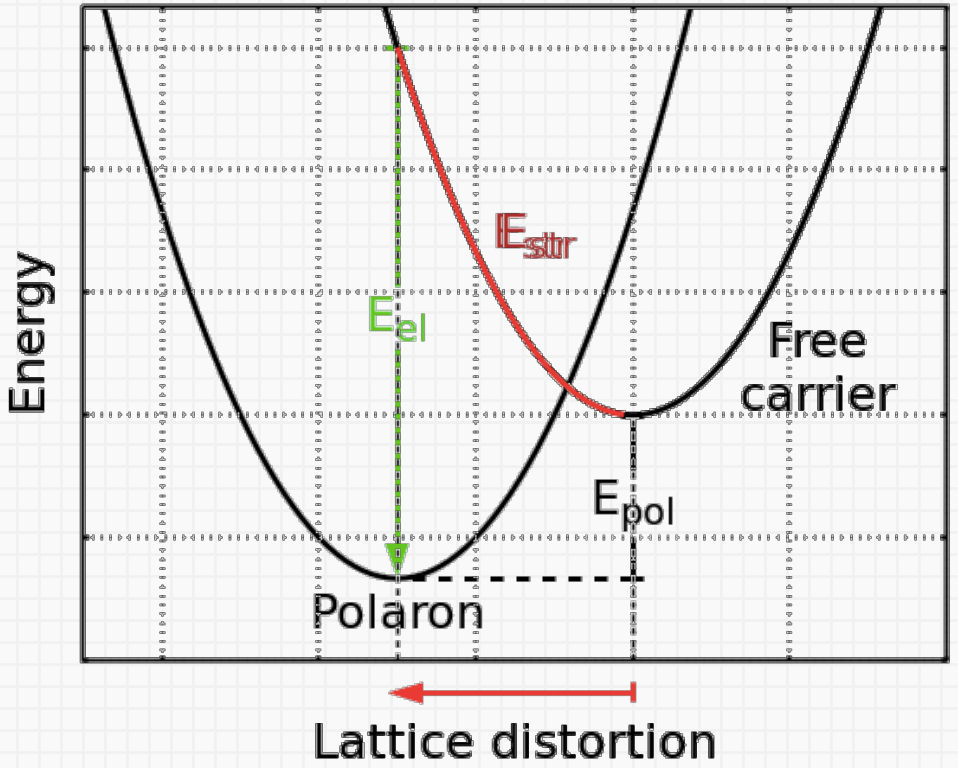
Livraghi, JPCC, 2011

Excess electrons: delocalized CB states or localized “polarons”?





O-vacancy @ rutile (110)
Di Valentin et al PRL 2006

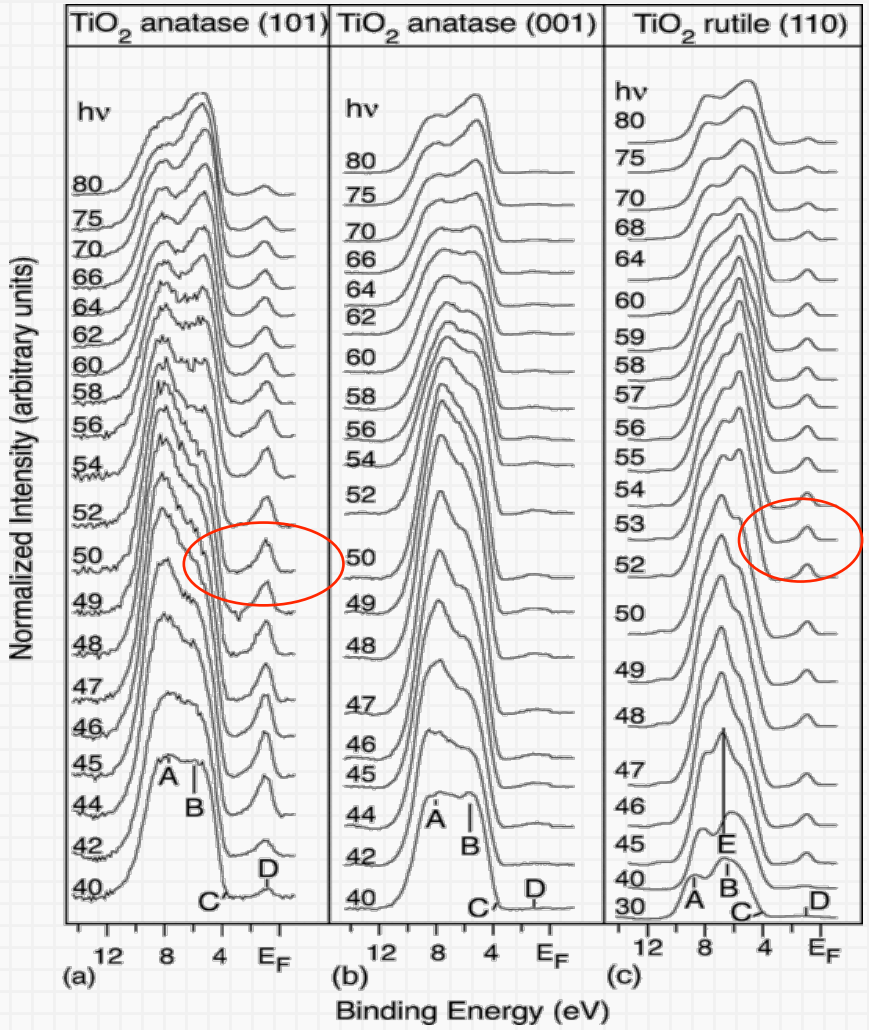


Deep gap state (GS)
=
Better localization
=
Small polaron

Shallow GS
=
Less localization
=
Large polaron

Small polarons in rutile; picture more complicated in anatase

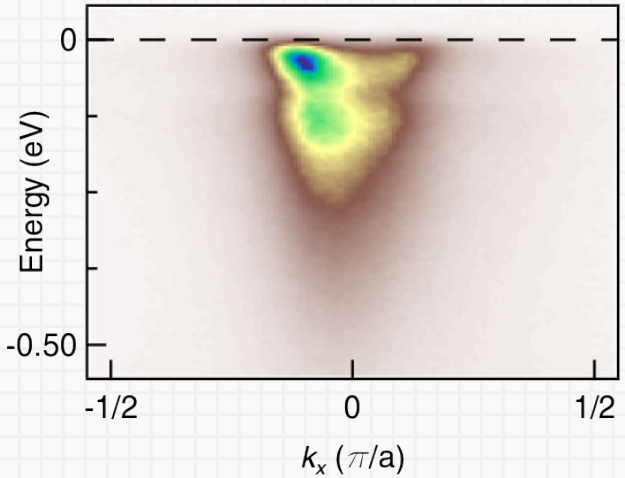
Evidence of both shallow and deep states in anatase



Deep gap state
~1 eV binding energy
indicates small polarons

No gap state
on anatase
(001)

ARPES anatase (001)



happens around $n_e^* \simeq 10^{19}$ cm^{-3}. Estimating the polaron radius r_p from the average separation between polarons $d \sim n^{-1/3} = 2r_p$, gives $r_p \sim 20$ Å. By comparison,

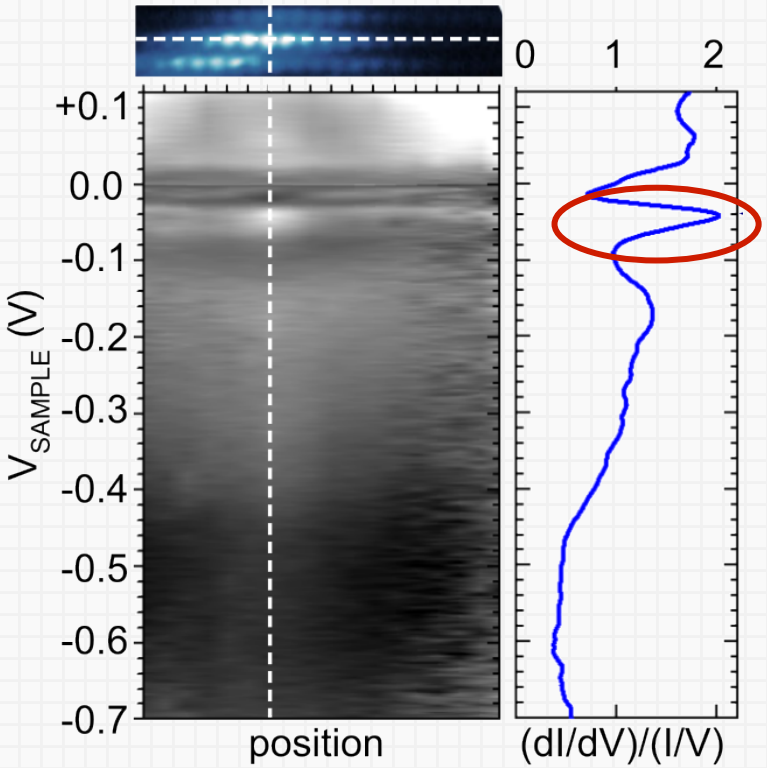
Shallow gap state
~40 meV binding energy indicates large polarons

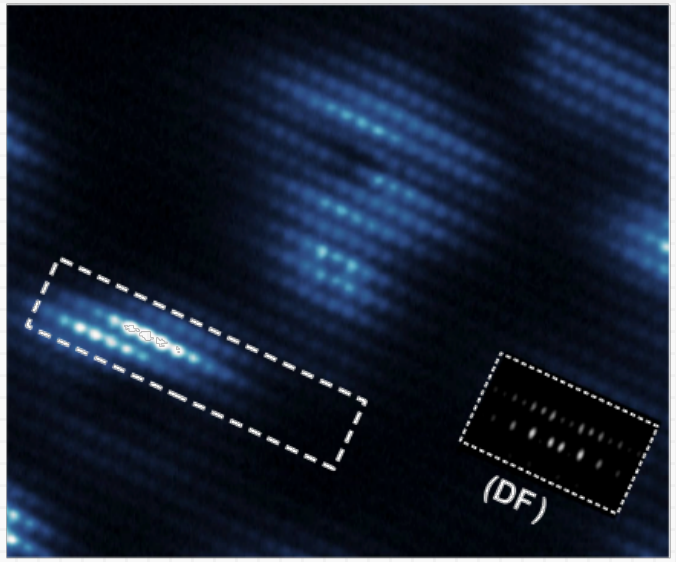
Thomas et al. PRB 2007

Moser et al PRL 2013

Evidences of both shallow and deep states in anatase

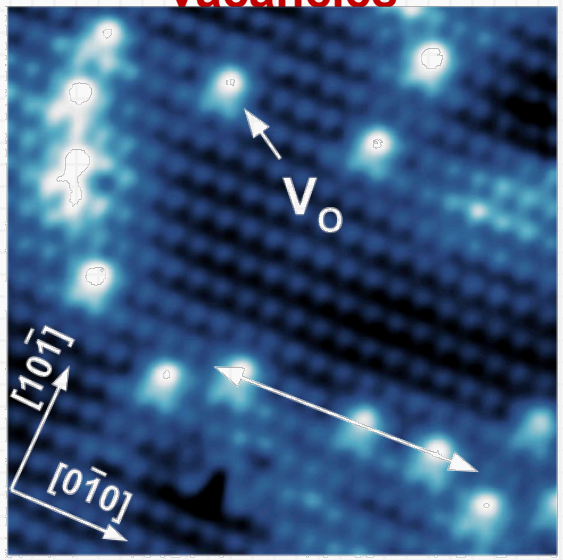
Shallow levels on subsurface Nb impurities



