



# First principles simulations of materials and processes in photocatalysis

**Annabella Selloni**

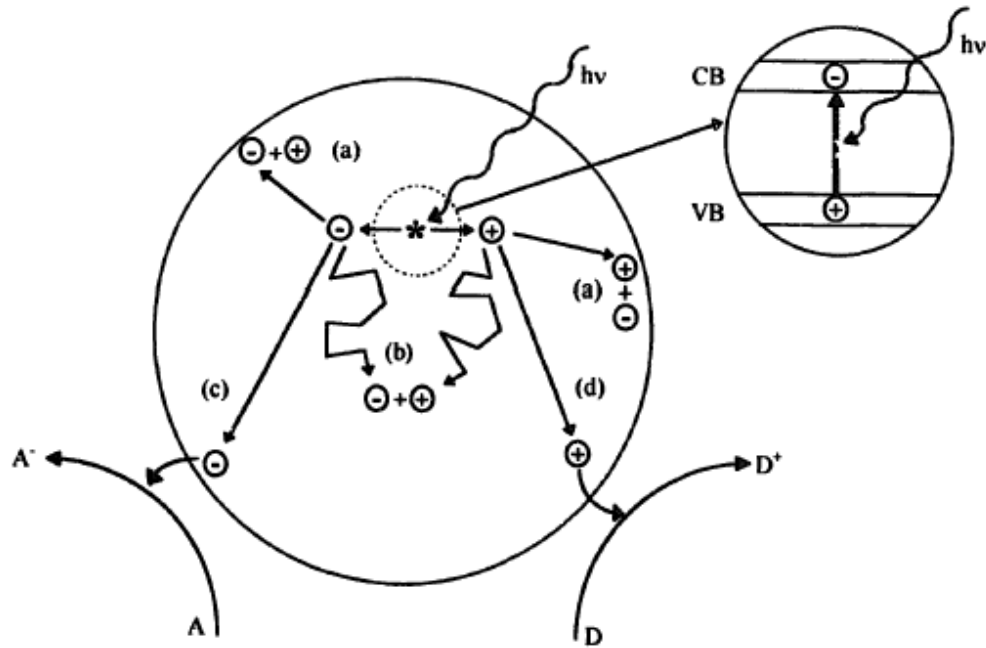
Department of Chemistry, Princeton University

## Work with:

Ulrich Aschauer, Jia Chen, Hongzhi Cheng, Cristiana Di Valentin, Weiyi Hou, Ye-Fei Li, Patrick Sit, Federico Zipoli

Expt: U. Diebold & co, TU-Wien

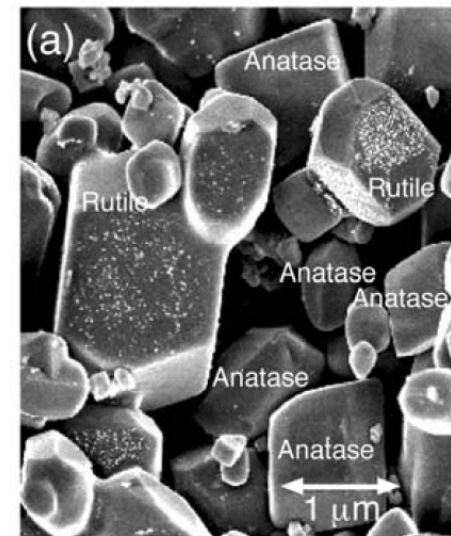
# Photocatalysis: the basic mechanism



Linsebigler, Lu, Yates, *Chem. Rev.* 95 (1995) 735

# Photocatalyst Materials

Mixture of  $TiO_2$  rutile  
and anatase



Ohno et al. *New J. Chem.* 26 (2002) 1167

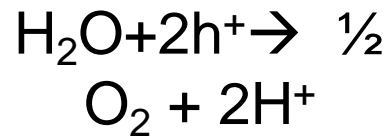
- **Rutile stable in bulk - Anatase in Nanoparticles**  
(Zhang, Banfield, *J Mater Chem*, 1998, 8, 2073)
- **Anatase photocatalytically more active than rutile**  
(Kavan, Grätzel, Gilbert, Klemenz, Scheel, *J Am Chem Soc*, 1996, 118, 671)

# Water splitting in PEC cell

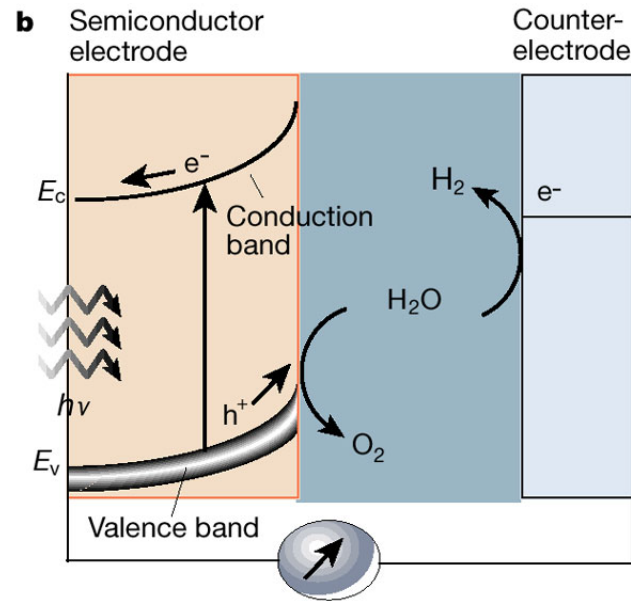


$$\Delta G = 2.46 \text{ eV/H}_2\text{O}$$

## Oxidation



N-type  
semiconductor, e.g.  
 $\text{TiO}_2$



## Reduction



Pt typically used as  
cathode

Issues: photo-oxidation inefficient  
Pt very expensive

# Challenges for theory/simulation

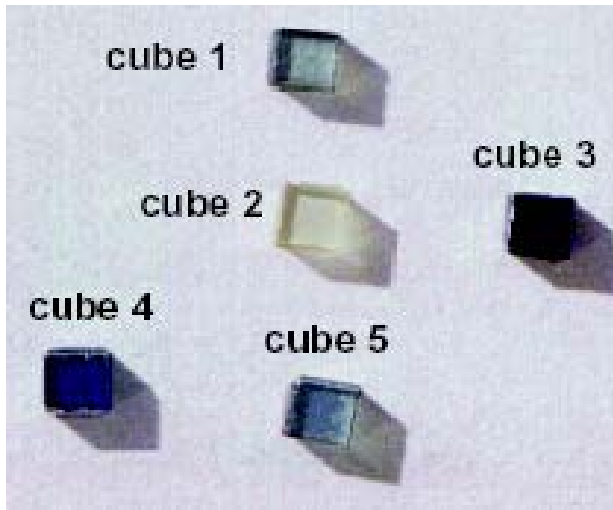
- Materials properties: electronic structure, excitations (electrons, holes, excitons), transport properties (defects, e-ph, ..)
- Solid-liquid interface, surface structure, interface electronic structure (level alignment at the interface)
- Electron & proton transfer reactions; chemical reactivity, pathways and barriers

# Outline

- Polaronic states in  $\text{TiO}_2$ :
  - surface/subsurface defects
  - Electron & holes in photo-excited anatase
- Interfacial electron transfer at the  $\text{TiO}_2$ -gas &  $\text{TiO}_2$ /water interfaces

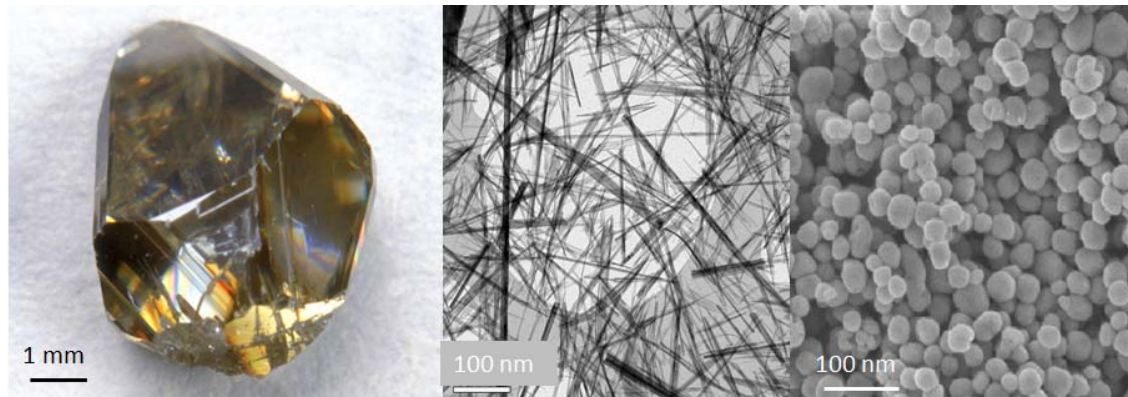
# Approach

- DFT with GGA-PBE and/or B3LYP/PBEO
- Minimum energy pathways and barriers via NEB
- First principles molecular dynamics (FPMD)
- Free energy barriers via thermodynamic integration
- Quantum ESPRESSO



Color change in rutile samples induced by increasing level of reduction (oxygen vacancies and Ti interstitials)

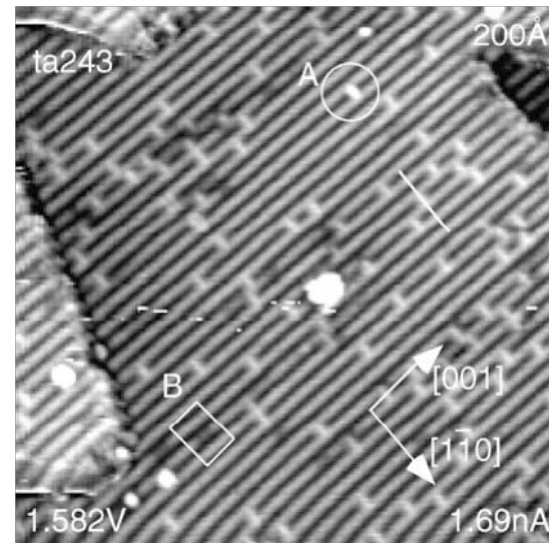
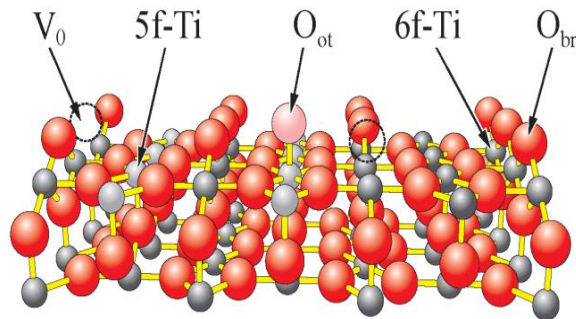
# Polaronic states in $\text{TiO}_2$



Anatase: from bulk to nano

# The paradigm: surface O-vacancy on rutile $\text{TiO}_2(110)$

## Rutile (110)



Empty state STM image of rutile (110) (bright rows  $\equiv$  Ti atoms)