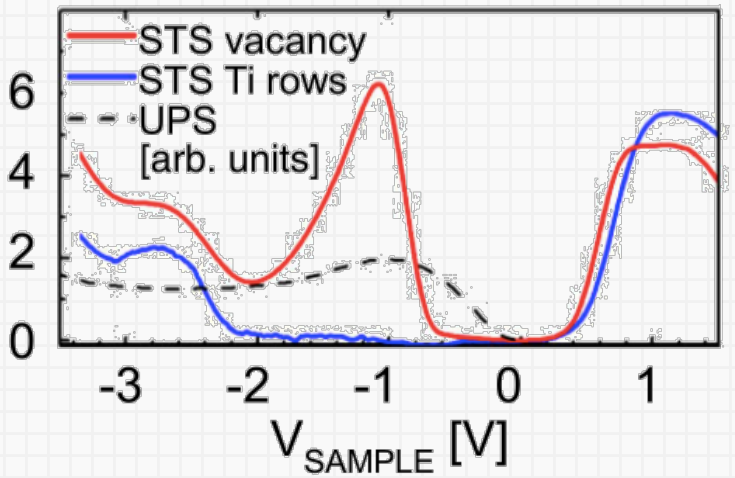


V_{SAMPLE} = - 0.5 V

Deep levels on surface O vacancies



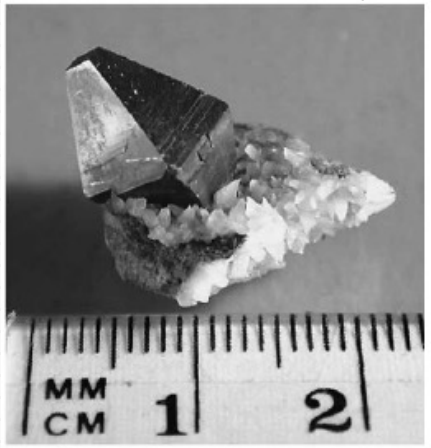
V_{SAMPLE} = + 0.8 V, 7x7 nm^2



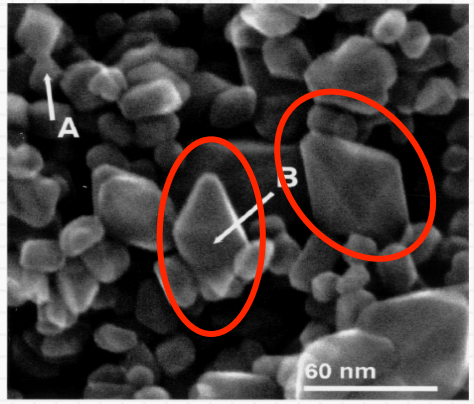
Setvin et al Phys Rev Lett 2014

TiO_2 anatase surface

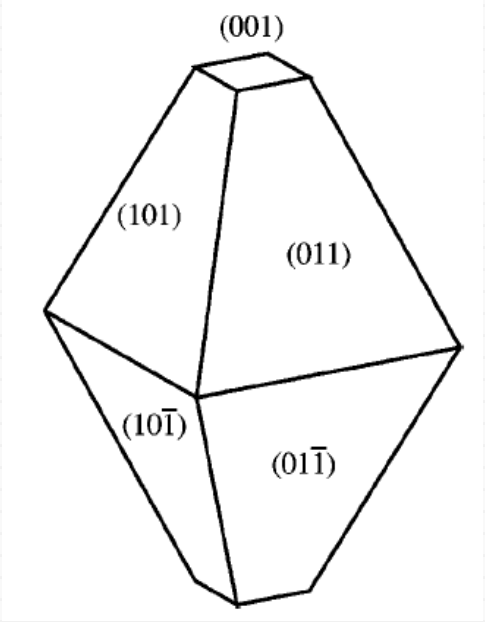
Natural Anatase crystal



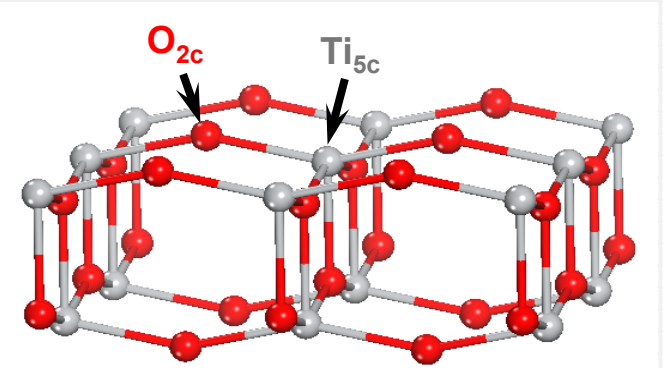
Diebold, *Surf Sci Rep*, 2003



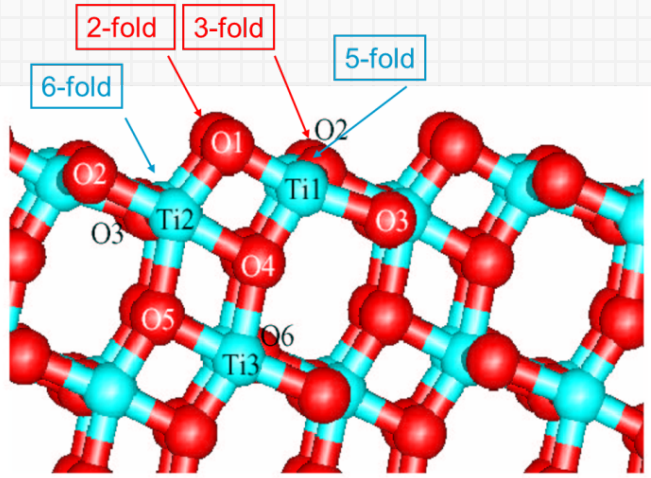
Calculated



Lazzeri et al., *Phys Rev B*, 2001



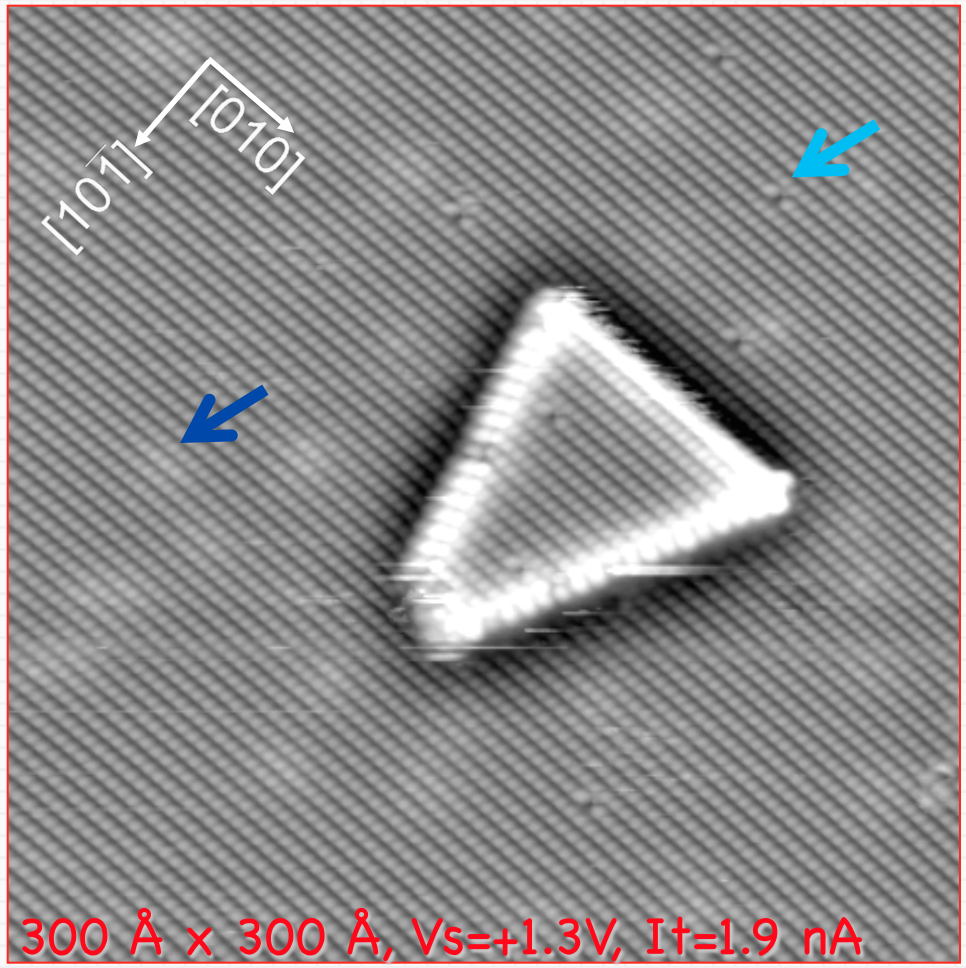
Minority TiO_2(001)

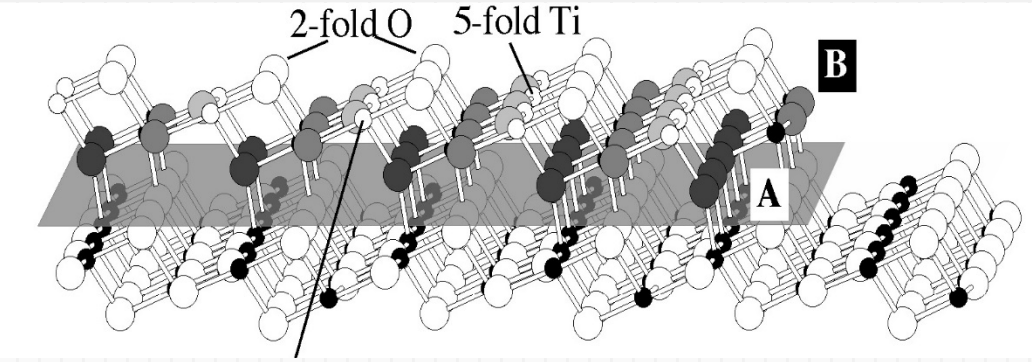


(101) surface: very stable, little reactive, dominates the anatase morphology

minority (001) surface is quite reactive

STM of cleaved Anatase (101)



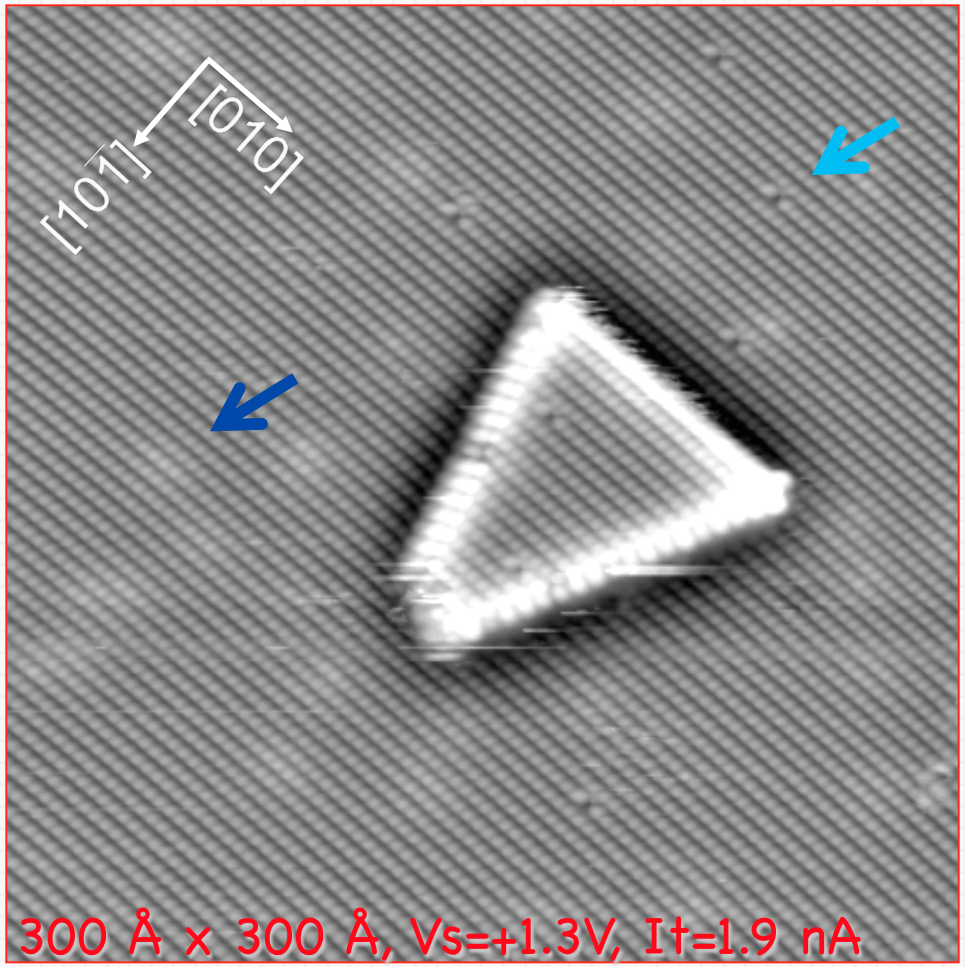


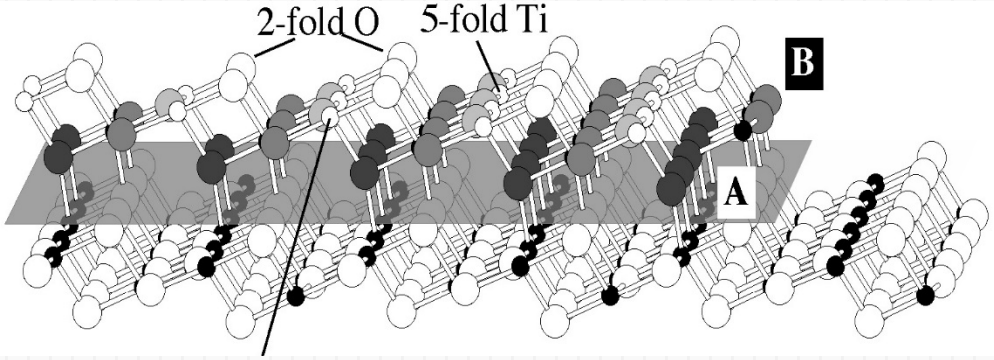
Anisotropic step edges
(Gong et al, Nature Mater. 2006)

Adsorbed water
(He et al, Nature Mater. 2009)

Subsurface impurities

No surface oxygen vacancies on cleaved Anatase (101)





Anisotropic step edges
(Gong et al, Nature Mater. 2006)

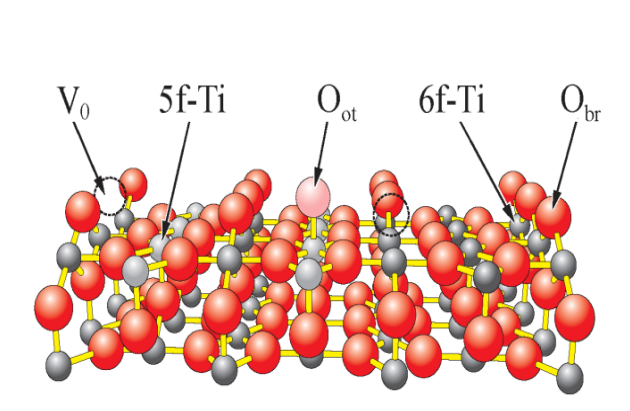
Adsorption of water
(He et al, Nature Mater. 2009)

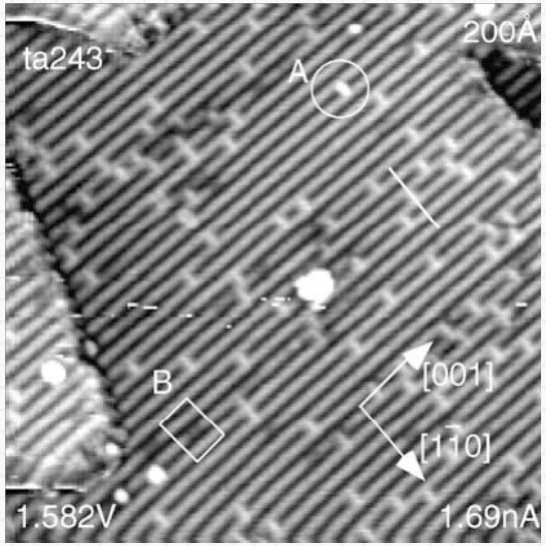
Subsurface impurities

He et al, PRL 2009

5-10% surface O-vacancies on rutile TiO_2(110)

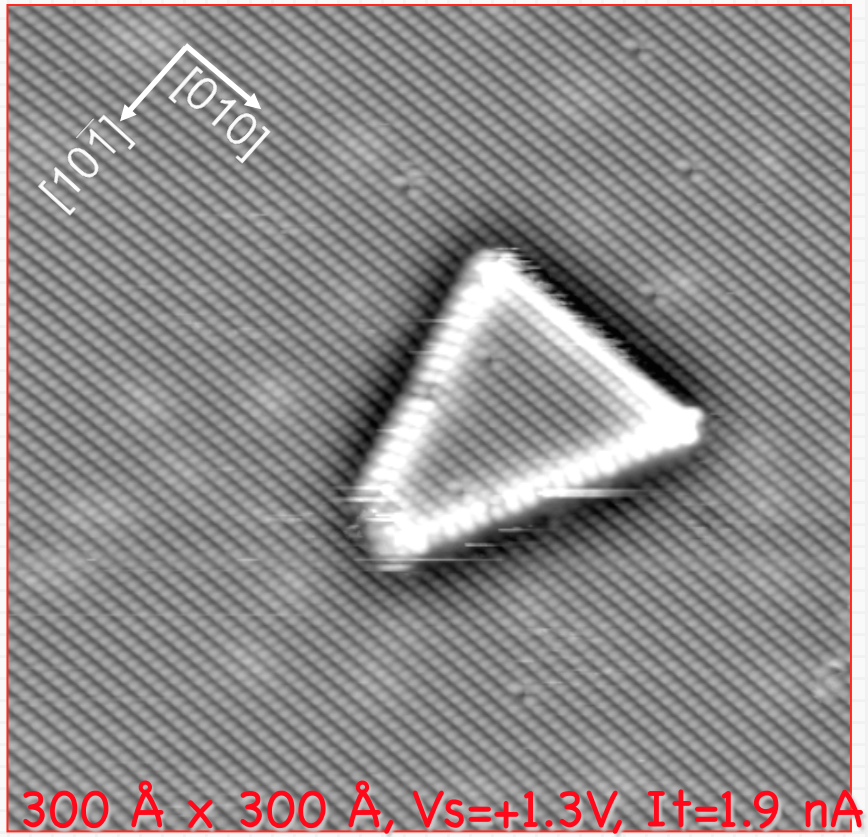
Rutile (110)



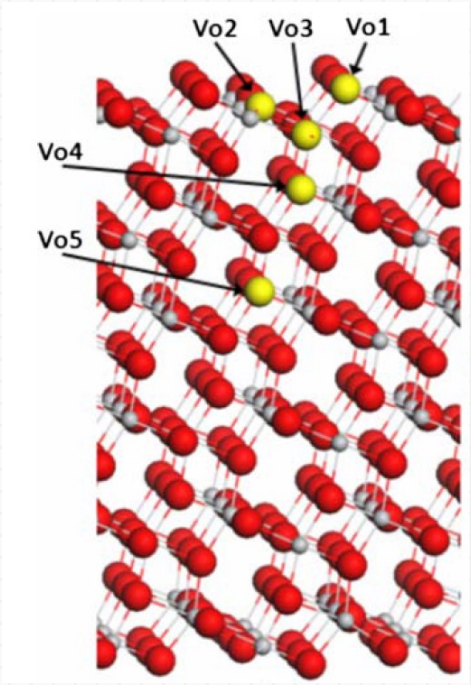


Empty state STM image of rutile (110) (bright rows ≡ Ti atoms)