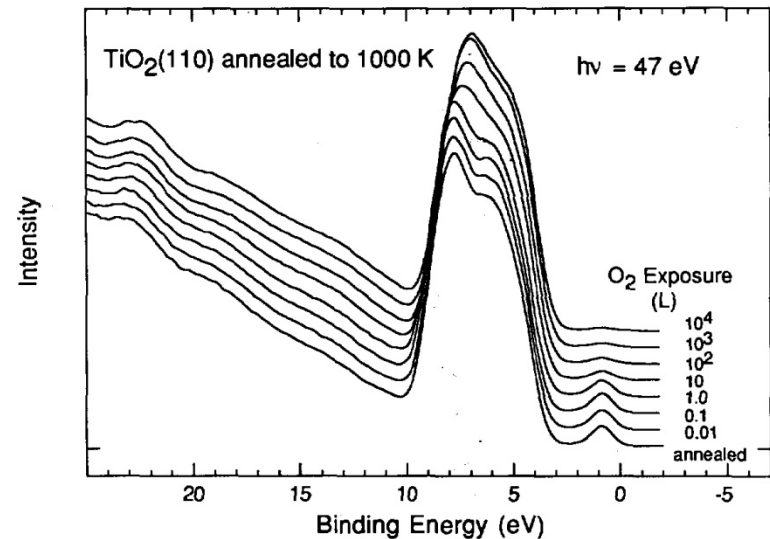


# The paradigm: surface O-vacancy on rutile $\text{TiO}_2(110)$

O-vacancy  $\rightarrow$  two excess electrons:  
delocalized or localized  $\text{Ti}^{3+}$  species?

- Experiments suggesting localized  $\text{Ti}^{3+}$  species:

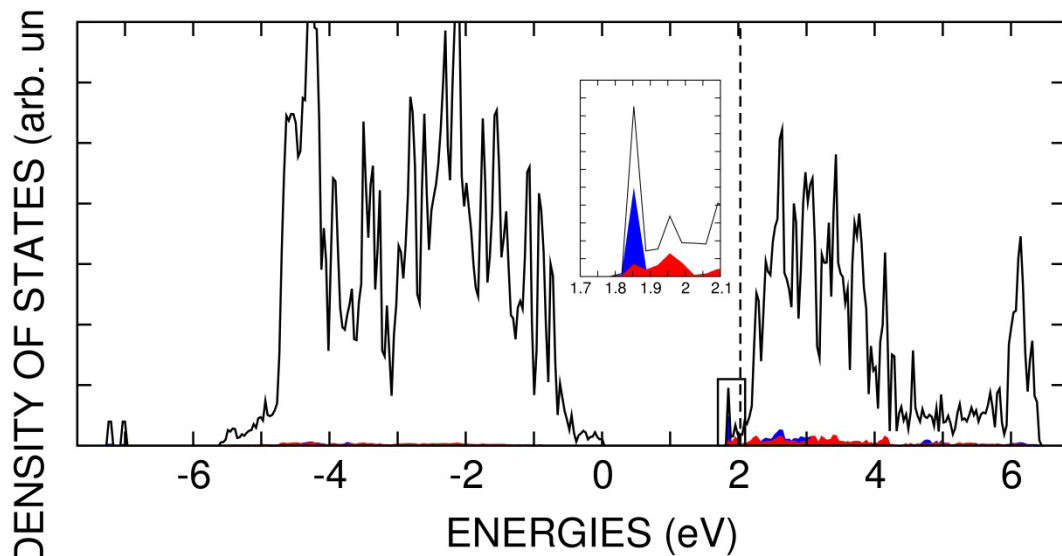
- EPR (bulk) shows paramagnetic defects with  $3d^1$  character
- UPS and EELS show states in the gap  $\sim 0.8$  eV below CB



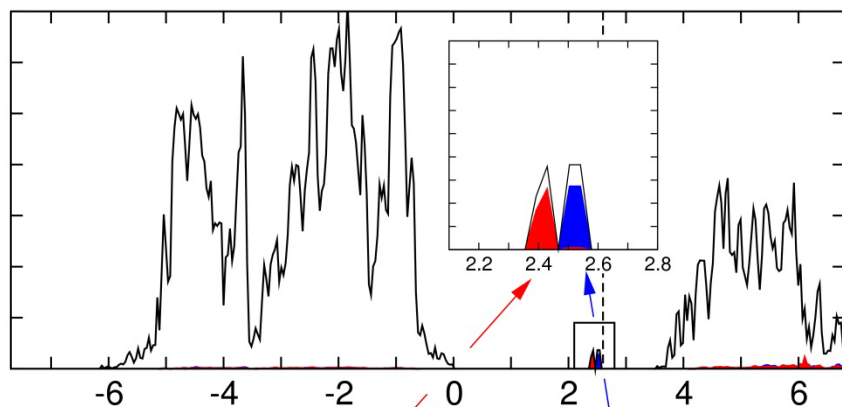
- Expts suggesting partially delocalized  $\text{Ti}^{3+}$  species

- defect charge shared by several surface and subsurface Ti sites according to Photoelectron Diffraction (PED)(Krüger et al, PRL 100 (2008)) and occupied state STM (Minato et al, JCP 130 (2009))

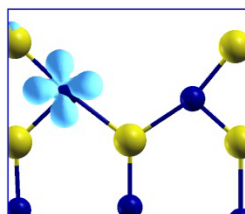
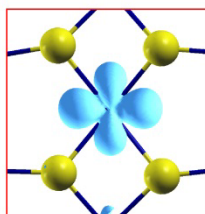
# Ti<sup>3+</sup> species in reduced TiO<sub>2</sub>(110): theory



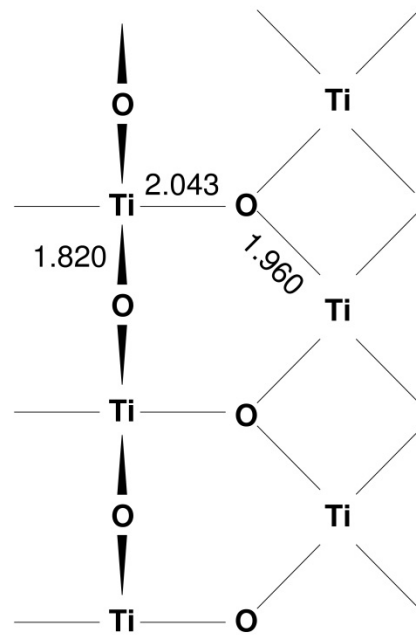
delocalized states at energies near the bottom of the CB and no gap state predicted by DFT-LDA and DFT-GGA calculations: in contrast with EPR, UPS & EELS experiments



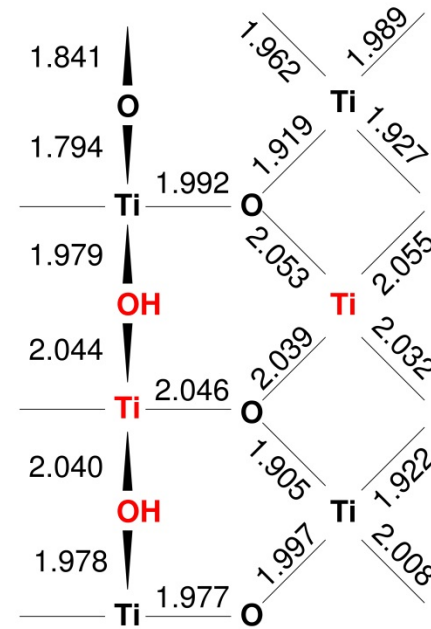
localized triplet state with energy in the band gap predicted by hybrid functional and DFT+U calculations (T= 0K)



# Polaronic nature of O vacancy states



CLEAN



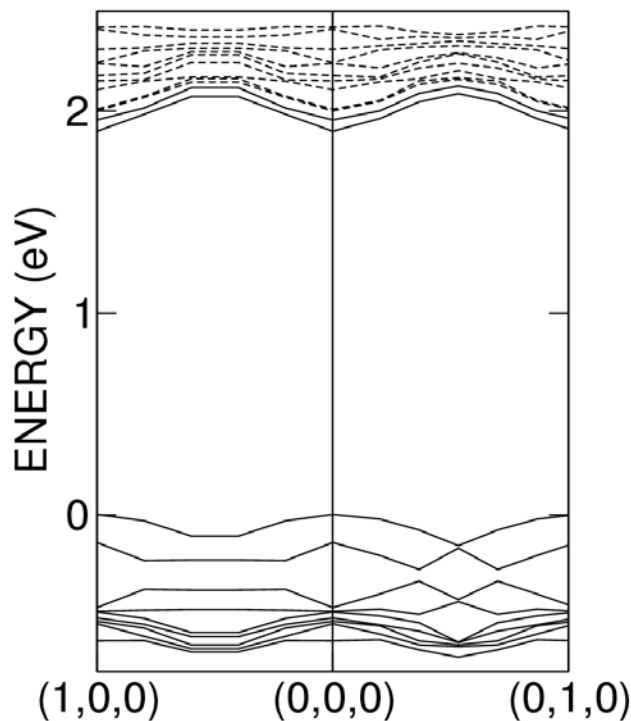
HYDROXYLATED

Polaronic distortion (and spin-polarization)  
essential for the formation of localized  
gap states

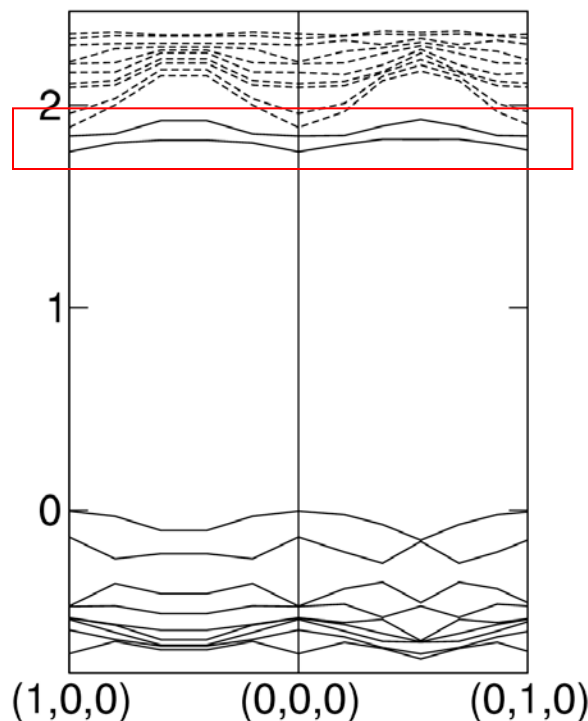
# Polaronic nature of O vacancy and OH groups