Vacancies are subsurface @ anatase



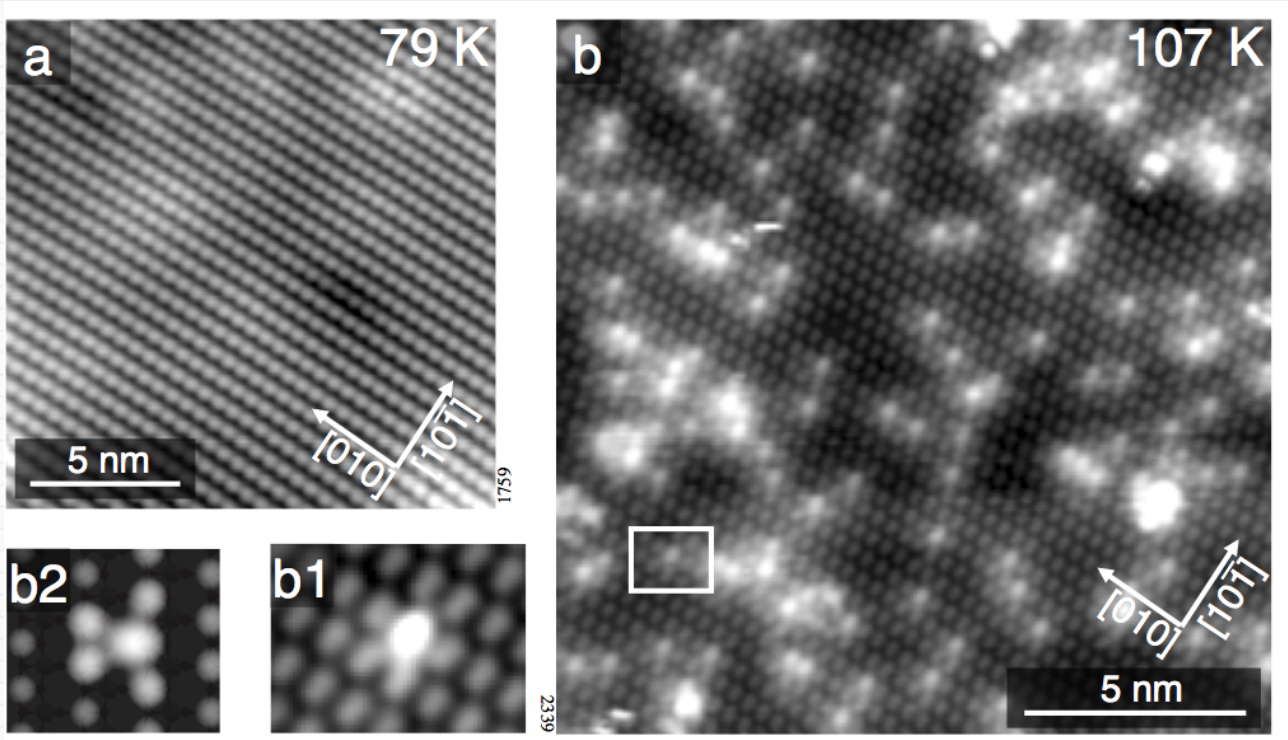
DFT calculations



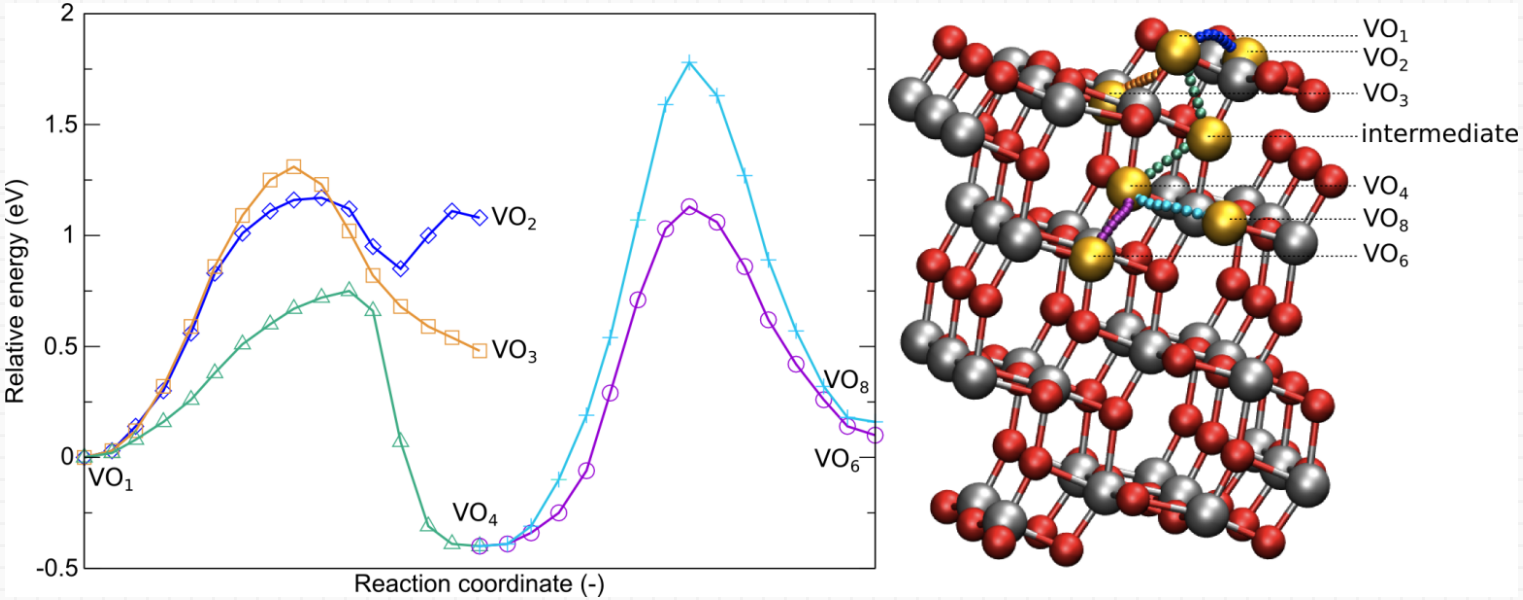
Vac.	E_{form} [eV]
Vo1	4.15
Vo2	5.40
Vo3	4.73
Vo4	**3.69**
Vo5	**3.65**
Bulk	**3.69**

He et al. PRL 102, **2009**, 106105; Cheng & AS., PRB 79(9), **2009**, 092101; Cheng & AS, J. Chem. Phys. 131(5), **2009**, 054703

Surface O-vacancies can be created by electron bombardment



Diffusion of O_{vac}'s *into* anatase



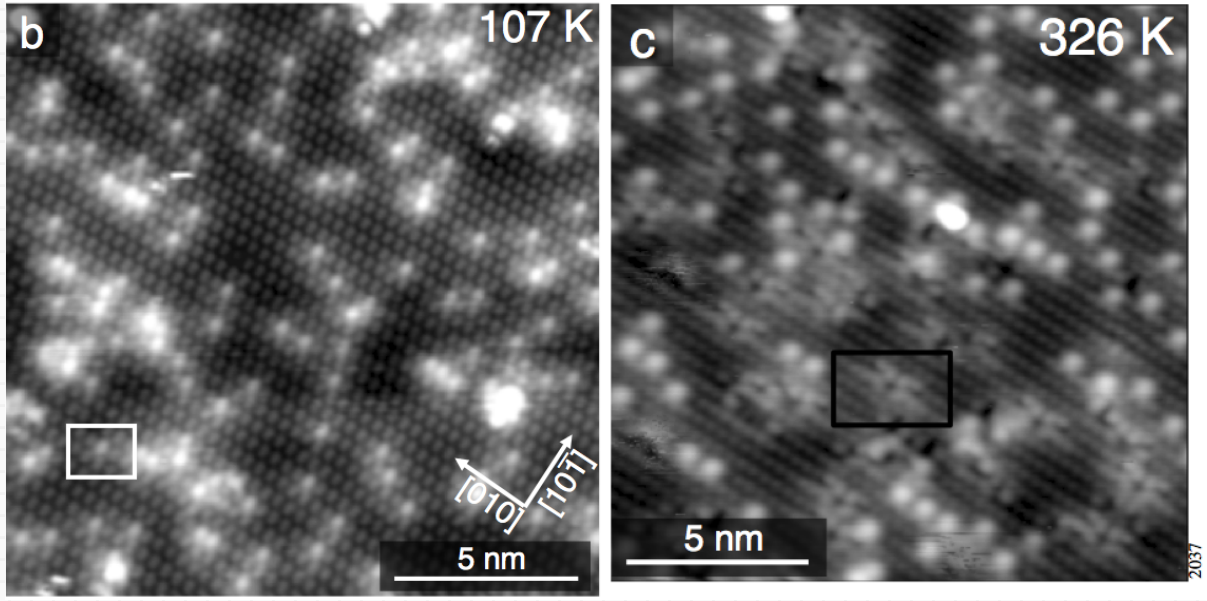
~ 0.75 eV barrier for O-vacancy surface→ sub-surface migration predicted by DFT-GGA

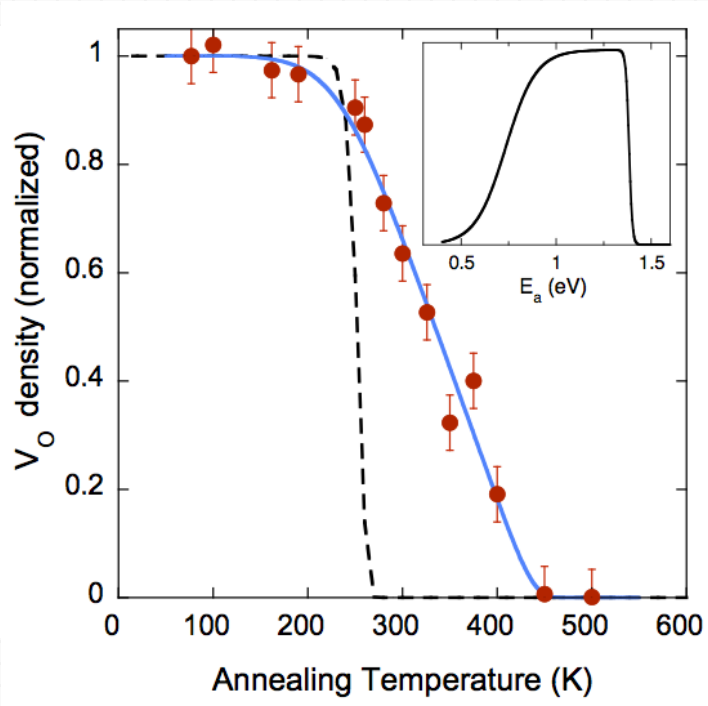
P. Scheiber, M. Fidler, O. Dulub,M. Schmid, U. Diebold, W. Hou, U. Aschauer, A. Selloni, (Sub)surface mobility of oxygen vacancies at the TiO_2 anatase (101) surface, *Phys. Rev. Lett.* **2012**, *109*, 136193.

Diffusion of O_{vac}'s *into* anatase
(STM images @78K)

After irradiation @ 100 K

10 min @ 325 K

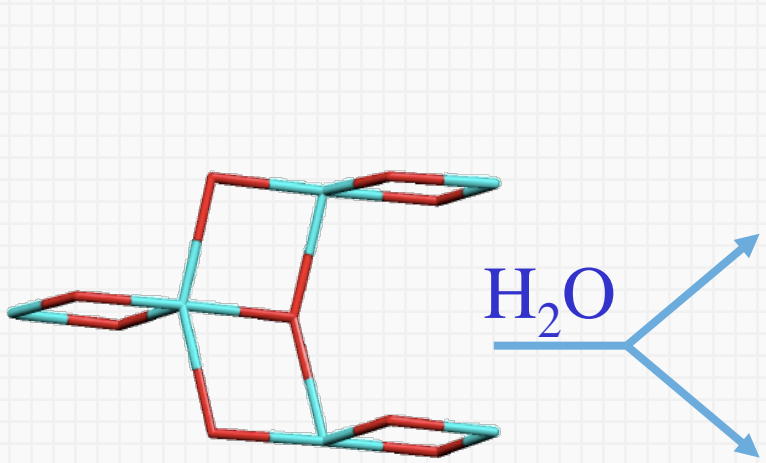




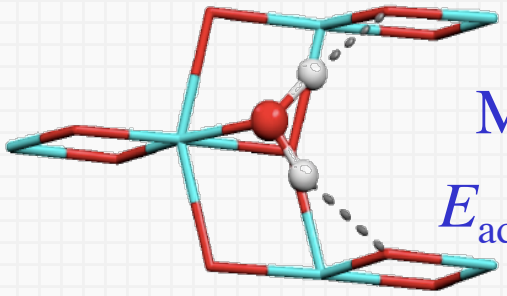
P. Scheiber, M. Fidler, O. Dulub,M. Schmid, U. Diebold, W. Hou, U. Aschauer, A. Selloni, (Sub)surface mobility of oxygen vacancies at the TiO_2 anatase (101) surface, *Phys. Rev. Lett.* **2012**, *109*, 136193.

H_2O on anatase (101)

Vittadini et al. PRL 81, 2954 (1998)

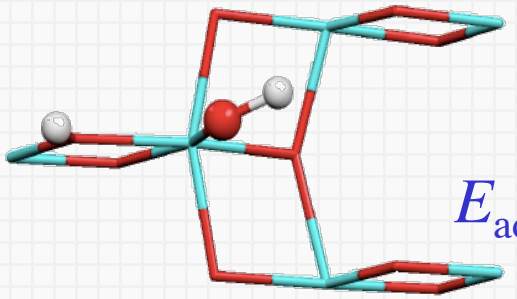


H_2O



Molecular:

E_{ads} = 0.74 eV

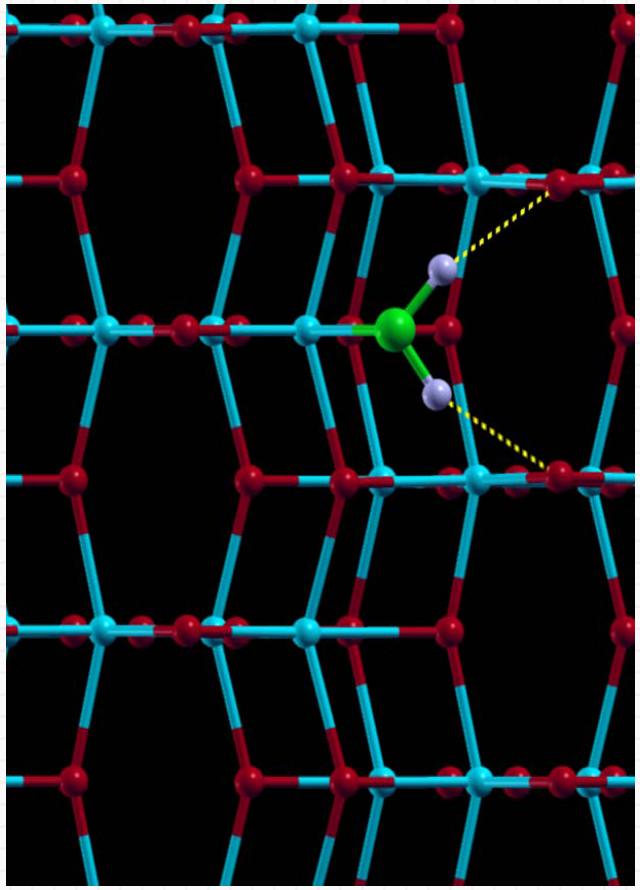


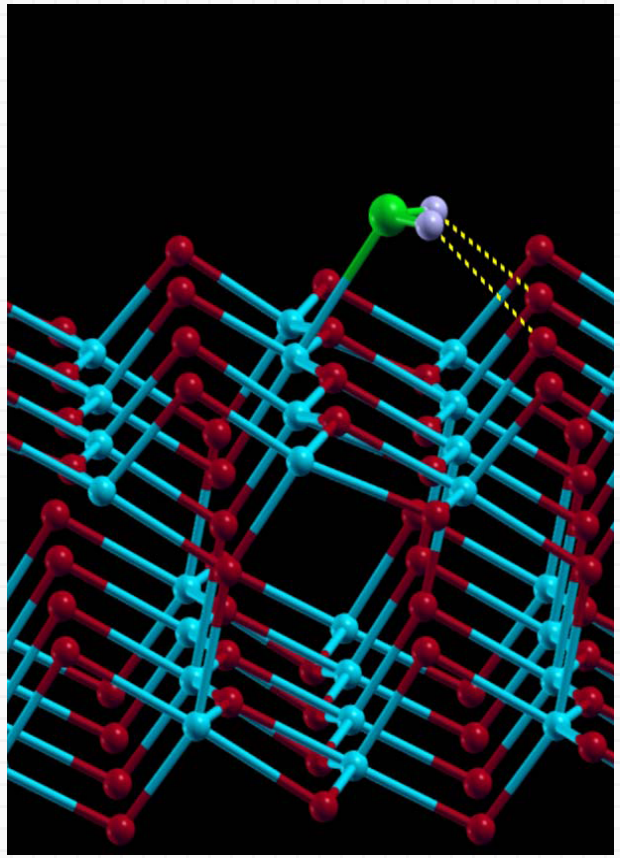
Dissociative:

E_{ads} = 0.2-0.3 eV

- Dissociation of H_2O on (101) surface is unfavored, in line with the stability of the surface.
- Molecular state stabilized by H-bonds with surface O_{2c}

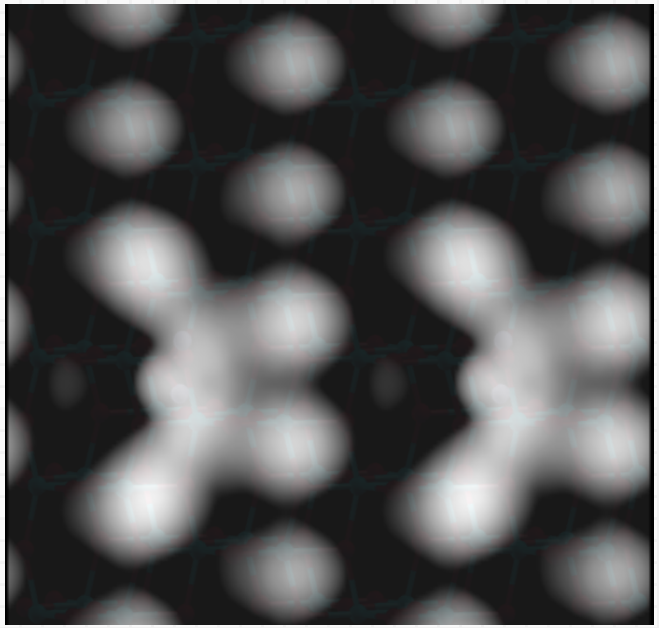
Structure of water monomer on anatase (101): two H-bonds with lattice O-2c atoms