SCF/GEOM

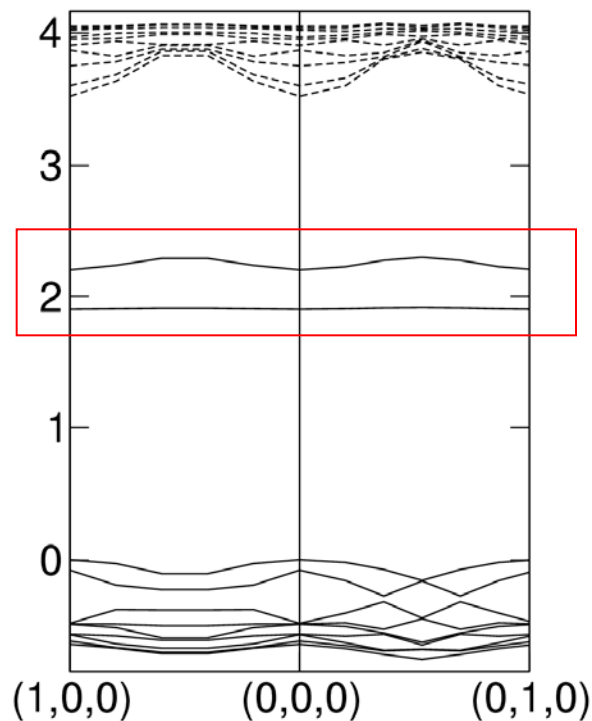
PBE/PBE



PBE/B3LYP



B3LYP/B3LYP

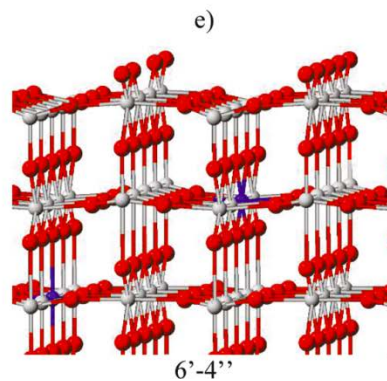
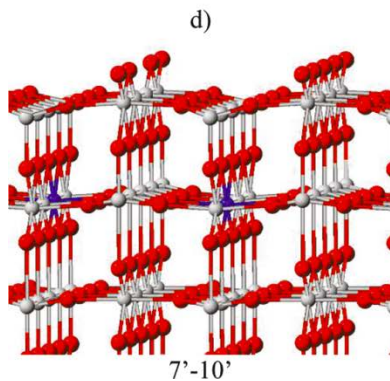
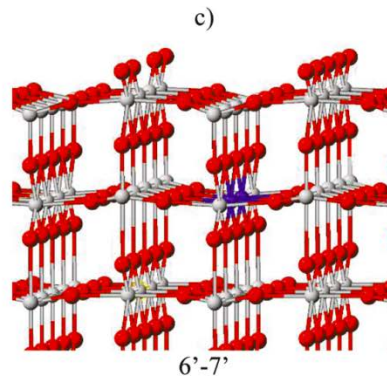
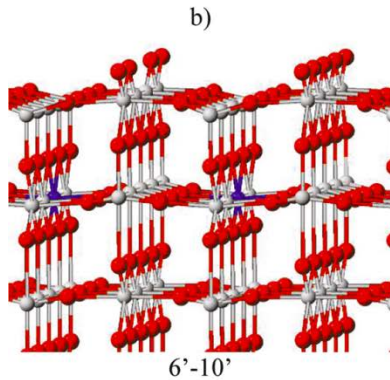
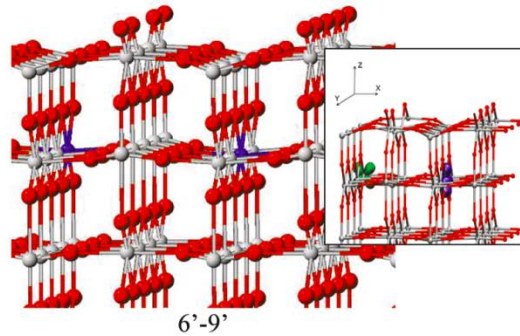


How to explain the partial delocalization seen by PED and STM?

# Ti<sup>3+</sup> species in reduced TiO<sub>2</sub>(110): theory

Distribution of Ti<sup>3+</sup> sites in reduced rutile TiO<sub>2</sub> (110)

DFT+U calculations:  
Deskins et al JPCC 115 (2011)



several possible  
nearly degenerate  
localization sites at  
the TiO<sub>2</sub> surface

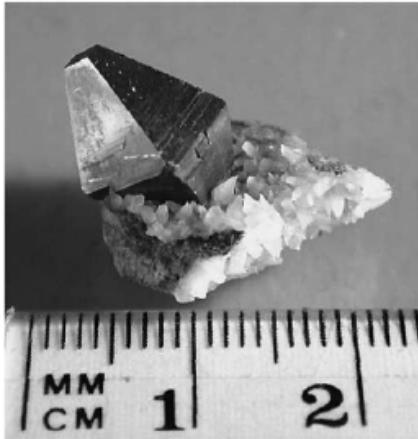
..electrons can  
hop between  
different sites

# Ti<sup>3+</sup> species in reduced TiO<sub>2</sub>(110)

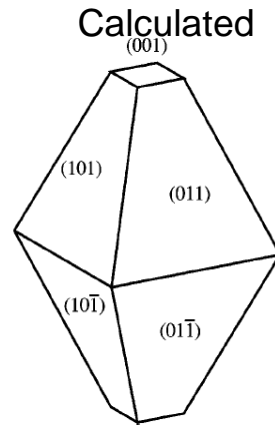
- At T= 0K localized states preferred; many possible localization sites, nearly degenerate in energy
- Electrons easily hop from one site to the other with small (< 0.1 eV) activation barrier at finite T → effectively partially delocalized state
- hybrid functionals or +U corrections essential to capture polaronic character of excess charges

# TiO<sub>2</sub> anatase surface

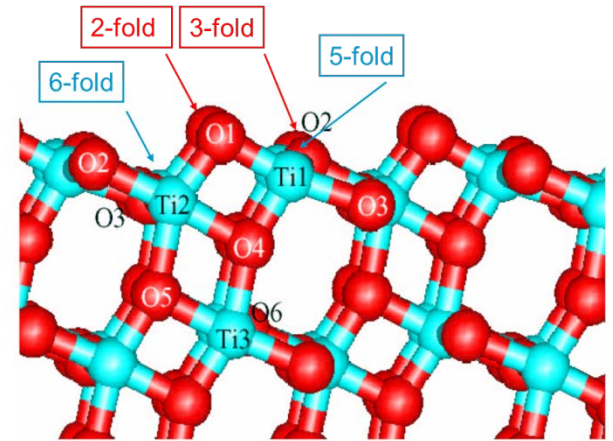
Natural Anatase crystal



Diebold, *Surf Sci Rep*, 2003

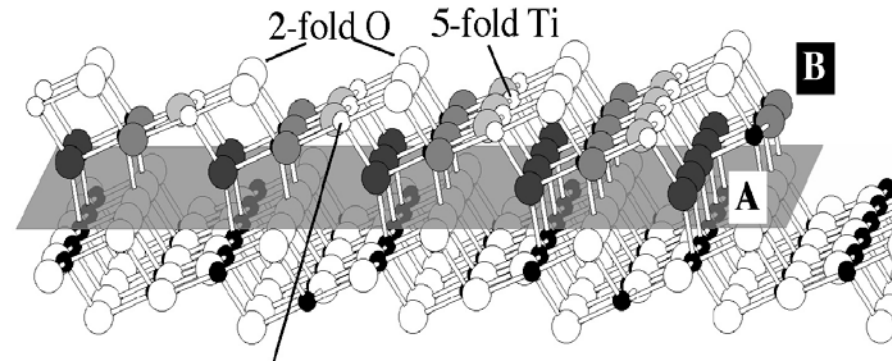
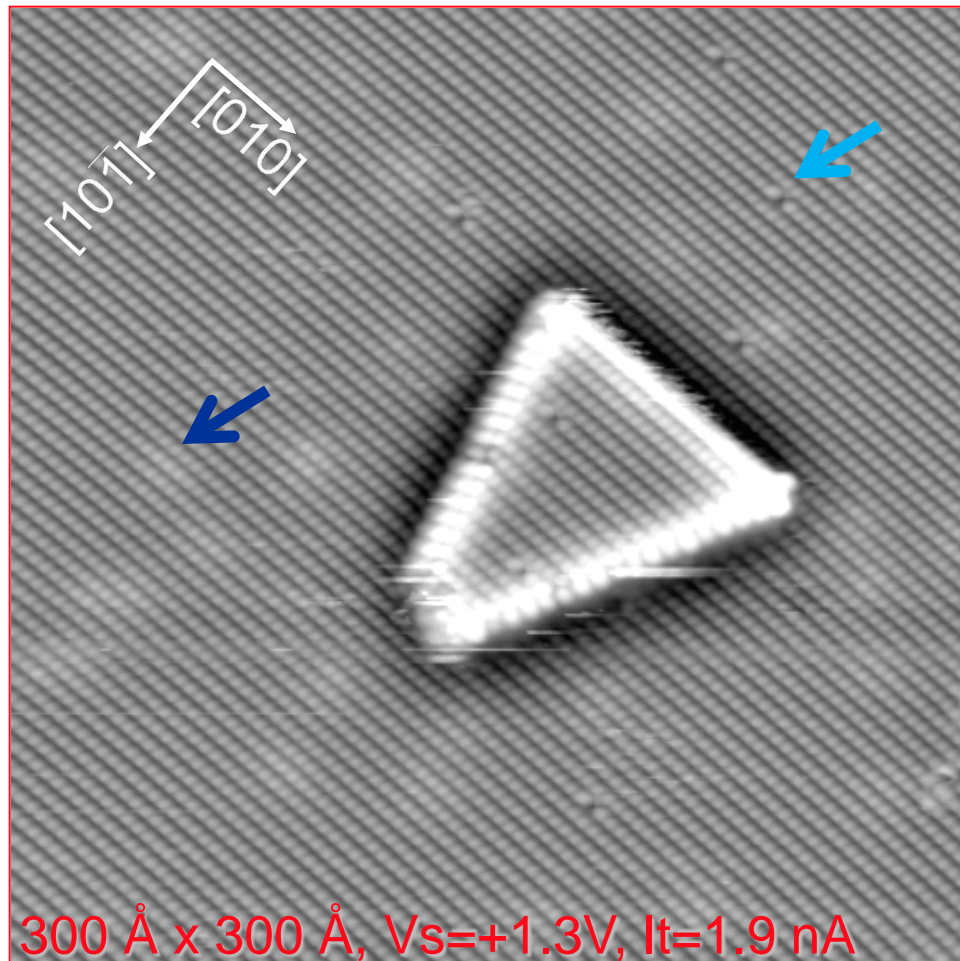