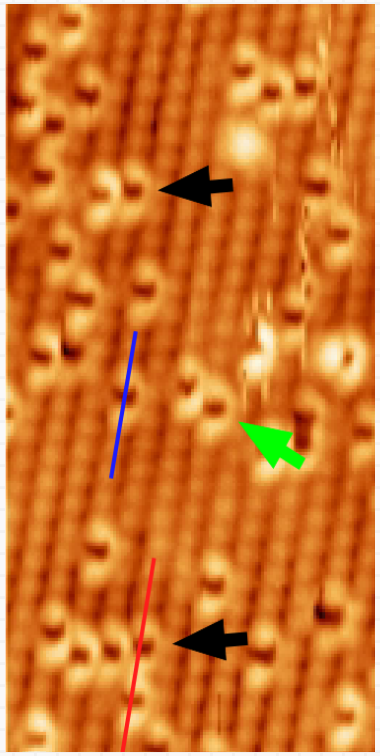


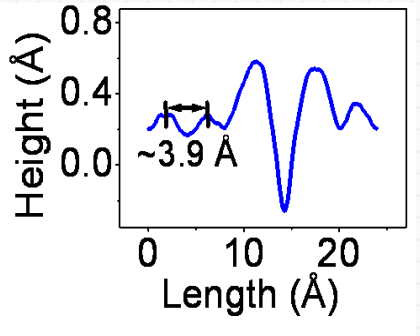


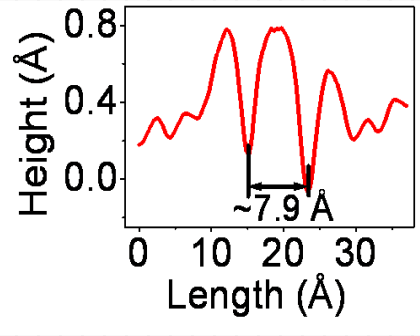
STM image of an adsorbed water molecule: calcs vs expt

He et al Nat Mat 2009



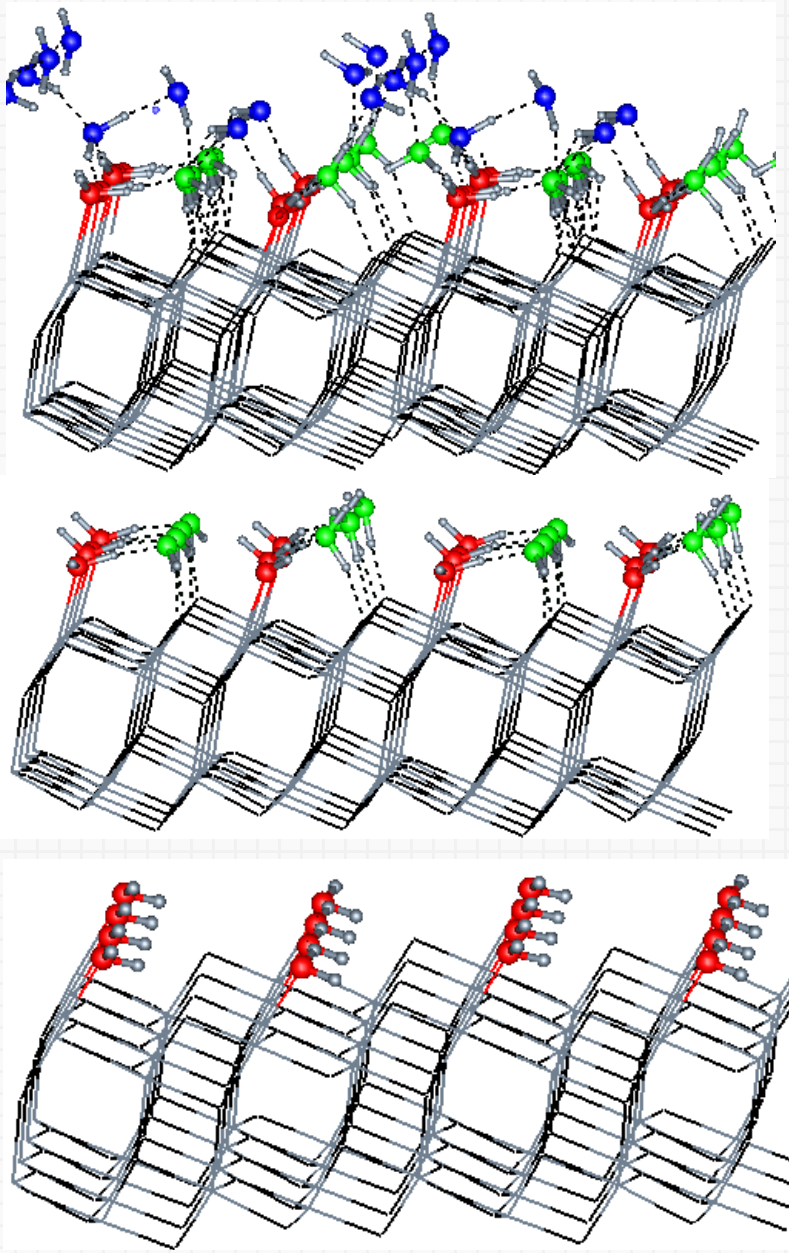




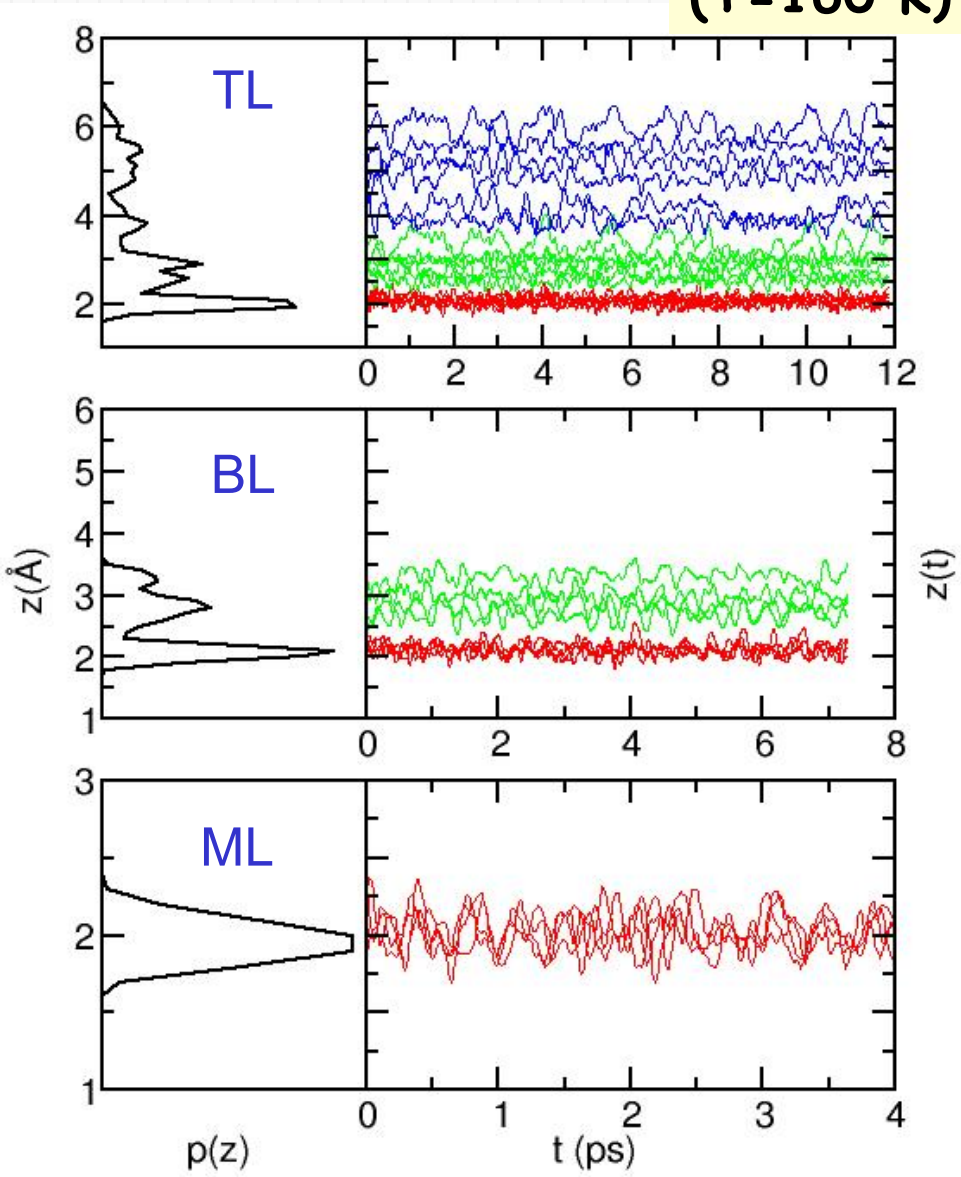


V=2.75 eV, constant density image (1e-4 a.u.)

1-3 water monolayers: ab initio MD



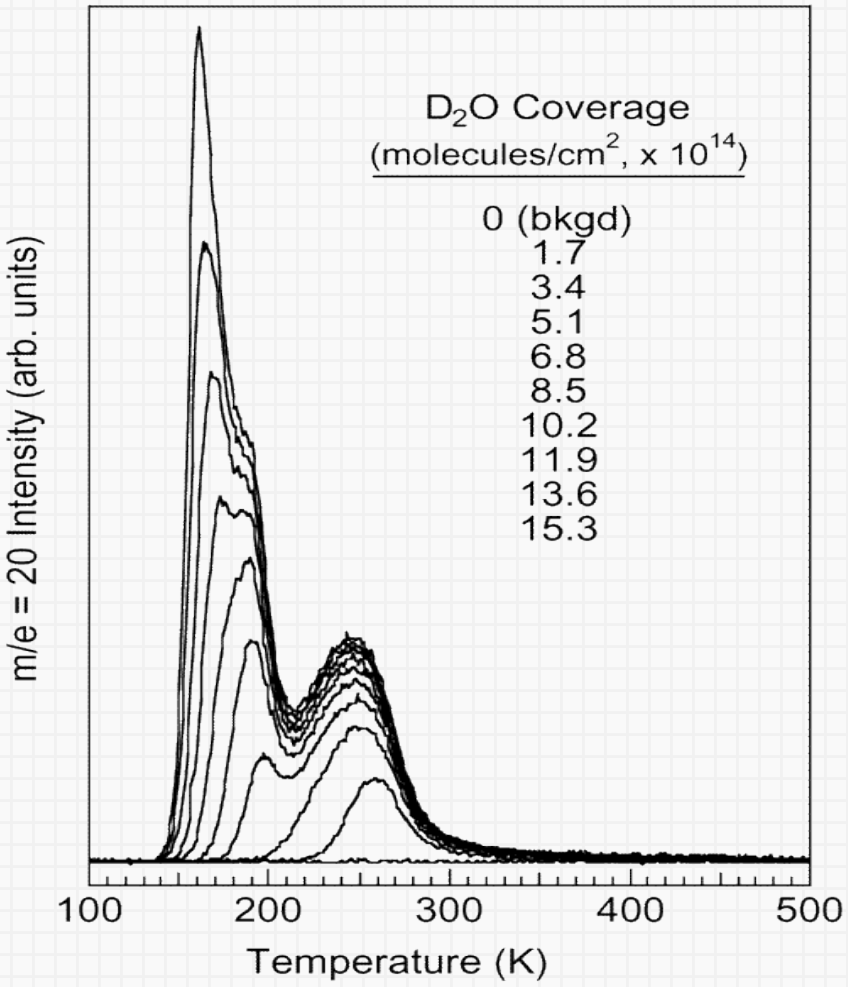
(T=160 K)



Tilocca & Selloni Langmuir 2004; JPCC 2012

Water on anatase TiO_2(101): expt

TPD spectrum



250 K: H_2O-Ti_{5c}

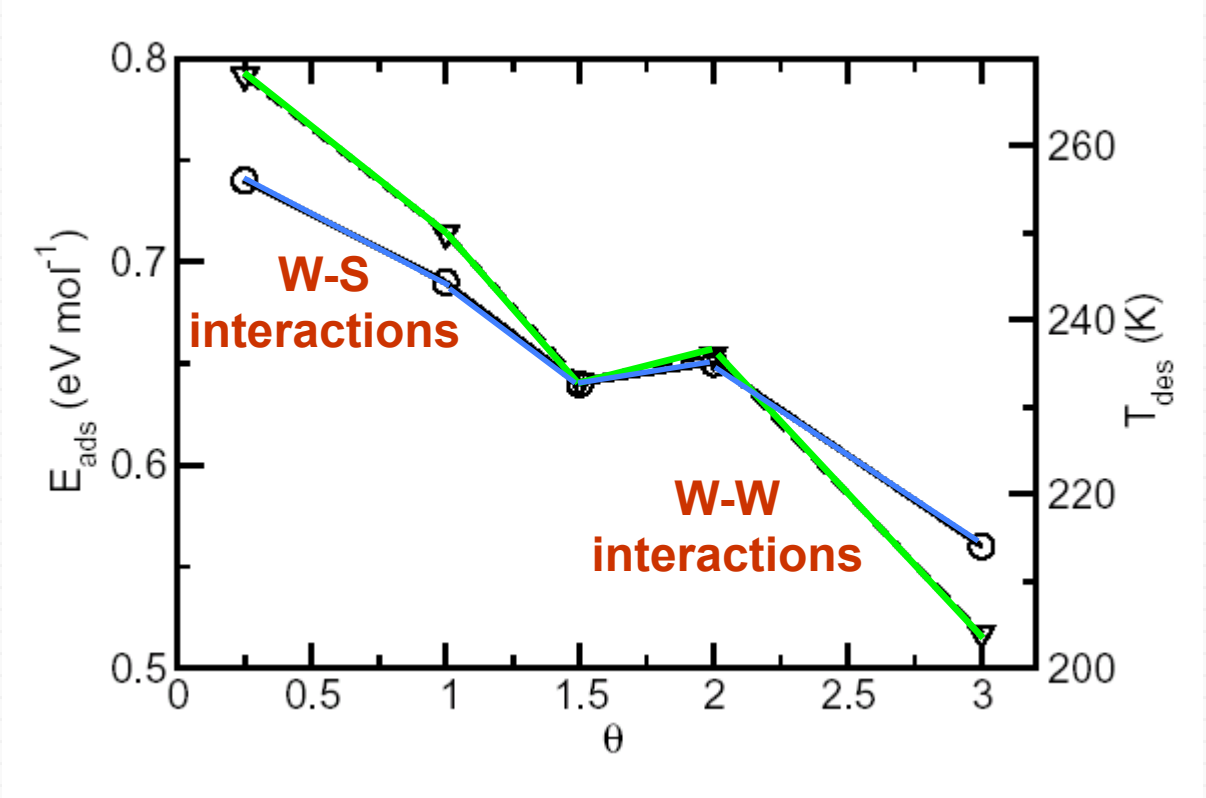
190 K: H_2O-O_{2c}

160 K: multilayer H_2O

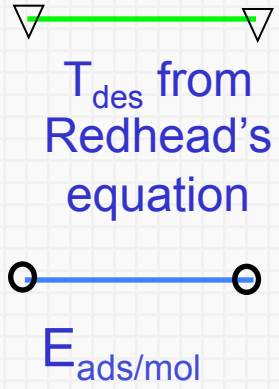
No dissociated H_2O

(Herman *et al*, JPC-B *107* 2788, 2003)

Water multilayer: adsorption energies



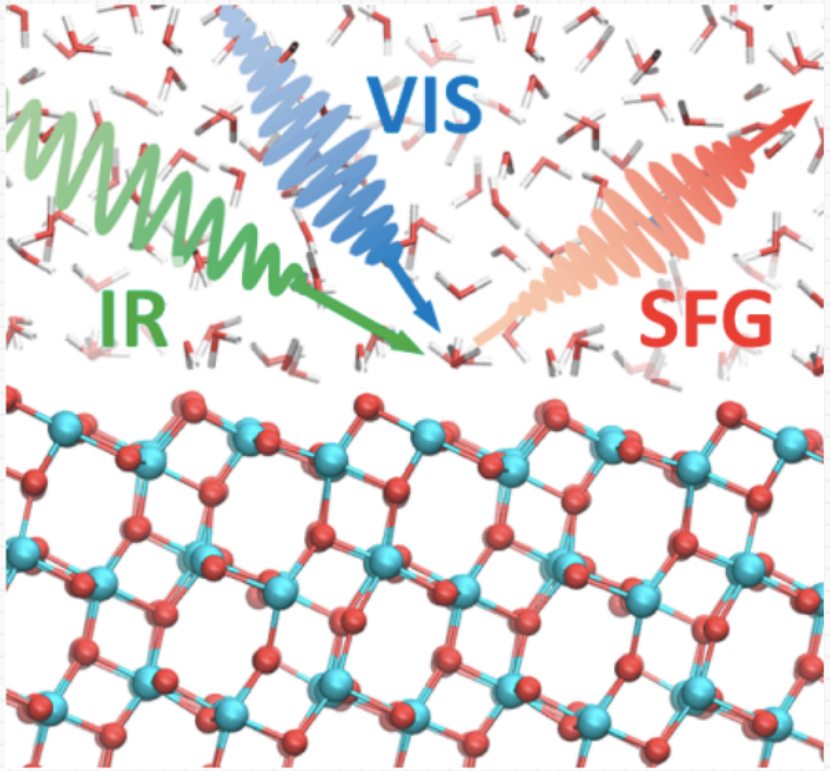
$E_{ads/mol} = \{ E(B) - E(A) - n \cdot E(H_2O) \} / n$



Trend in estimated desorption T in agreement with TPD experiments

Tilocca & Selloni Langmuir 2004; JPCC 2012

….however: evidence of both dissociated and molecular water at the TiO_2/water interface



SFG on polycrystalline globular anatase, 50-200 nm

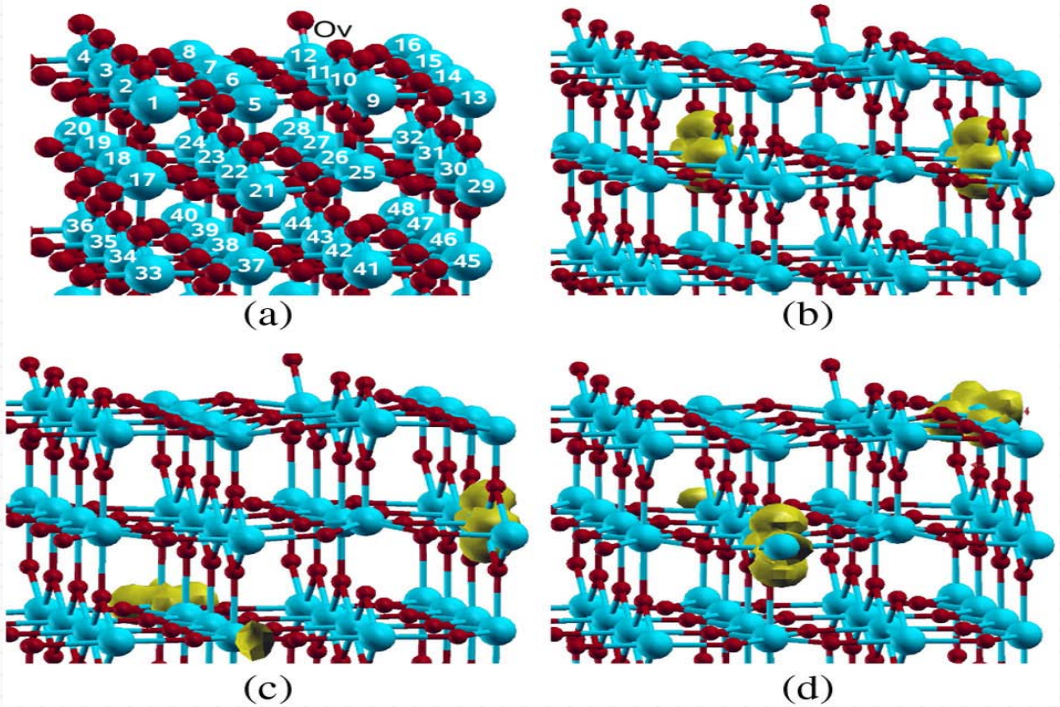
Shultz et al JACS *126*, 8094, 2004; *127*, 9736, 2005

Backus et al., JPCL 2017, 8, 2195

Outline

- TiO_2 as a prototypical material in photocalysis: surfaces, defects, reactivity
- Excess and photoexcited electrons at anatase TiO_2 surfaces and aqueous interfaces: **trapping and dynamics**
- Formation and structure of "black TiO_2"

Directly simulate effect of thermal fluctuations of TiO_2 lattice on carrier trapping by First Principles MD



Charge transfer dynamics induced by O-vacancies on TiO2(110) – Kowalski et al PRL 2010

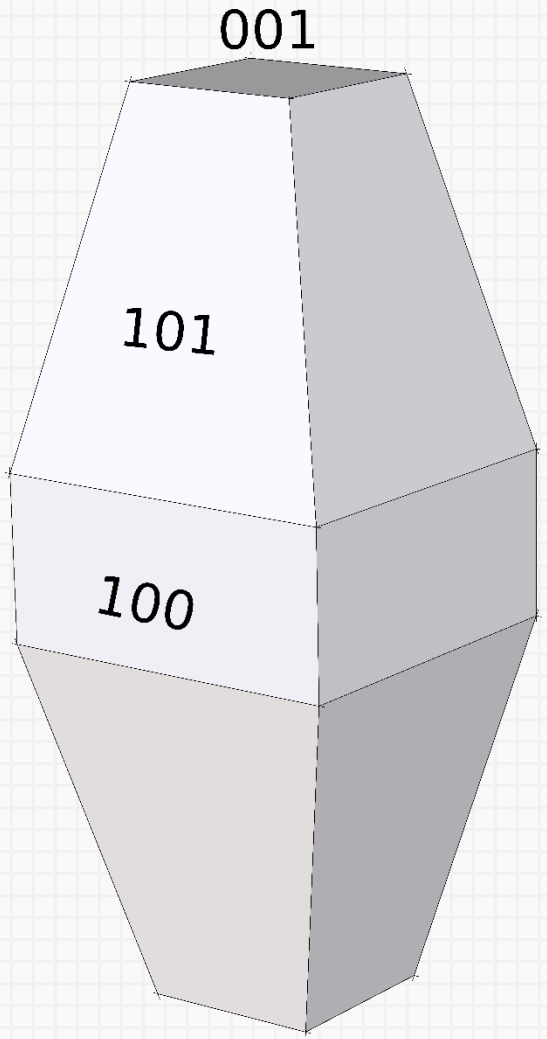
Assumes motion is adiabatic (strong coupling between hopping sites)

Very long (likely ~ ns) simulations needed to reliably estimate mobilities

Computational details

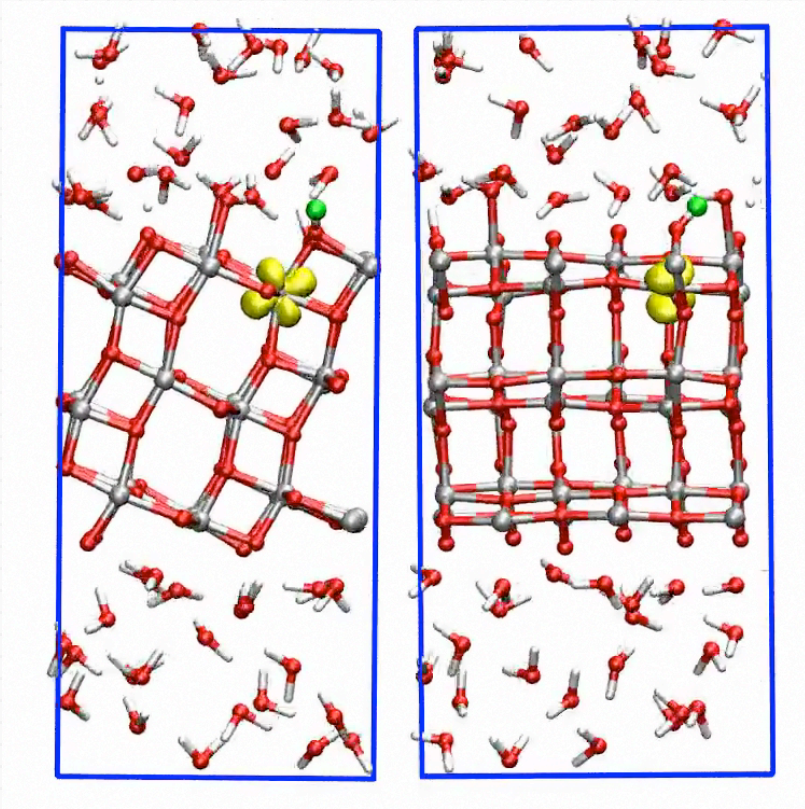
- DFT+U based AIMD simulations (10-20 ps):
  - U = 3.3 eV
  - U = 3.9 eV

  ] expected range from ab initio theories
- (101), (001) and (100) surfaces
- Common step edges on (101) surface
- In vacuo and water
- Photoexcited electron (PE), bridging hydroxyl ($O_{br}H$), bulk dopants (H, Nb)

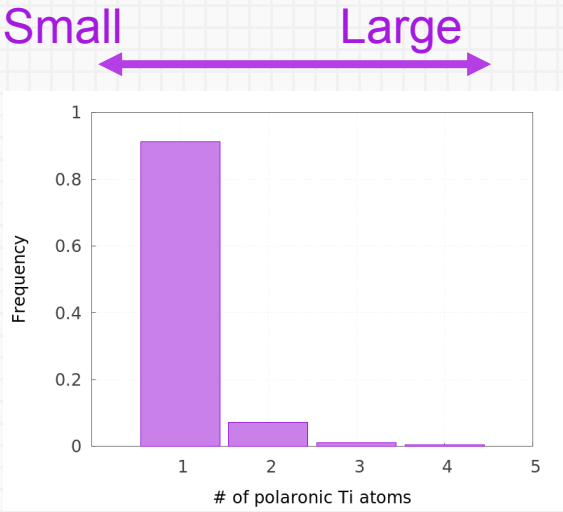


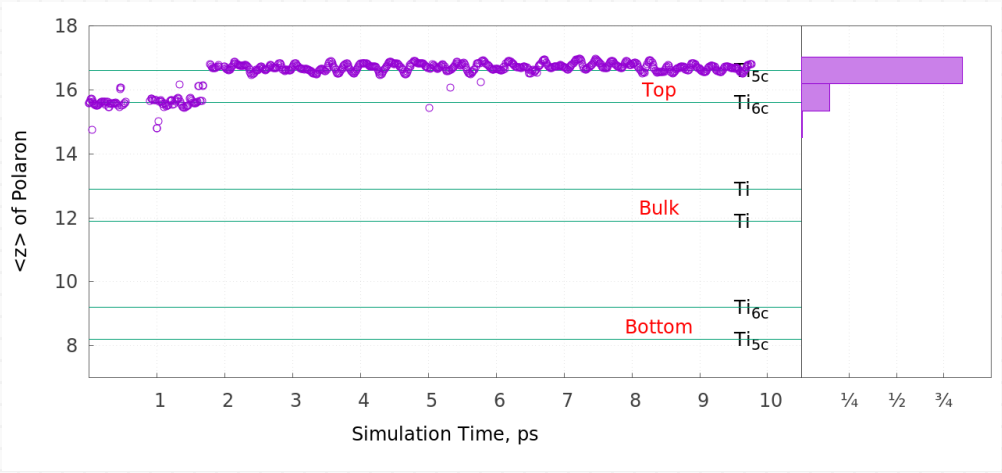
Bridging hydroxyl ($O_{br}H$) on (101) surface

T=400 K, U =3.9 eV



localization on Ti-5c and formation of $Ti^{3+} – O_{br}H$



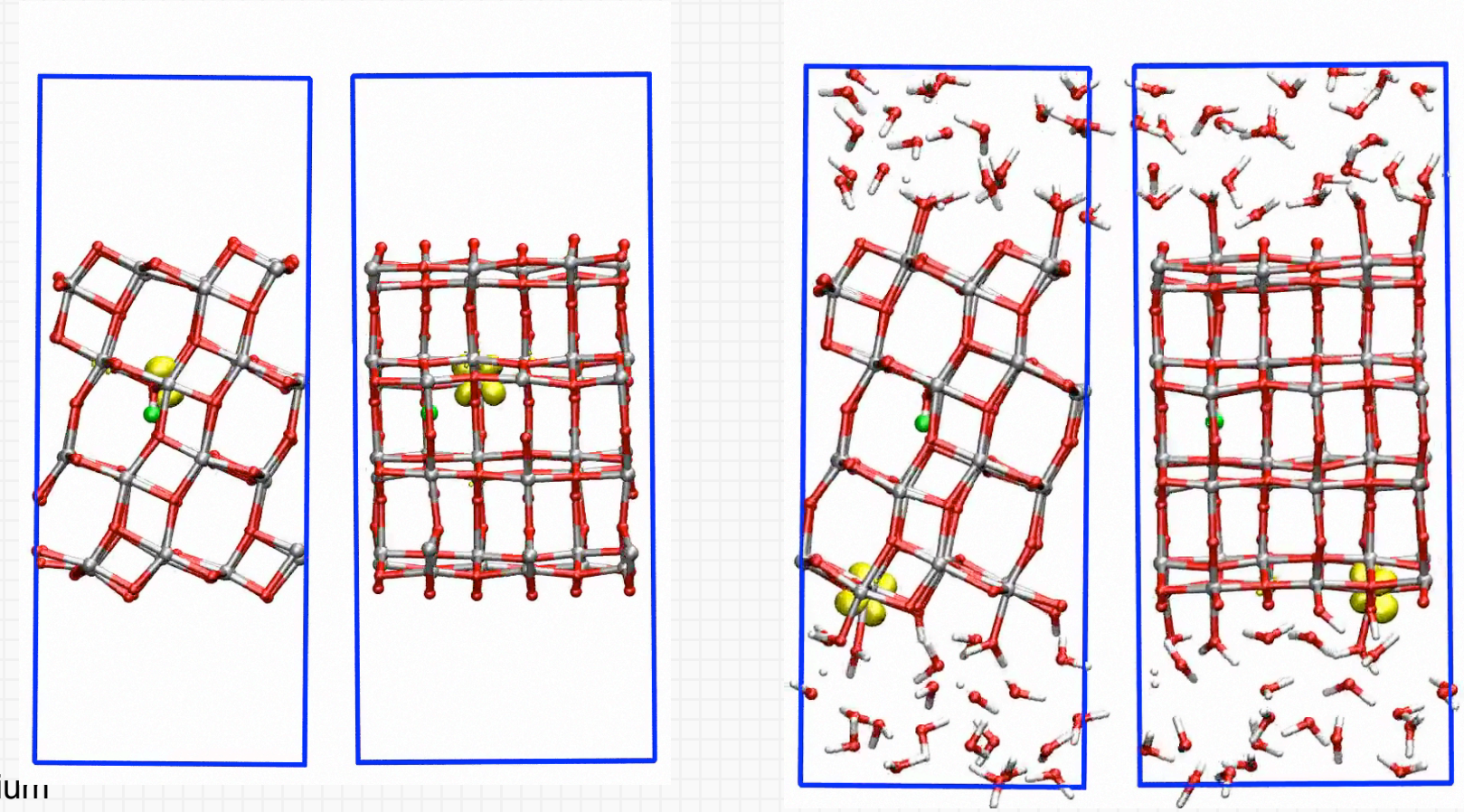


Titanium
Oxygen
H
H_{ads}

Excess electron in Ti3d states→ Ti^{3+}

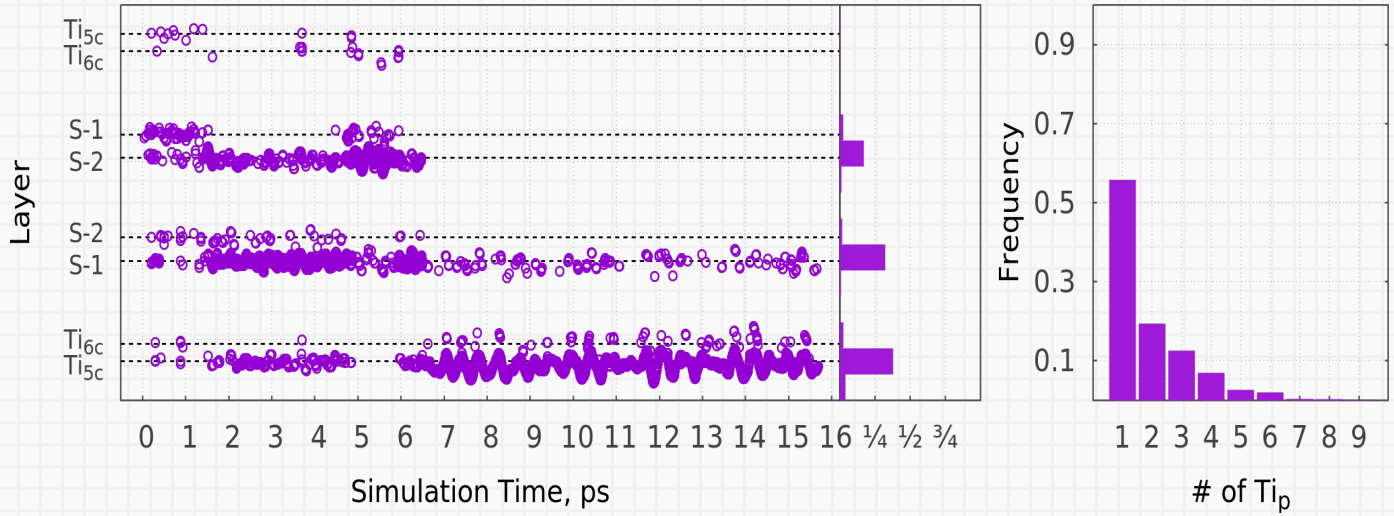
H-doped anatase (101):