Lazzeri et al., *Phys Rev B*, 2001



(101) surface dominates the anatase morphology

# STM of cleaved Anatase (101)



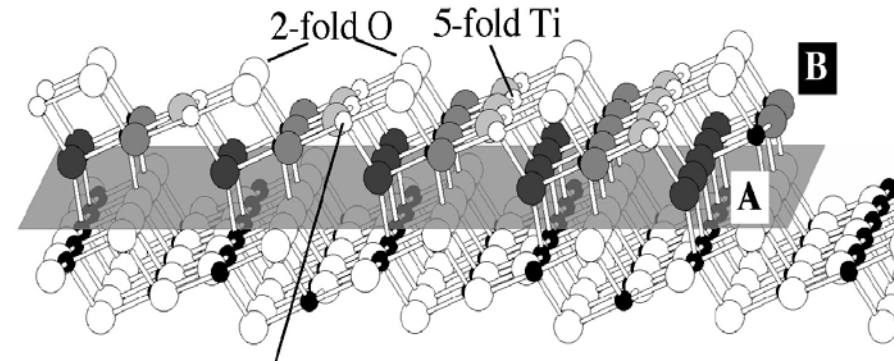
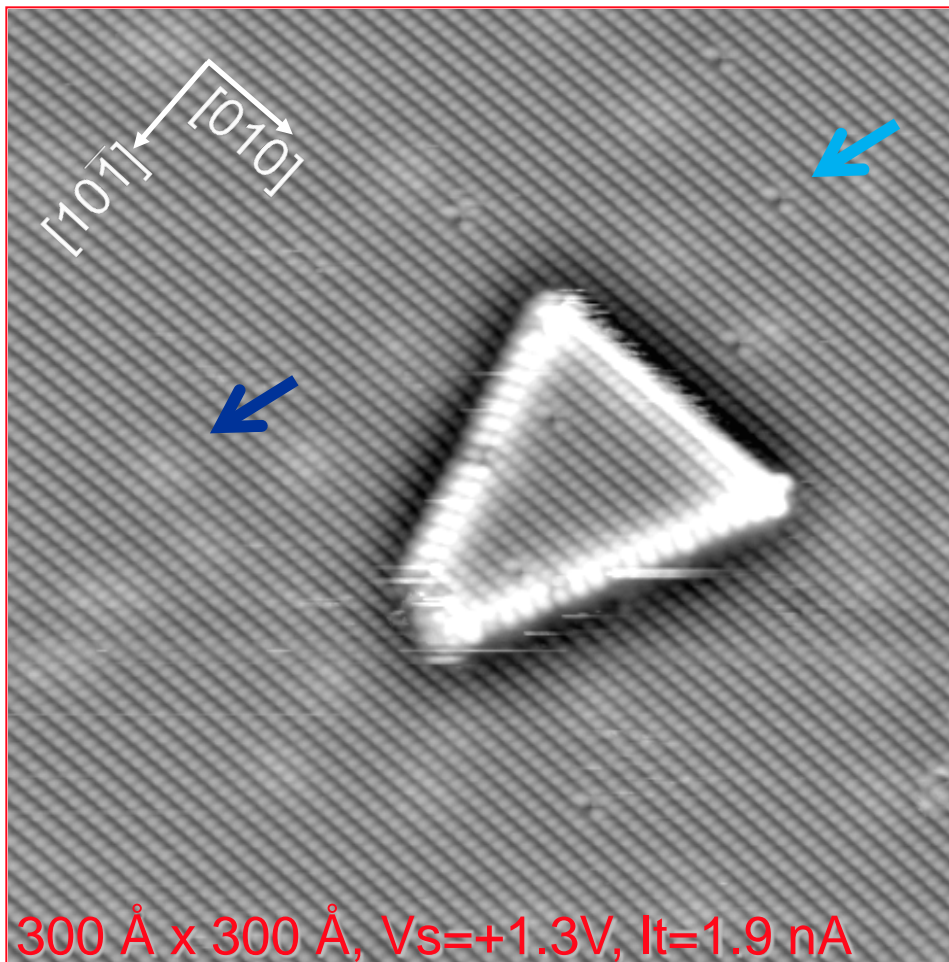
Anisotropic step edges  
(Gong et al, Nature Mater. 2006)

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

Subsurface impurities



# No surface oxygen vacancies on cleaved Anatase (101)



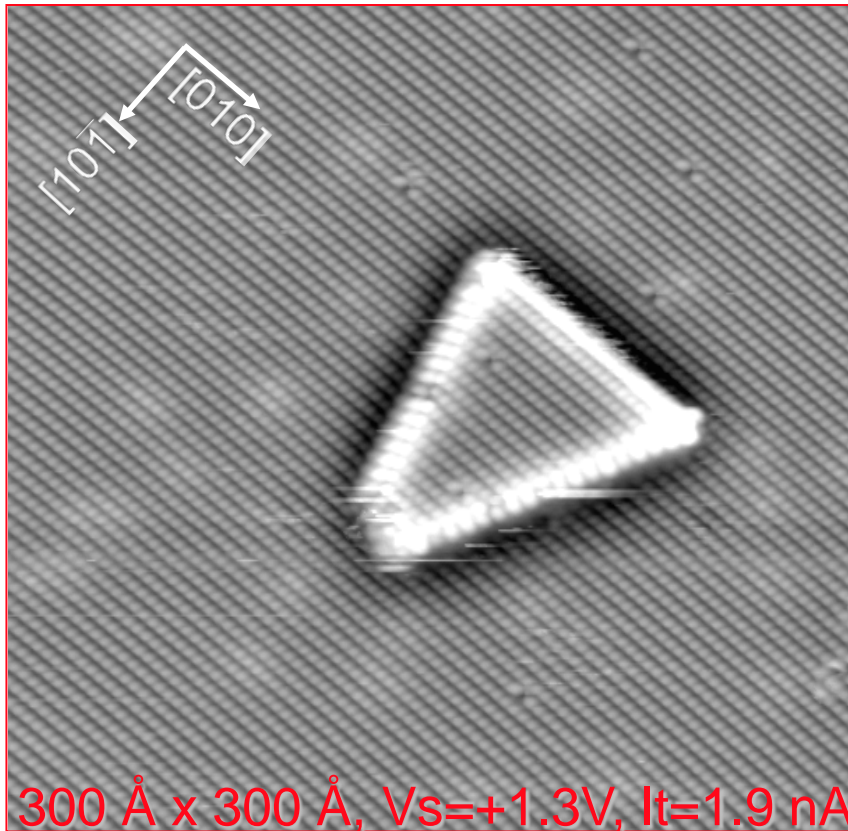
Anisotropic step edges  
(Gong et al, Nature Mater. 2006)

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

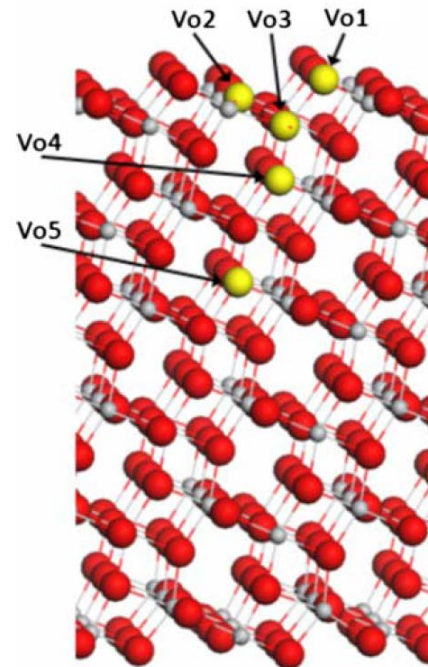
Subsurface impurities

He et al, PRL 2009

# Vacancies are subsurface



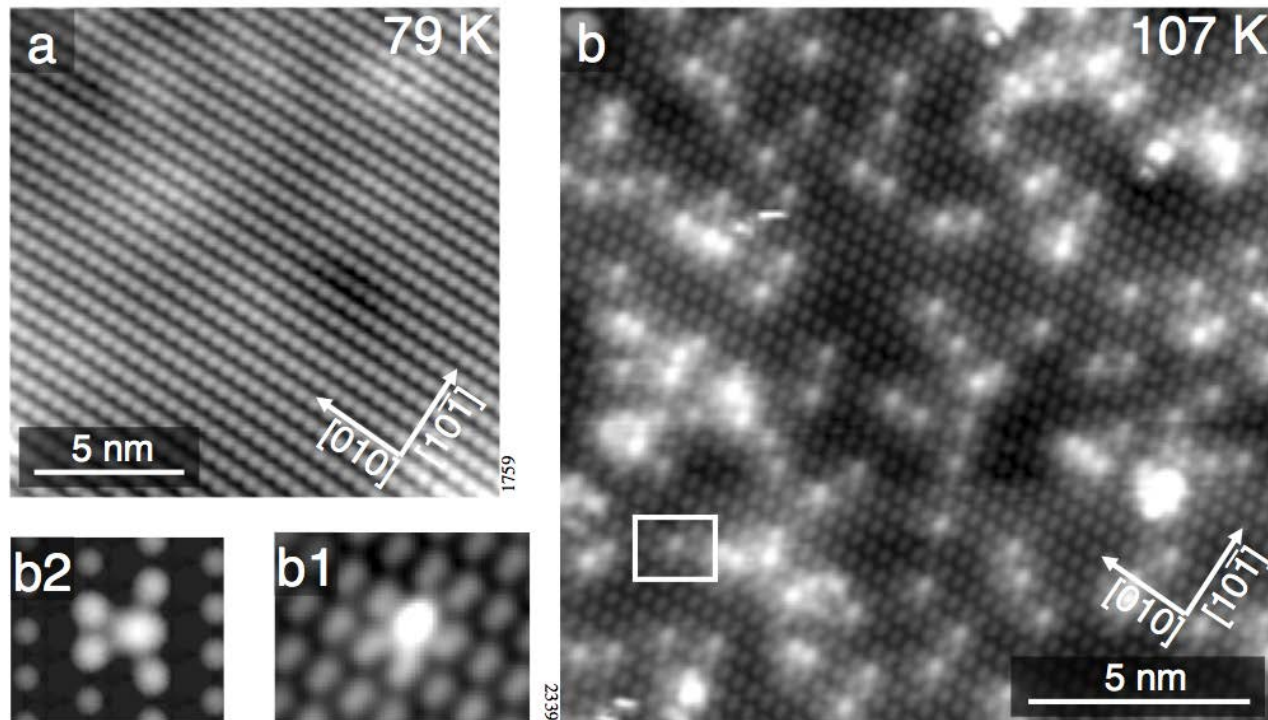
## DFT calculations



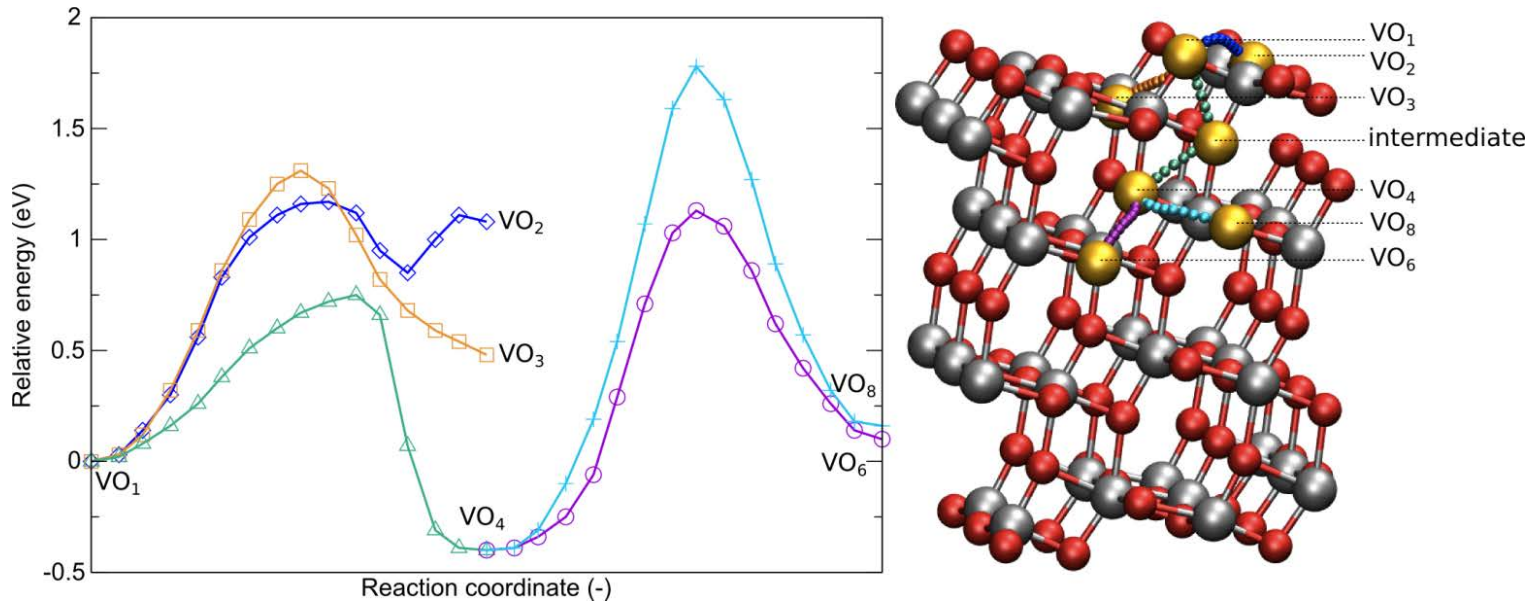
Vac.	$E_{\text{form}}$ [eV]
Vo1	4.15
Vo2	5.40
Vo3	4.73
<b>Vo4</b>	<b>3.69</b>
<b>Vo5</b>	<b>3.65</b>
<b>Bulk</b>	<b>3.69</b>

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 $O_{\text{vac}}$ 's *into* anatase

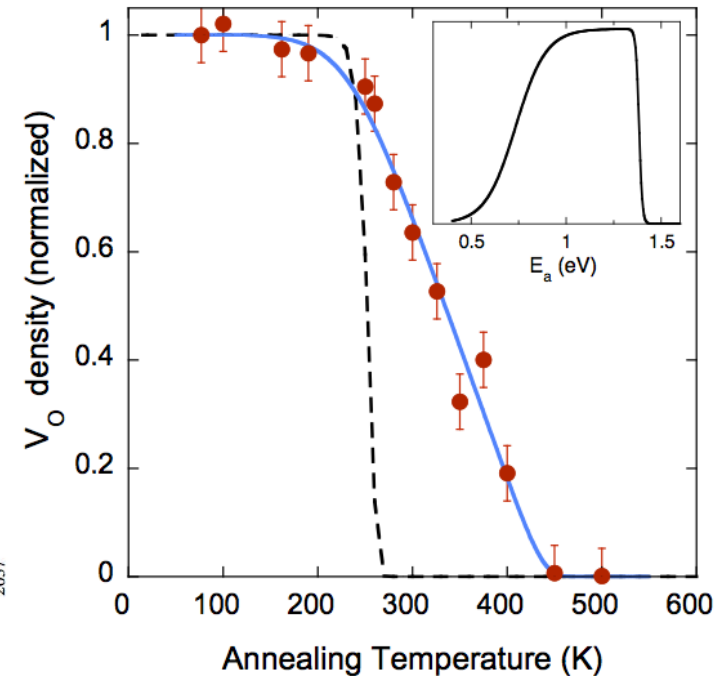
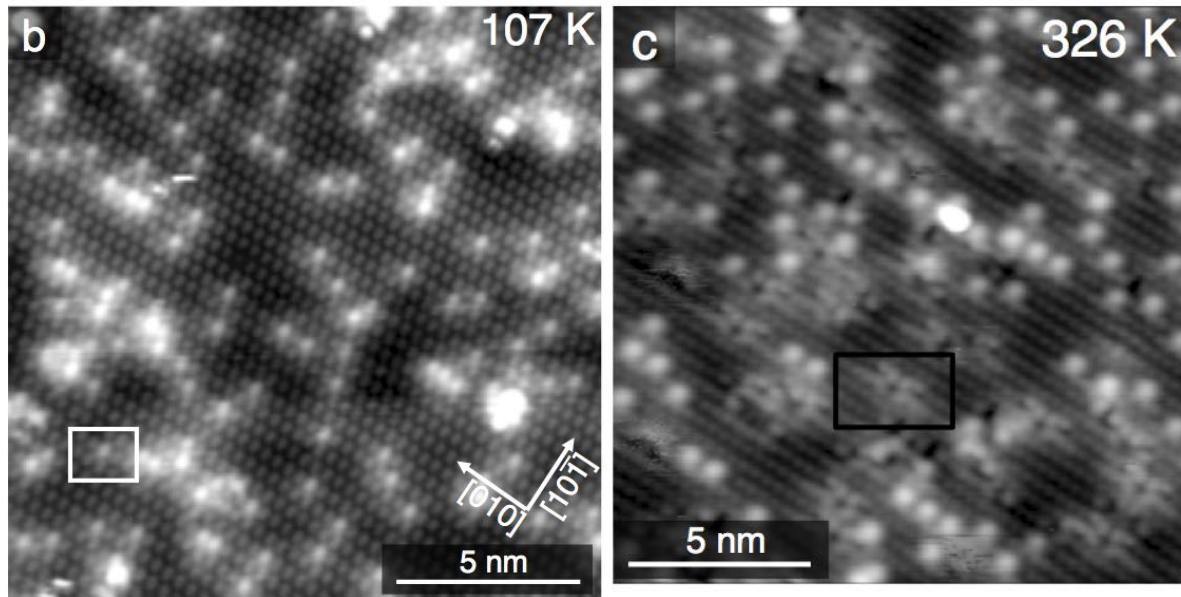


**~ 0.75 eV barrier for O-vacancy surface → sub-surface migration predicted by DFT-GGA**

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

After irradiation @ 100 K

10 min @ 325 K

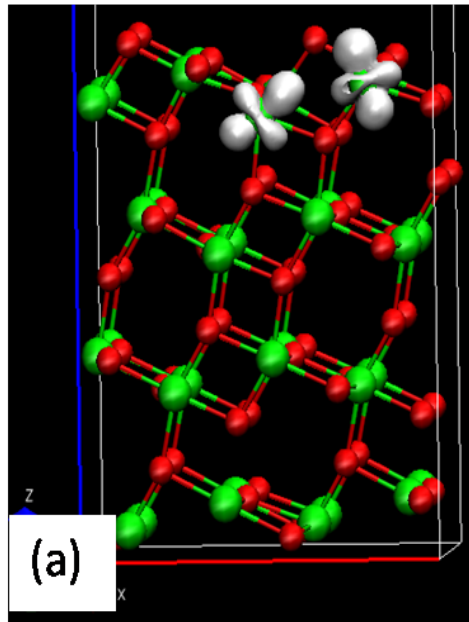


P. Scheiber, M. Fidler, O. Dulub, M. Schmid, U. Diebold, W. Hou, U. Aschauer, A. Selloni, (Sub)surface mobility of oxygen vacancies at the  $\text{TiO}_2$  anatase (101) surface, *Phys. Rev. Lett.* **2012**, *109*, 136193.

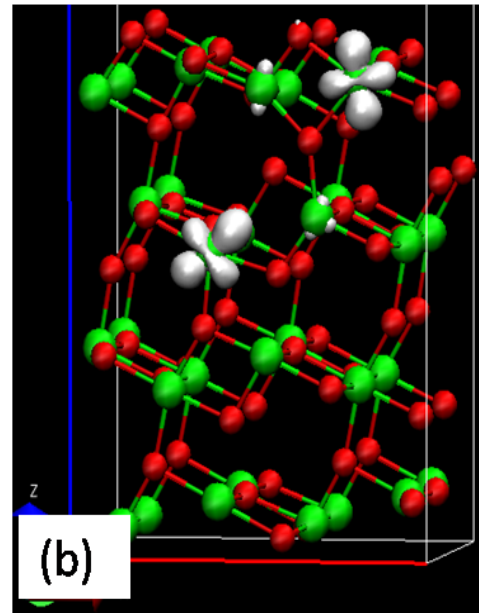
# Surface & subsurface O vacancy @ anatase (101): DFT + U calculations

$U = 3.5 \text{ eV}$   
(calculated)