e^- - H^+ vs e^- - surface interaction

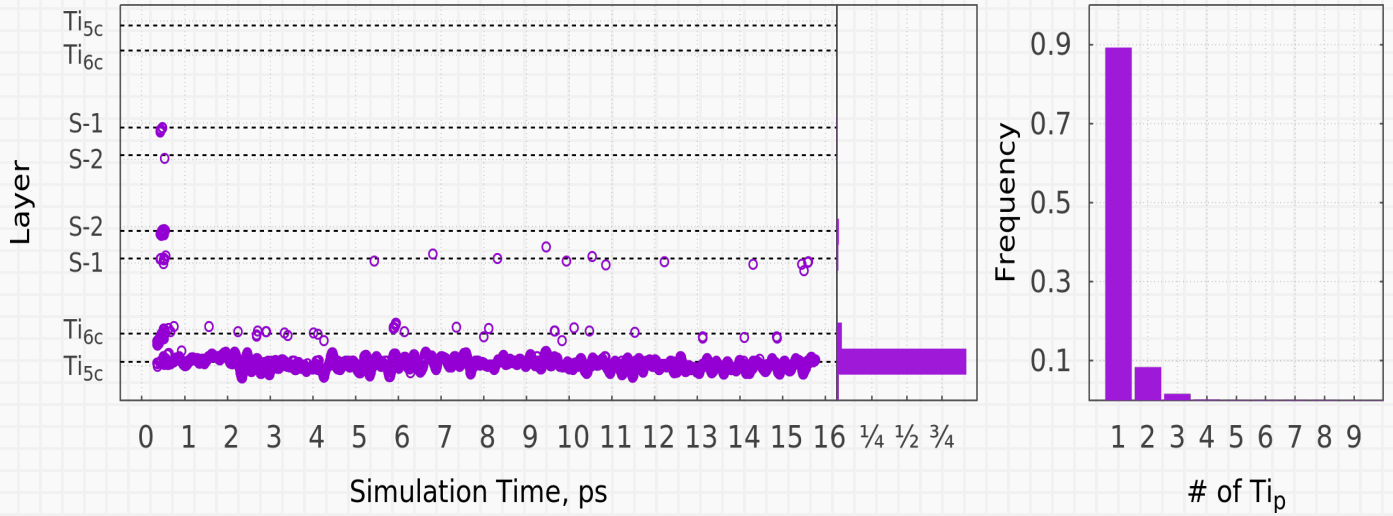


H-doped (101) (T = 400 K, U= 3.9 eV)

in vacuo

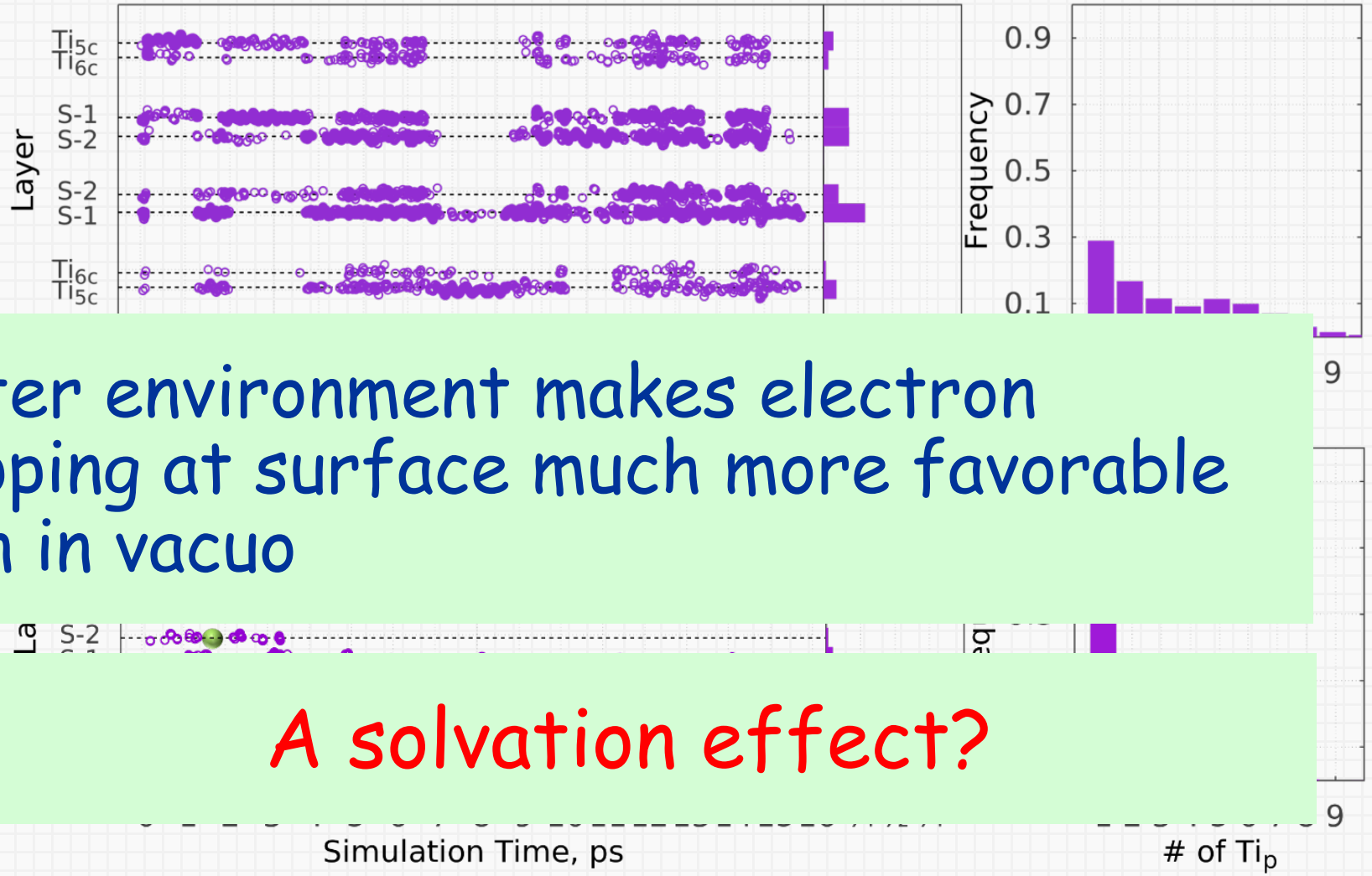


solvated



Nb-doped (101) (T =400 K, U = 3.9 eV)

in vacuo

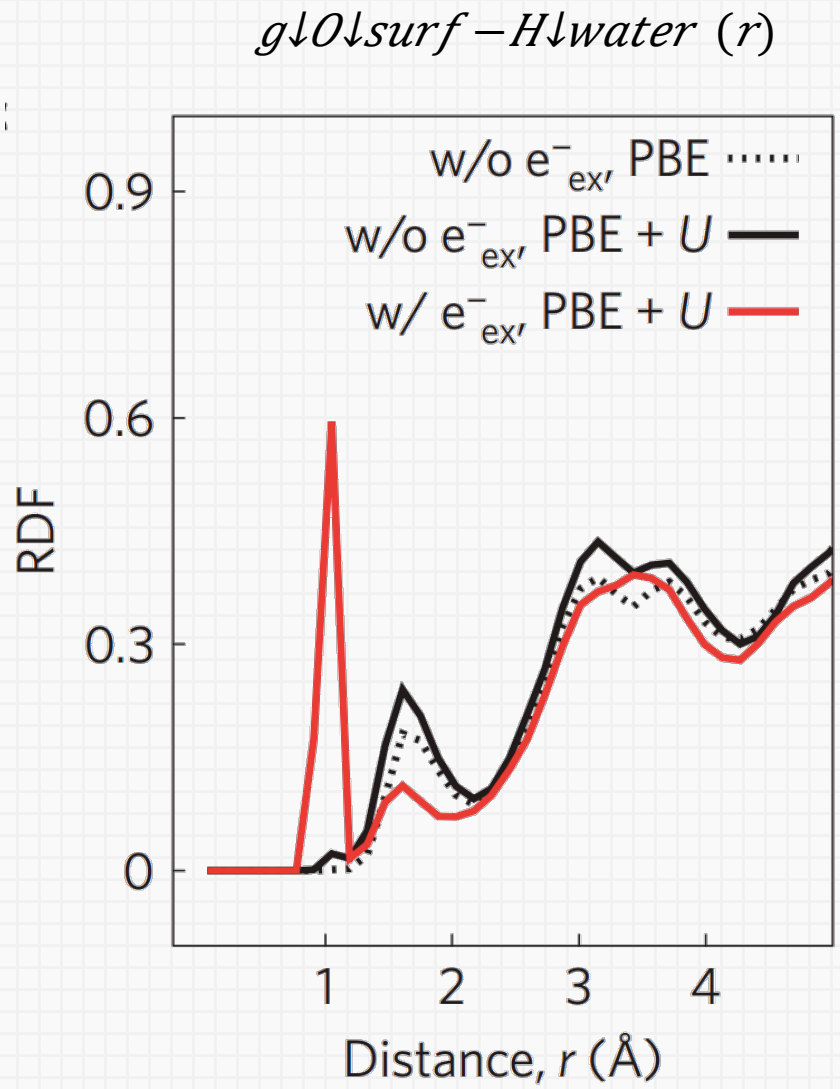


solv

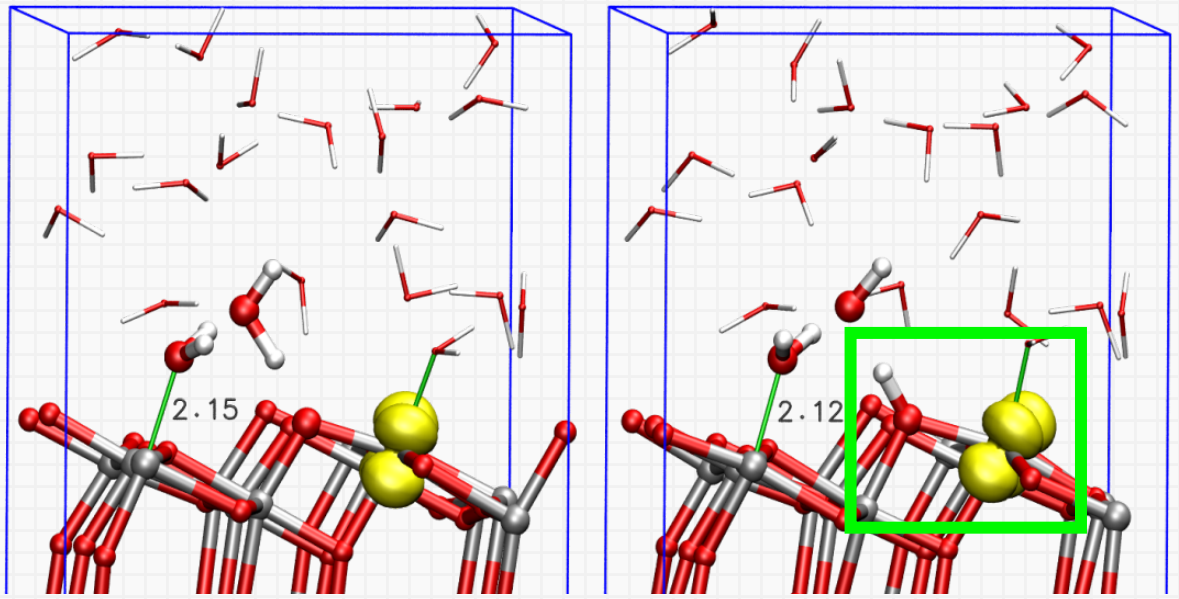
Water environment makes electron trapping at surface much more favorable than in vacuo

A solvation effect?

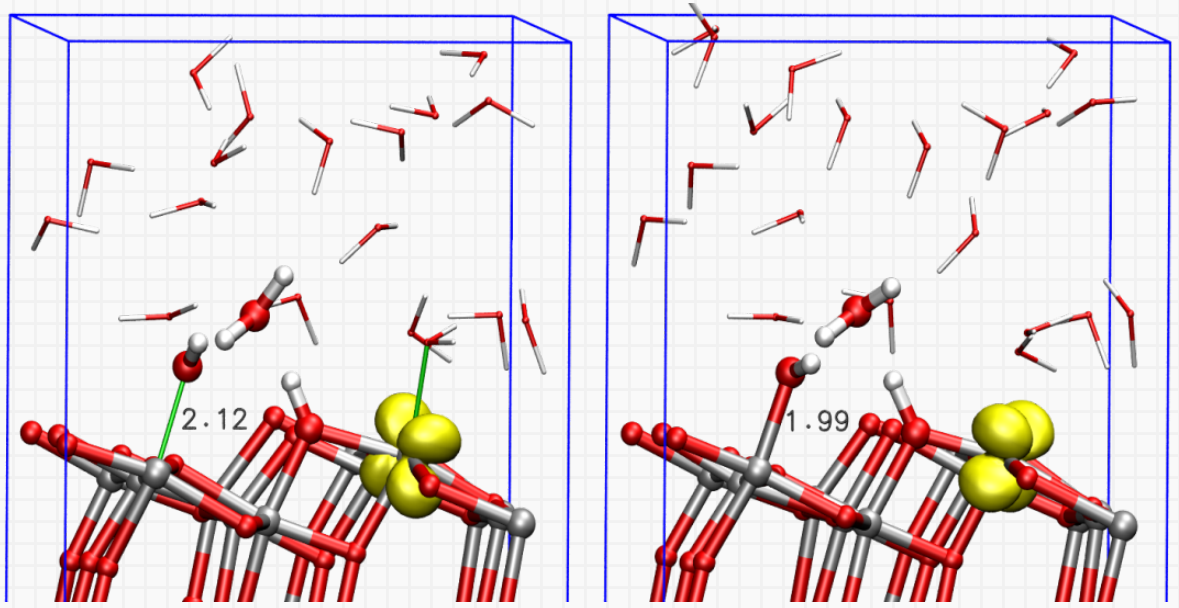
Polaron is stabilized by water dissociation



Photoexcited electron, U = 3.9 eV

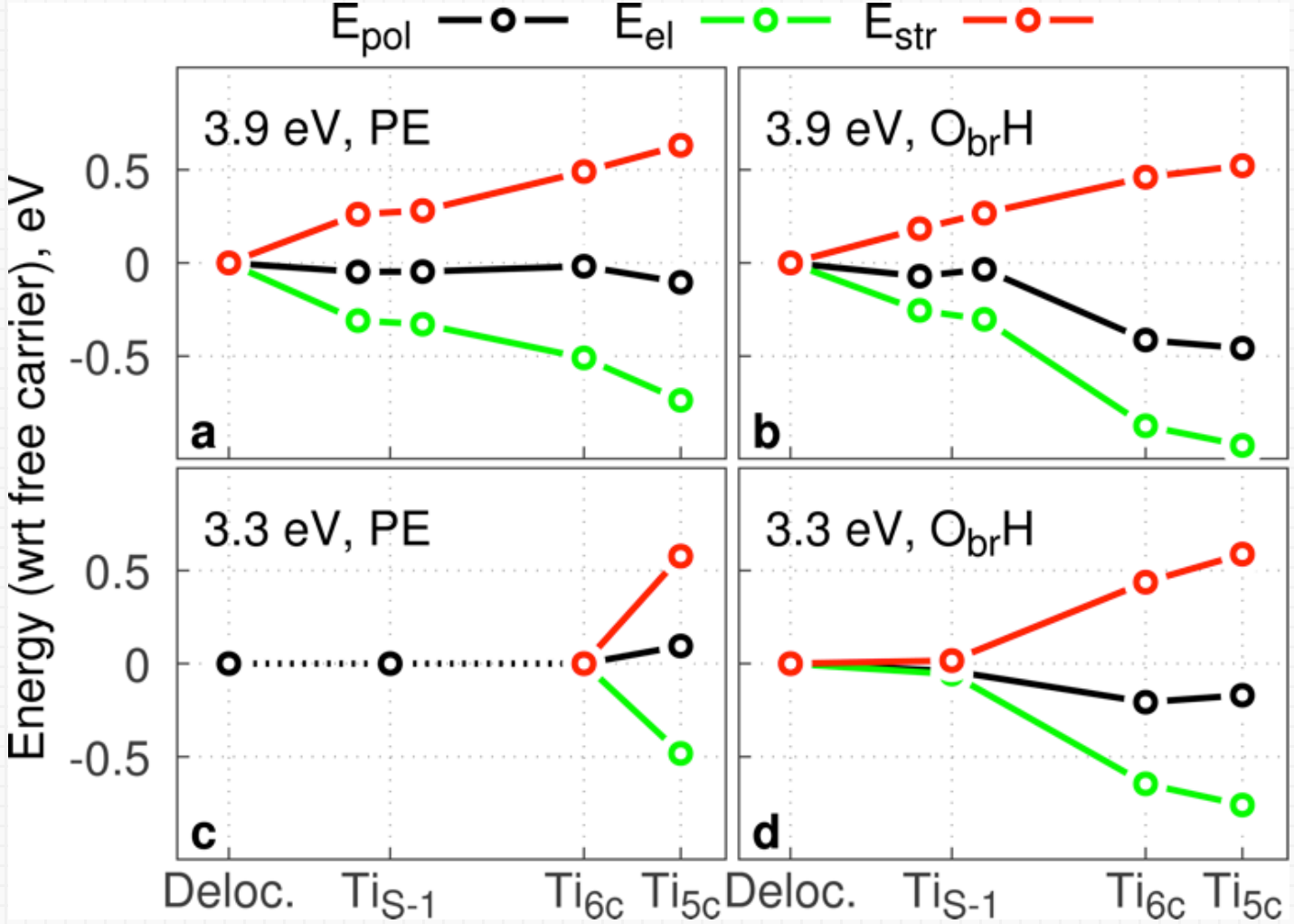


I II



III IV

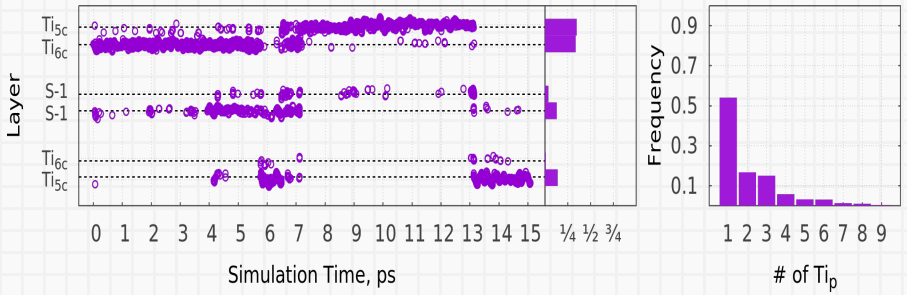
U dependence: Polaron formation energies
(T = 0 K, vacuum)



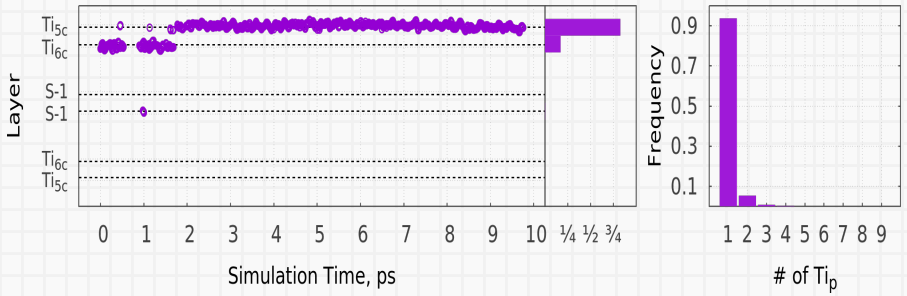
U dependence – aqueous interface

Ti^{3+} – $O_{br}H$

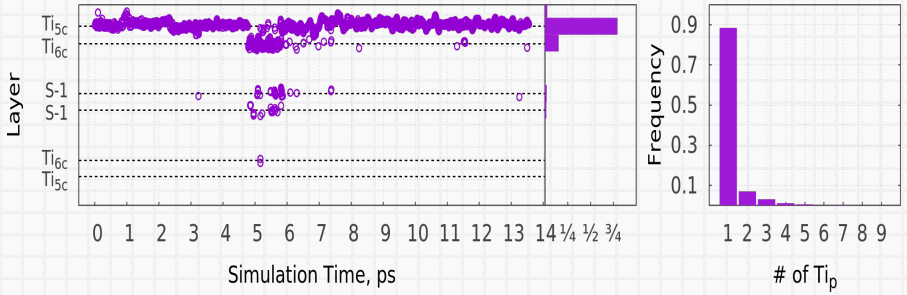
3.3 eV, 400K



3.9 eV, 400K

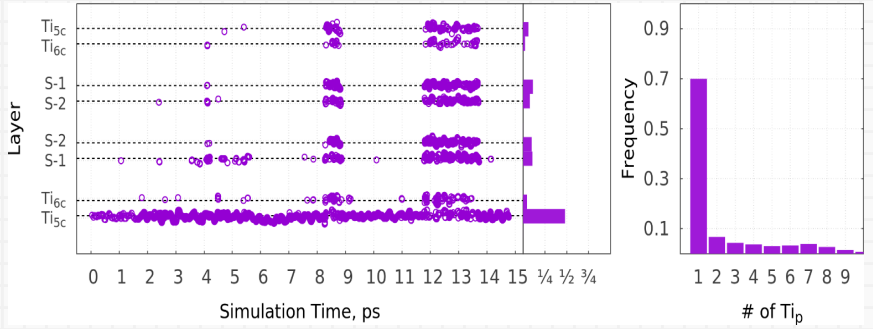


3.9 eV, 600K

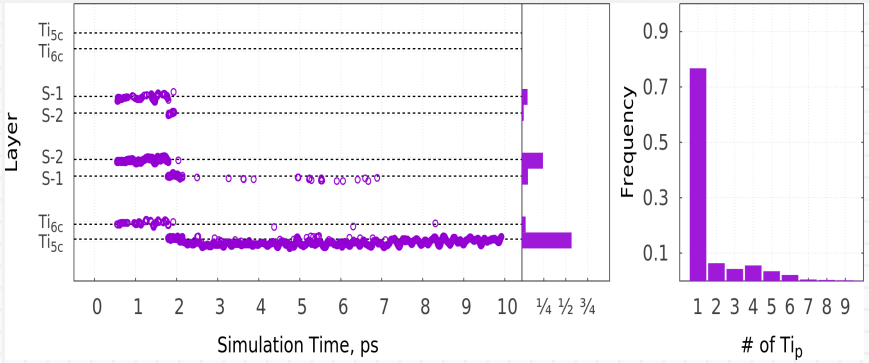


Photoexcited electron

3.3 eV, 400 K

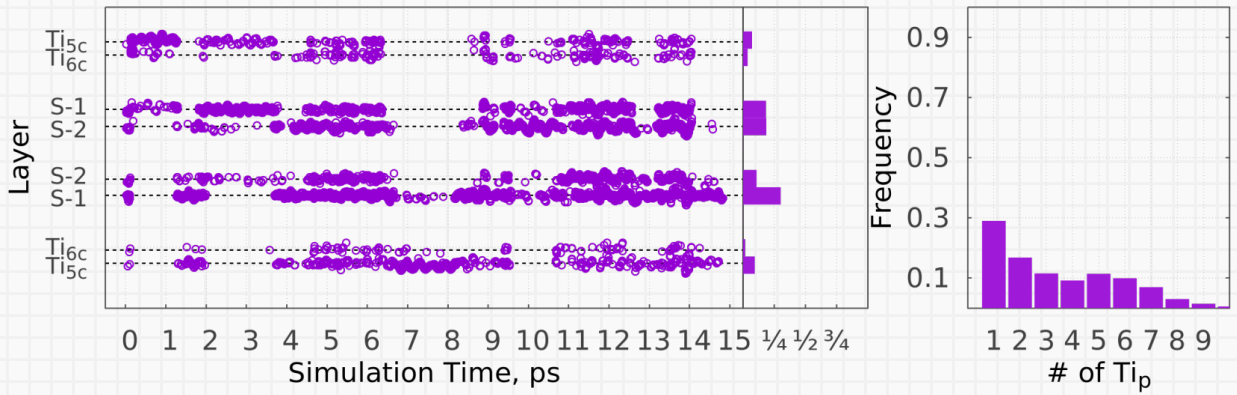


3.9 eV, 400 K

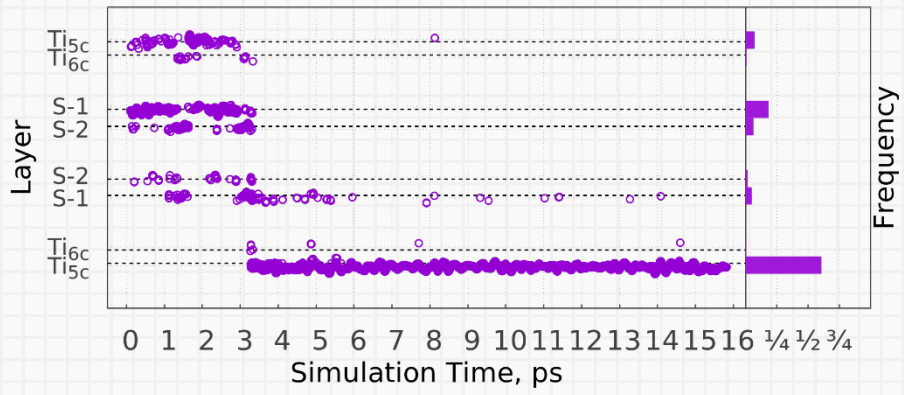


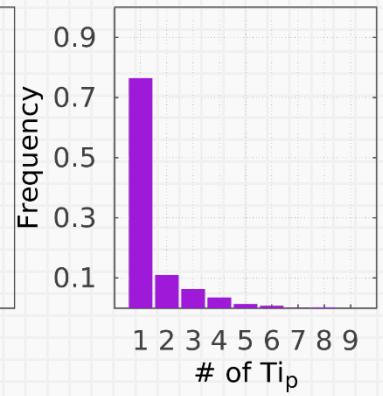
Size Effects – Nb - doped (101)