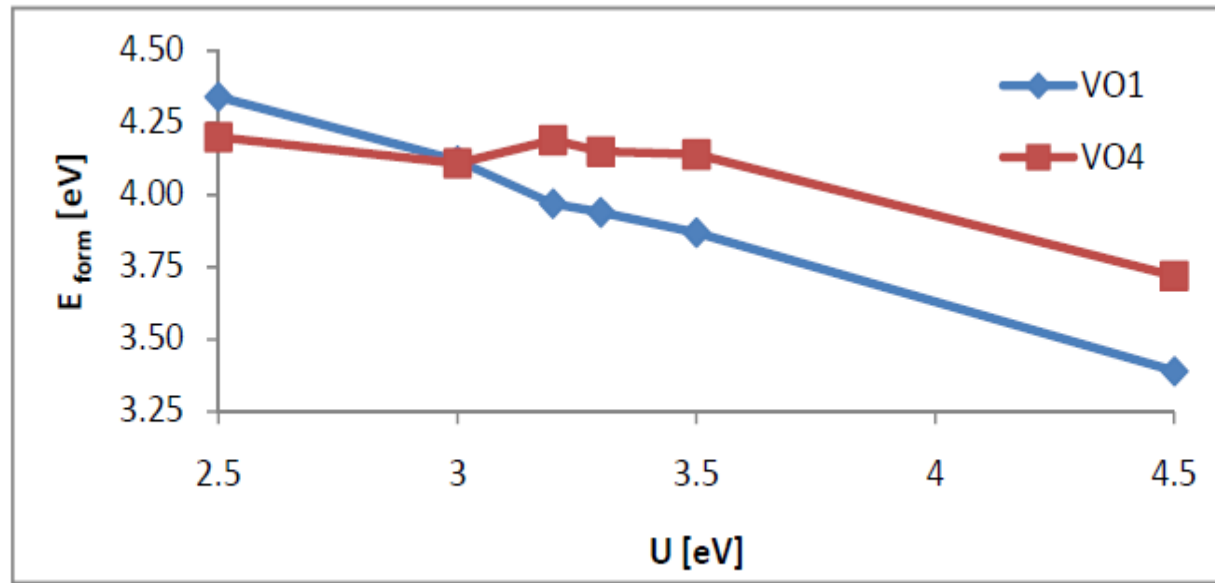
Surface  $V_{O1}$ ,  
 $S=1$



Subsurface  
 $V_{O4}$ ,  $S=1$



# Surface & subsurface O vacancy @ anatase (101): DFT + U calculations

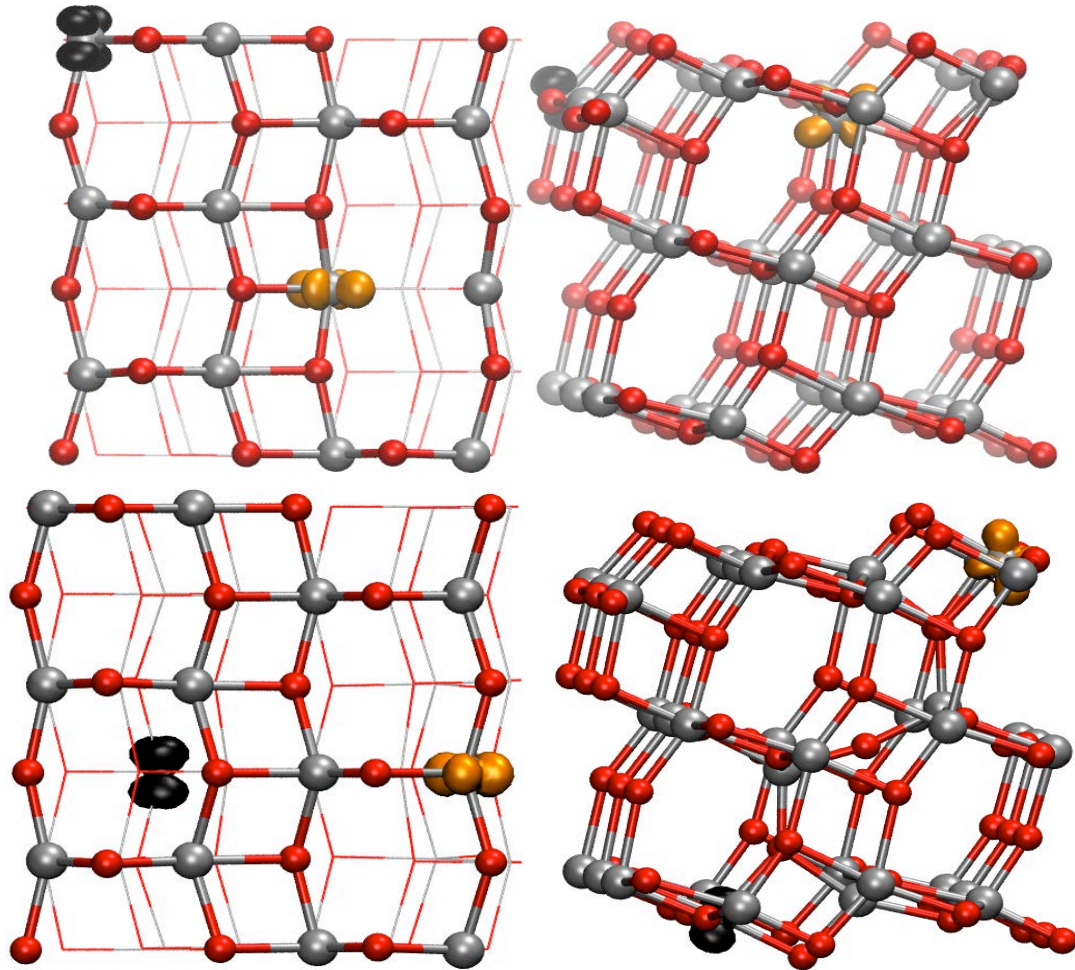


Polaronic effect over-estimated?

Temperature?

???

# Surface & subsurface O vacancy @ anatase (101): PBE0 calculations



**Surface Vo:  
 $E = 0.$**

**Subsurface Vo:  
 $E = - 0.61 \text{ eV}$**



# Bulk and surface polarons in anatase

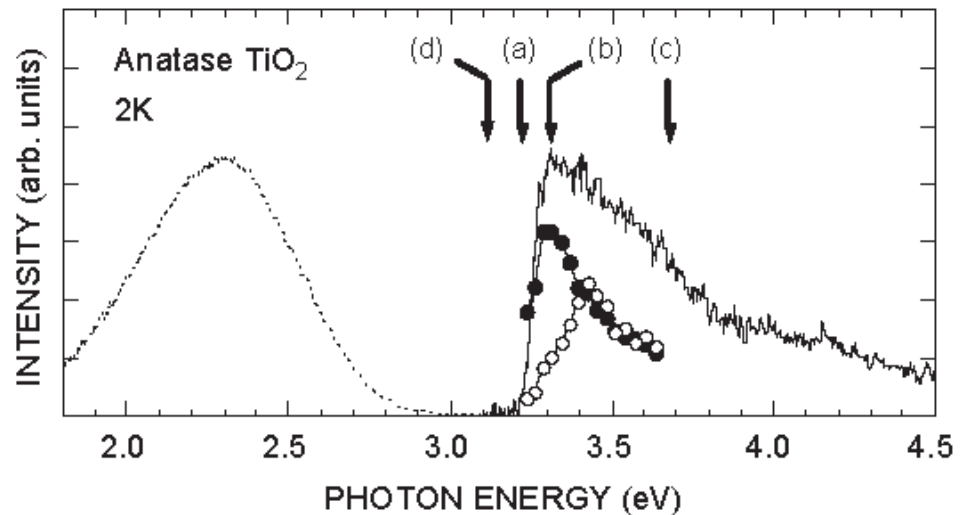
Do electrons & holes localize in the absence of structural defects or impurity centers?

# Electrons, holes and e-h pairs in photoexcited (defect-free) anatase TiO<sub>2</sub>

➤ Role in photocatalysis

➤ Experimental evidence of trapped holes and self-trapped excitons

Luminescence band from self trapped (triplet) excitons: peak at 2.3 eV & 2-3  $\mu$ s decay time



# Compare electron & hole states in the bulk and at the surface



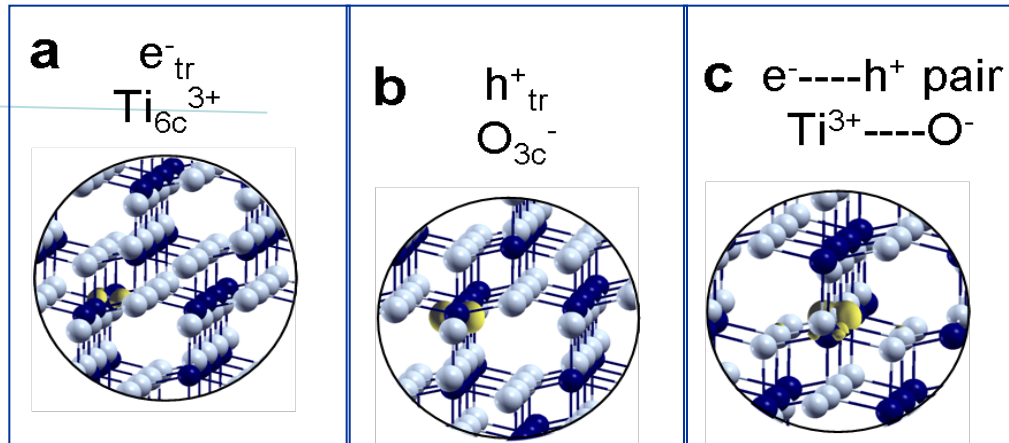
Cristiana Di Valentin

- Add a single electron or a single hole or excite a *triplet exciton* in a bulk supercell or large anatase (101) slab
- B3LYP functional (CRYSTAL09)

	HOMO-LUMO	S <sub>0</sub> →T <sub>1</sub> (vertical)	S <sub>0</sub> →T <sub>1</sub> (adiab.)	$\Delta E_{\text{trap}}$
Bulk	3.9	4.08	3.50	0.58