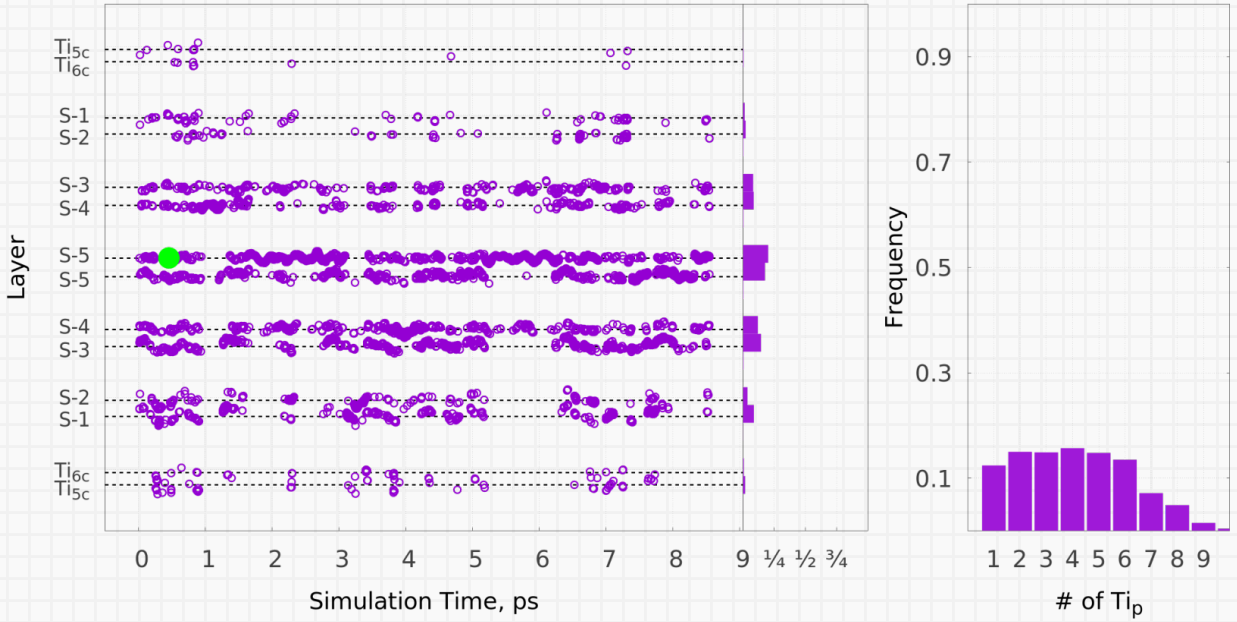
In vacuo

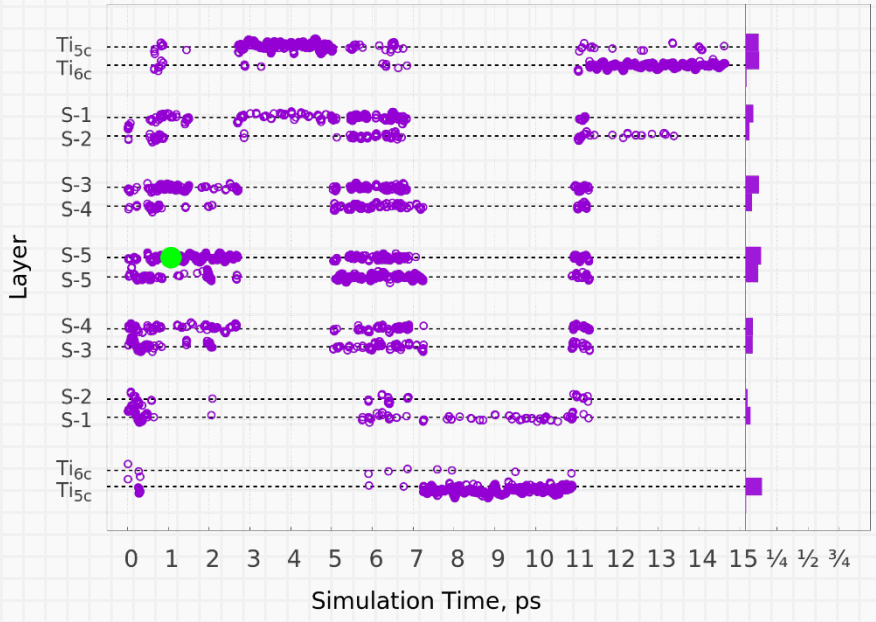


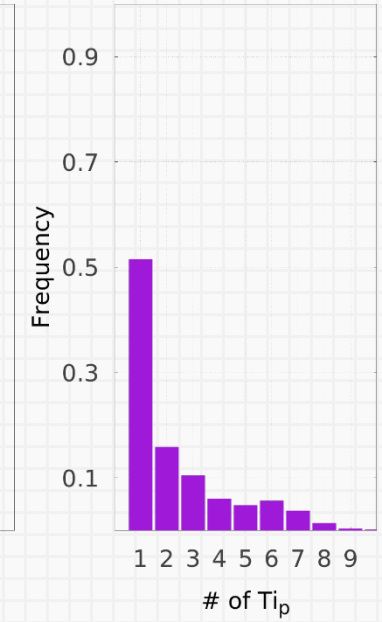
In water



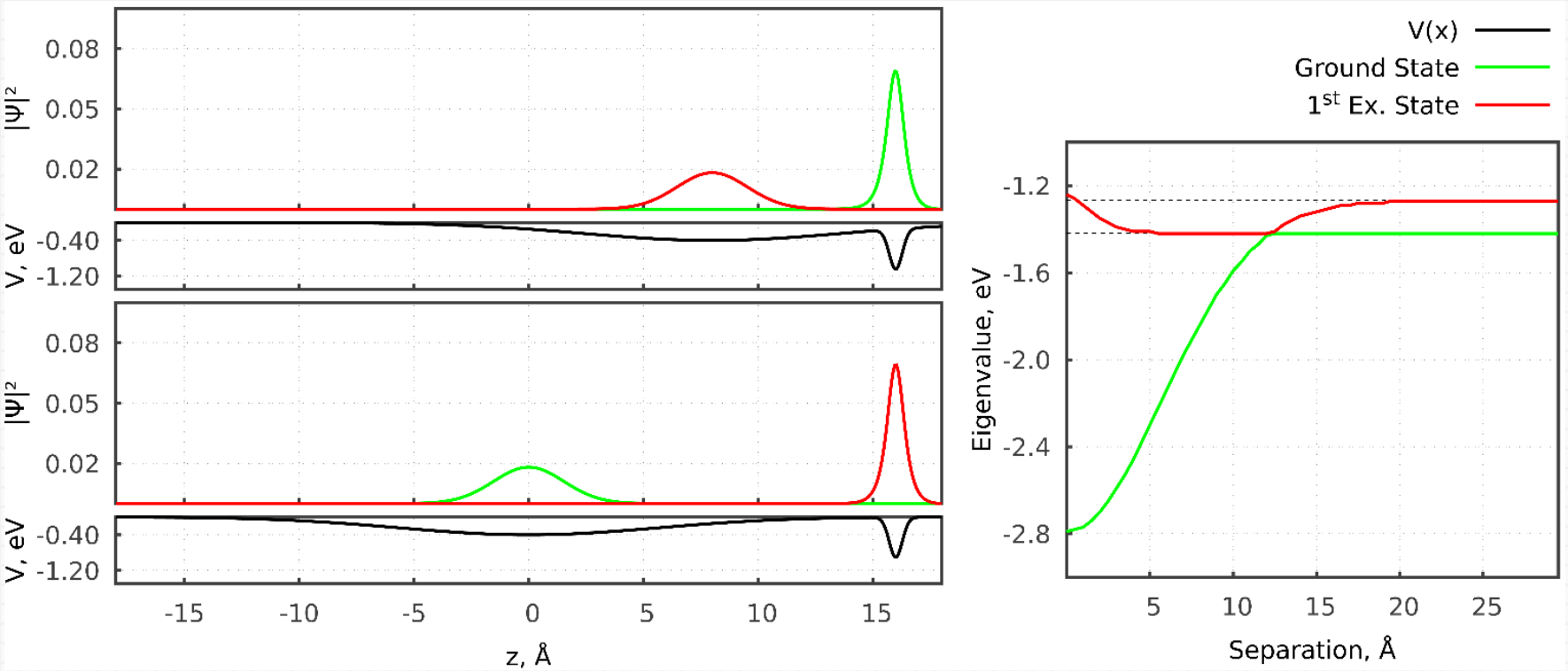




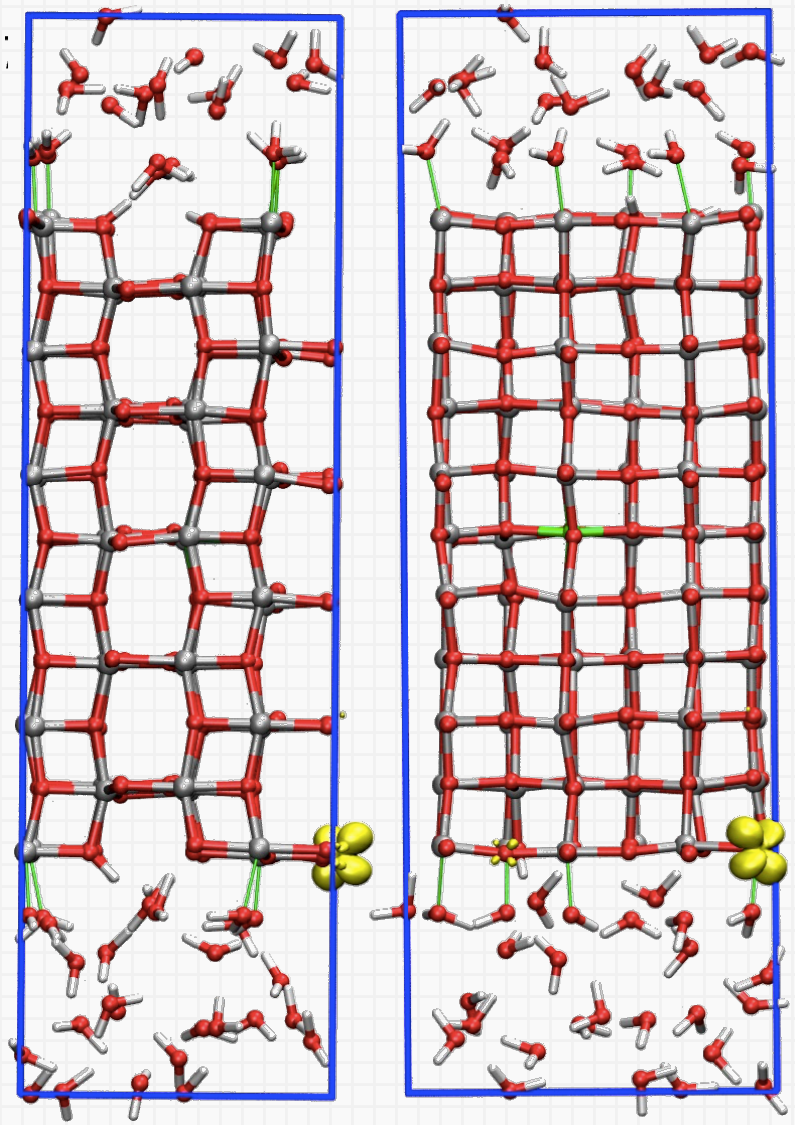


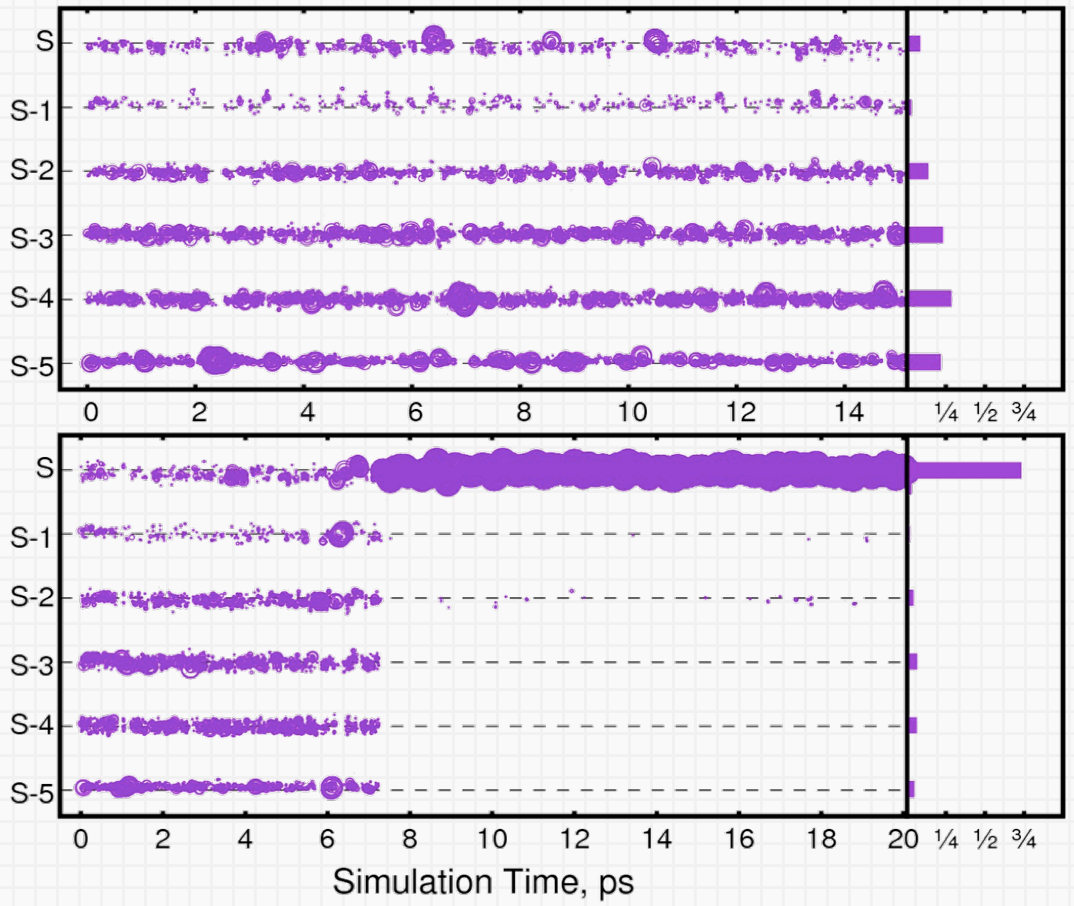


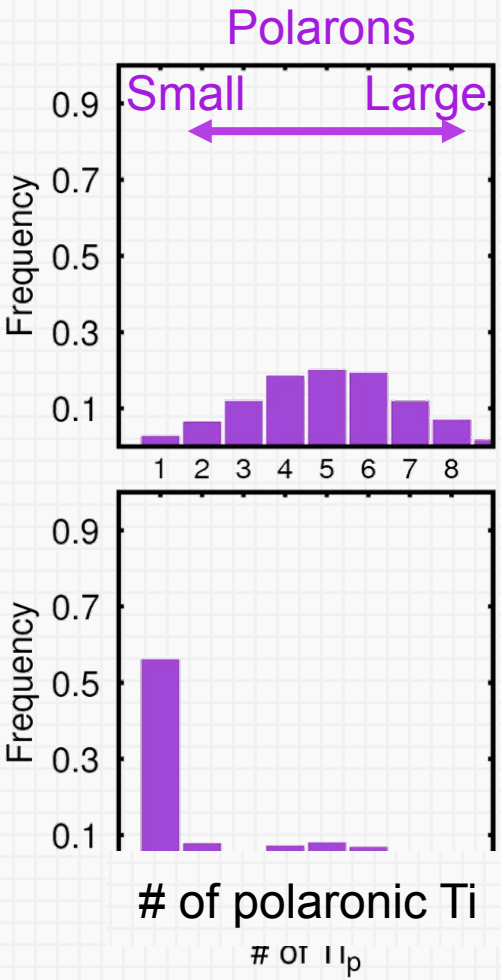
Particle in a box + 2 wells



Facet dependence - (100) Surface



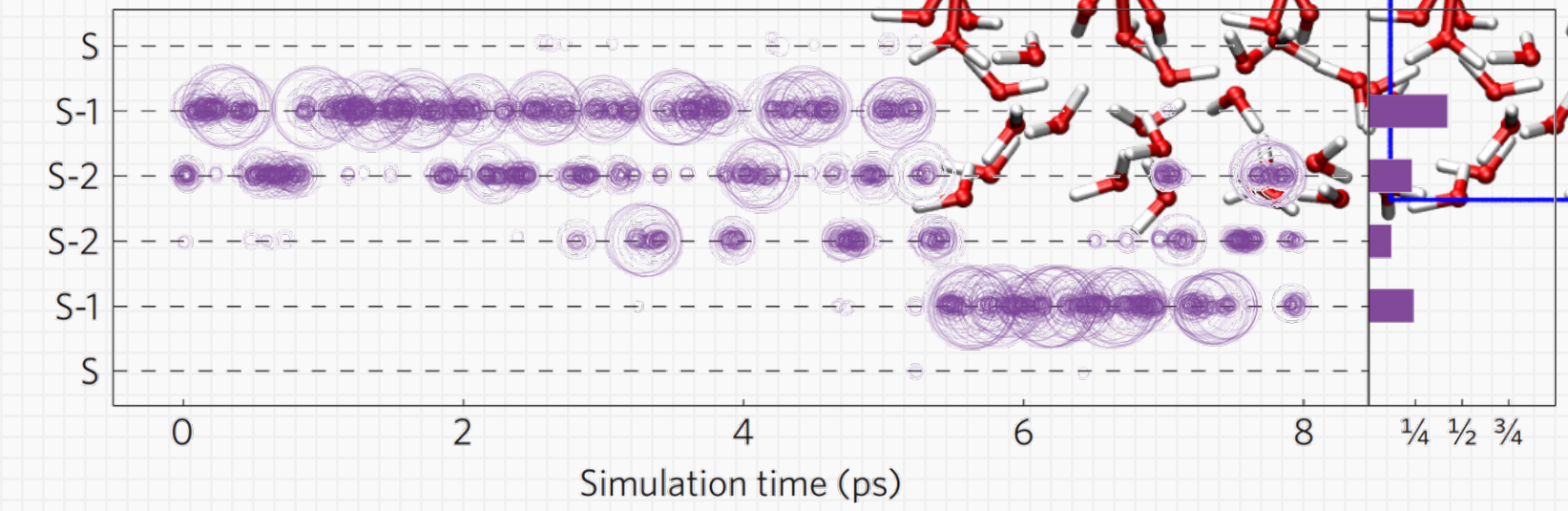




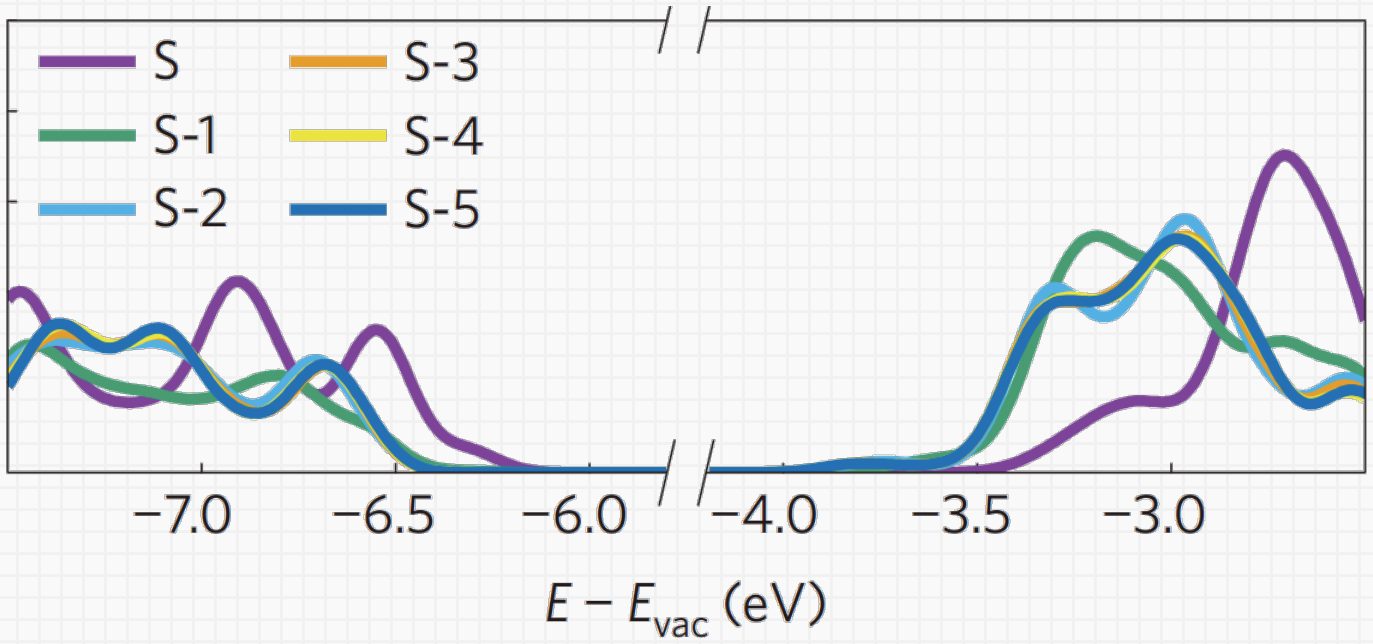
Even with a thick slab, doped with Nb in the bulk electrons can get trapped on (100) surface.

(001) Surface

- Excess electron avoids surface layers.
- It is typically delocalized throughout an inner (001) plane, and hops between different planes frequently.



(001) Surface does not have free, low-lying orbitals



Contribution of the surface layers to the CBM vanishes for the (001) surface (on both 1x1 and 1x4 surfaces)

Ohno et al New J Chem 2002

face and on the {110} face, respectively. For anatase particles, it is suggested that the oxidation site is mainly on the {001} face and the reduction site is mainly on the {011} face.

Summary

- Electron localization on the surface triggers water dissociation on otherwise inert surfaces
- (101) and (100) surfaces accommodate electrons well; (001) avoids them strongly, explaining observed oxidative behavior of the (001) surface vs reductive behavior of the others

THANK YOU

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY

BROOKHAVEN NATIONAL LABORATORY

PICSciE

NERSC