# Polaron states in anatase $\text{TiO}_2$

**Bulk  
Anatase**



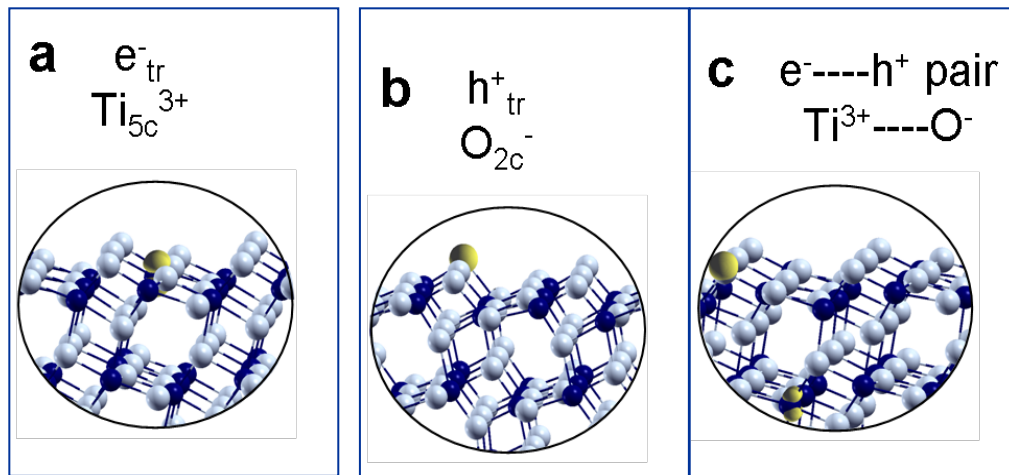
$\Delta E_{\text{trap}}(\text{eV})$

**0.23**

**0.74**

**0.58**

**(101)  
surface**



$\Delta E_{\text{trap}}(\text{eV})$

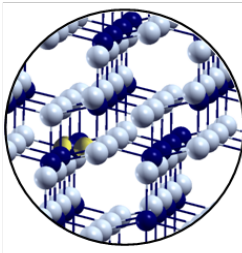
**0.62**

**1.45**

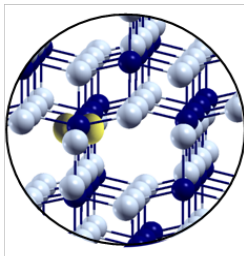
**-----**

# BULK

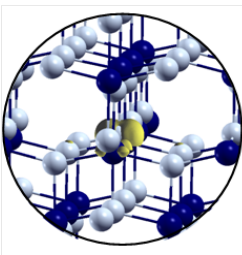
**a**  $e^-_{tr}$   
 $Ti_{6c}^{3+}$



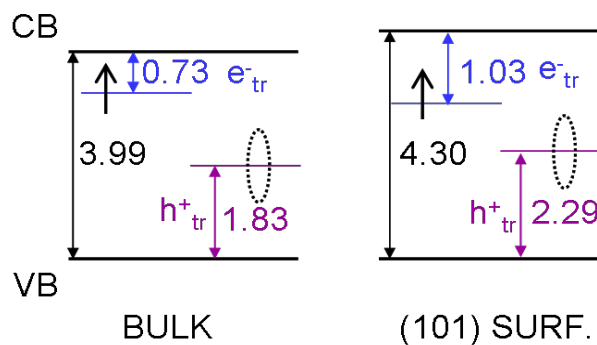
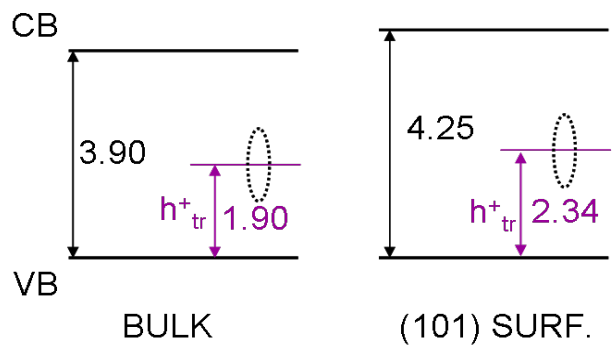
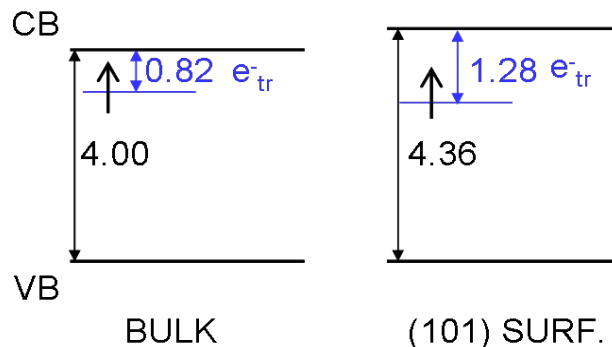
**b**  $h^+_{tr}$   
 $O_{3c}^-$



**c**  $e^- \text{---} h^+$  pair  
 $Ti^{3+} \text{---} O^-$

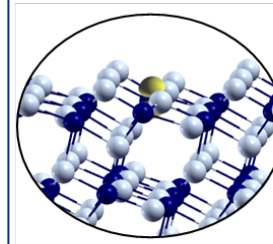


# One particle levels

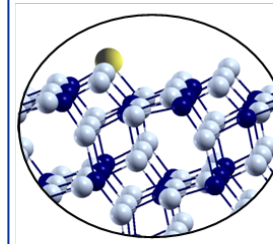


# SURFACE

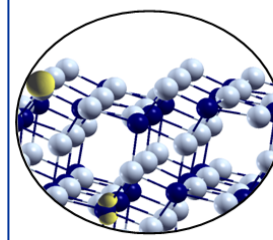
**a**  $e^-_{tr}$   
 $Ti_{5c}^{3+}$



**b**  $h^+_{tr}$   
 $O_{2c}^-$



**c**  $e^- \text{---} h^+$  pair  
 $Ti^{3+} \text{---} O^-$



# Some conclusions

- Self-trapped excitons/holes in photo-excited anatase
- surface polarons energetically more stable than bulk polarons → photoexcited carrier tend to migrate to the surface
- deep hole levels → decreased oxidation power

# Experimental Evidences

10, 196403 (2013)

PHYSICAL REVIEW LETTERS

week ending  
10 MAY 2013



## Tunable Polaronic Conduction in Anatase TiO<sub>2</sub>

S. Moser,<sup>1,2</sup> L. Moreschini,<sup>1</sup> J. Jaćimović,<sup>2</sup> O. S. Barišić,<sup>3</sup> H. Berger,<sup>2</sup> A. Magrez,<sup>2</sup> Y. J. Chang,<sup>1,4</sup> K. S. Kim,<sup>1</sup>  
A. Bostwick,<sup>1</sup> E. Rotenberg,<sup>1</sup> L. Forró,<sup>2</sup> and M. Grioni<sup>2</sup>

<sup>1</sup>Advanced Light Source (ALS), Berkeley, California 94720, USA

<sup>2</sup>Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut de Physique des Nanostructures, CH-1015 Lausanne, Switzerland

<sup>3</sup>Institute of Physics, Bijenička c. 46, HR-10000 Zagreb, Croatia

<sup>4</sup>Department of Physics, University of Seoul, Seoul, 130-743, Korea

(Received 26 February 2013; published 7 May 2013)

Large polaron, Shallow donor level ~ 10 meV

**TABLE 1: Oxidation Potentials ( $E_{ox}$ ) of Oxidizing Species during TiO<sub>2</sub> Photocatalytic One-Electron Oxidation Reactions**

oxidizing species	$E_{ox}/V$ versus NHE
$h_{VB}^+$	+2.96 <sup>a</sup>
$h_{tr}^+$	+1.6–1.7 <sup>b</sup>
$\cdot OH_{free}$	+2.72 <sup>c</sup>
$\cdot OH_{ads}$	+1.5 <sup>d</sup> , >+1.6 <sup>e</sup>

Majima et al., JPCC 111, 5259 (2007)

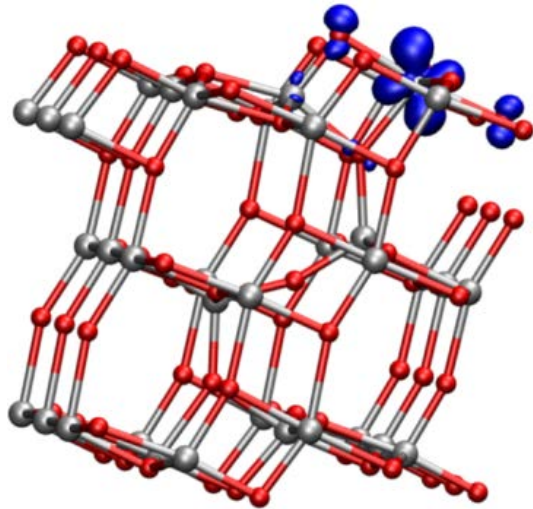
# $O_2$ adsorption on anatase (101)

- $O_2$  used as an electron scavenger in photocatalysis
- $O_2$  does not adsorb on stoichiometric surface
- Adsorption through surface →  $O_2$  charge transfer

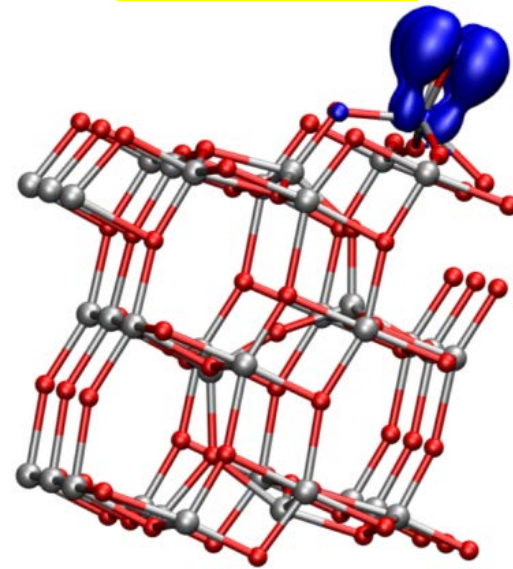


# $O_2$ adsorption on reduced anatase (101) & influence of subsurface defects

Clean surface



Adsorbed  $O_2$



Selectivity: stronger adsorption close to subsurface defect

Adsorbed  $O_2$  is a peroxide  $O_2^{2-}$ ,  $d_{O-O} \sim 1.46 \text{ \AA}$

~Same results with GGA, DFT+U, and hybrids

# What is the state of adsorbed O<sub>2</sub> on reduced titania: peroxide (O<sub>2</sub><sup>2-</sup>) or superoxide (O<sub>2</sub><sup>-</sup>) ??

Generation of superoxide ions at oxide surfaces

Masakazu Anpo<sup>a</sup>, Michel Che<sup>b</sup>, Bice Fubini<sup>c</sup>, Edoardo Garrone<sup>c</sup>, Elio Giamello<sup>c</sup> and Maria Cristina Paganini<sup>c</sup>

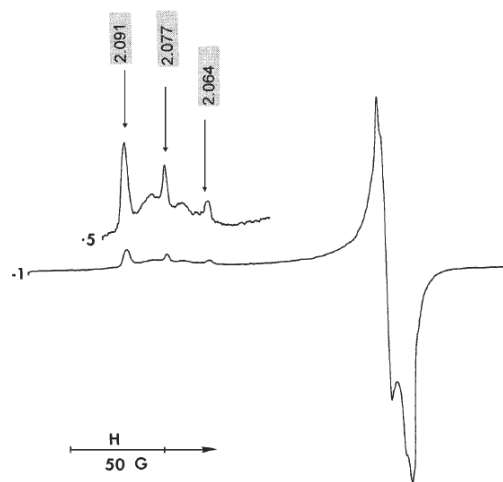
<sup>a</sup> Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Gakuen-cho 1-1, Sakai, Osaka 599-8531, Japan

<sup>b</sup> Laboratoire de Réactivité de Surfaces, Université P. et M. Curie (Paris VI), 4 Place Jussieu, 75252 Paris, France

<sup>c</sup> Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 9, 10125, Torino, Italy

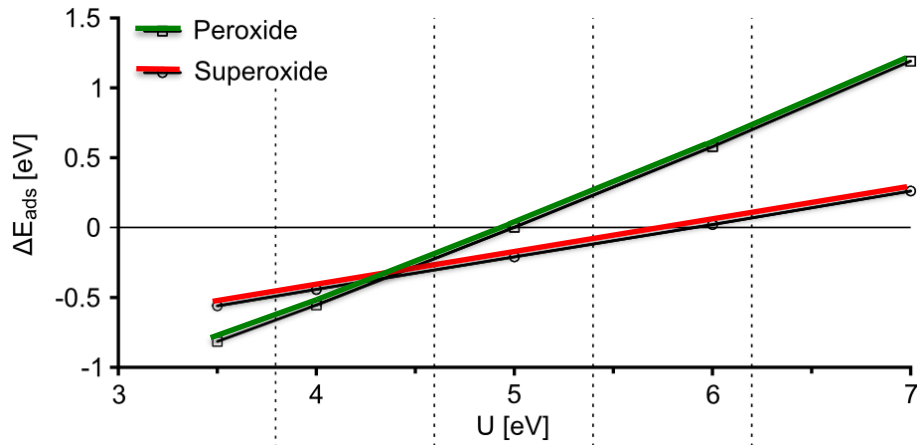
The superoxide radical anion O<sub>2</sub><sup>-</sup> is both an important intermediate in heterogeneous catalytic oxidation and a useful probe for positive charges in ionic solids, such as metal oxides and zeolites. The paper illustrates the main circumstances under which stable superoxide anions are formed at surfaces: (i) direct surface-oxygen electron transfer; (ii) photoinduced electron transfer; (iii) surface intermolecular electron transfer; (iv) decomposition of hydrogen peroxide.

Keywords: superoxide ions, radical ion, oxide surfaces, EPR study, hydrogen peroxide



Evidence of superoxide  
O<sub>2</sub><sup>-</sup> in EPR

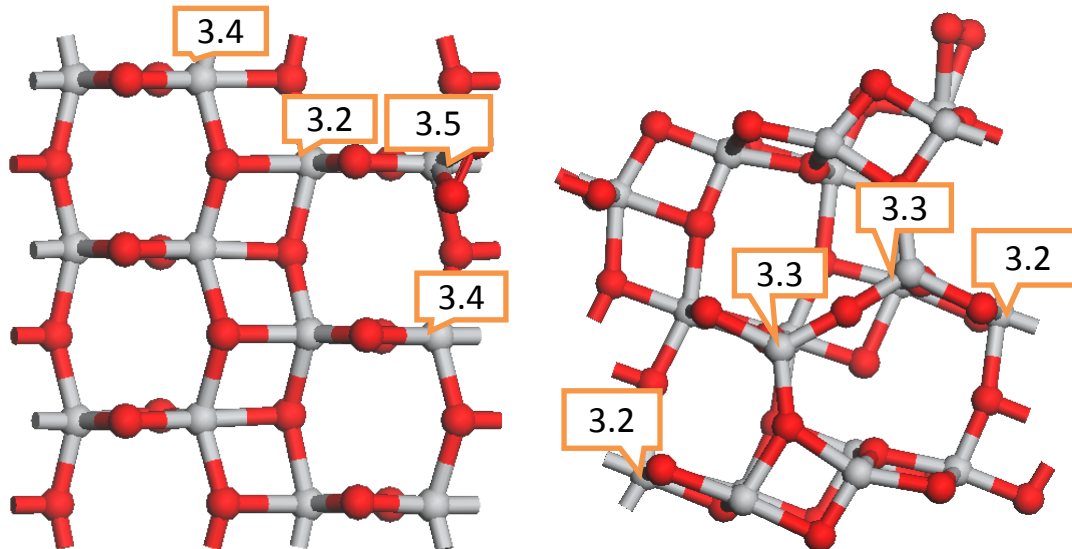
# Is the greater stability of the peroxide vs superoxide state an artifact of DFT-GGA?



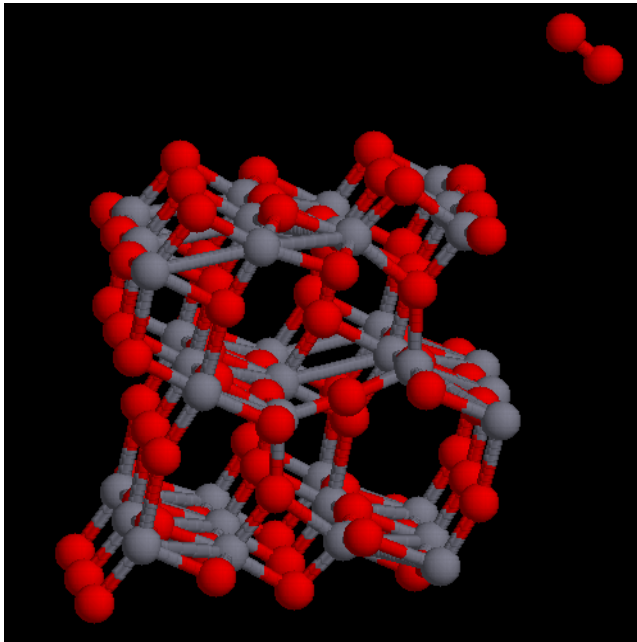
- $U$  moves states in the gap down
- Charge transfers from surface to  $\text{O}_2$  more difficult
- Less adsorption strength

## Self consistent determination of $U$

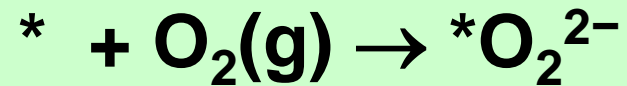
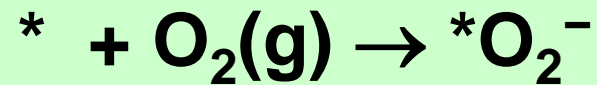
Cococcioni, Gironcoli, *Phys Rev B*, 2005, 71, 035105



# Electron transfer from reduced TiO<sub>2</sub> to O<sub>2</sub>

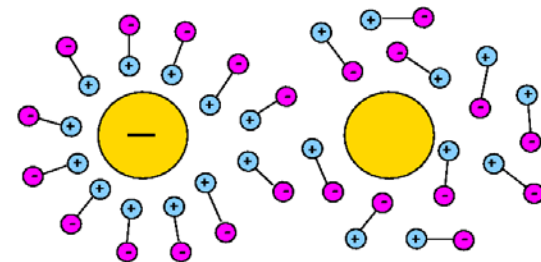
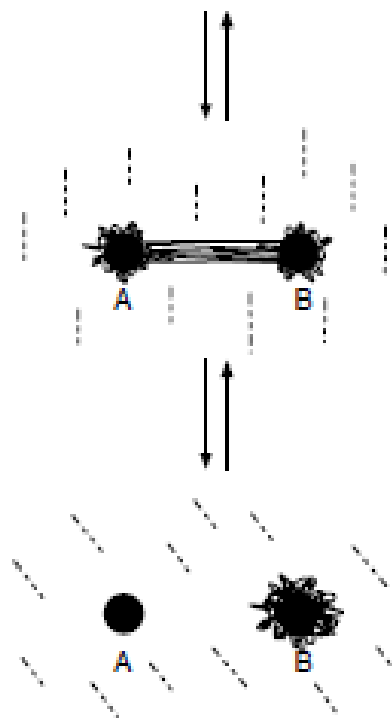
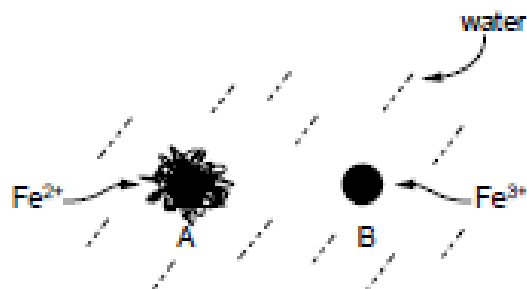
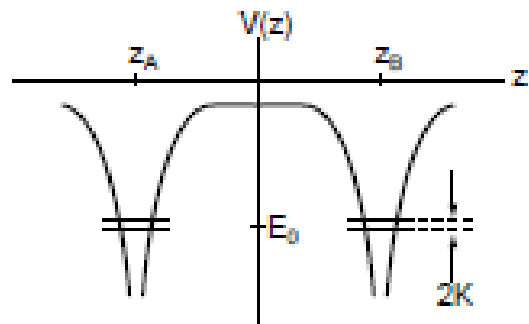
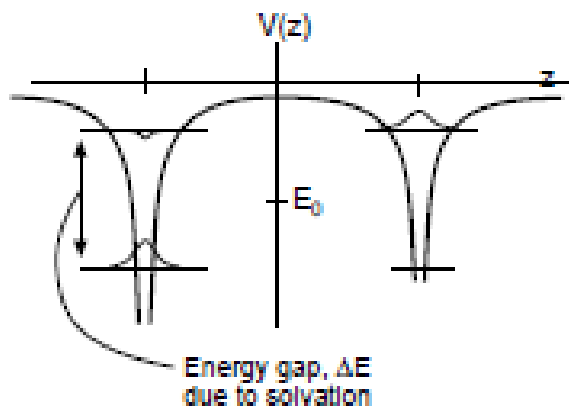


O<sub>2</sub> approaching a reduced  
TiO<sub>2</sub> surface

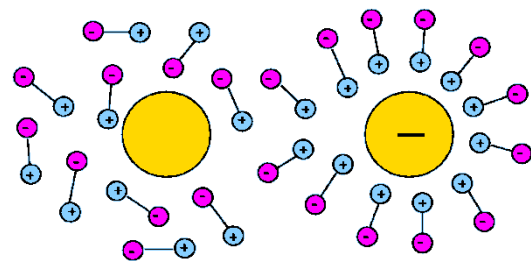


Hybrid functional  
(PBE0) calculations

# The paradigm of Electron Transfer: the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ in water



Transition state



# Electron Transfer

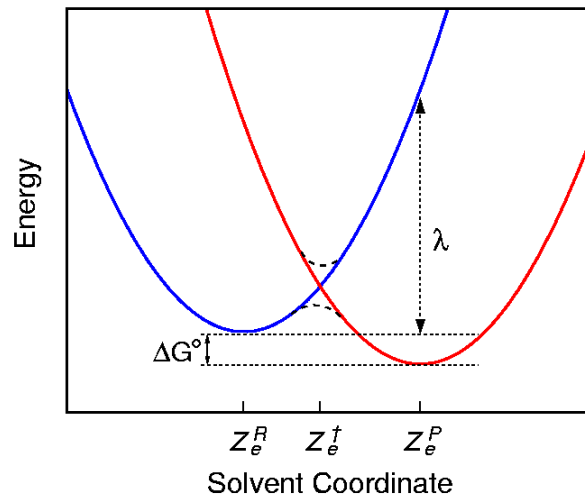
Diabatic states:

(1)  $D_e^- A_e$

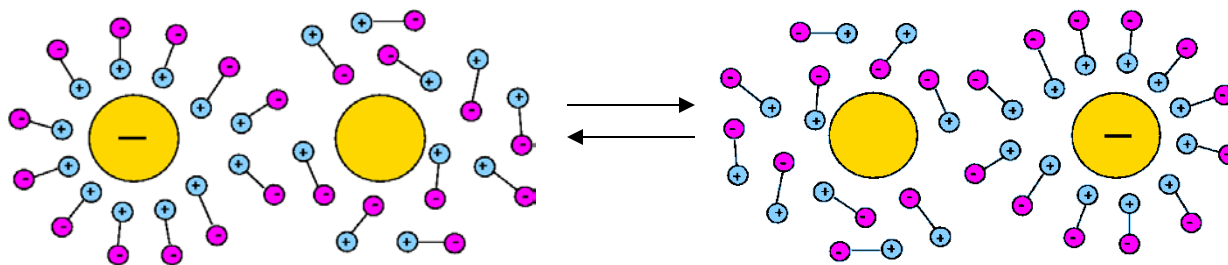
(2)  $D_e A_e^-$

Solvent coordinate

$$z_e = \int d\mathbf{r} (\rho_2 - \rho_1) \Phi_{in}(\mathbf{r})$$



Marcus theory



Nonadiabatic ET rate:  $k = \frac{2\pi}{\hbar} V_{12}^2 (4\pi\lambda k_B T)^{-1/2} \exp\left[-\Delta G^\ddagger / (k_B T)\right]$

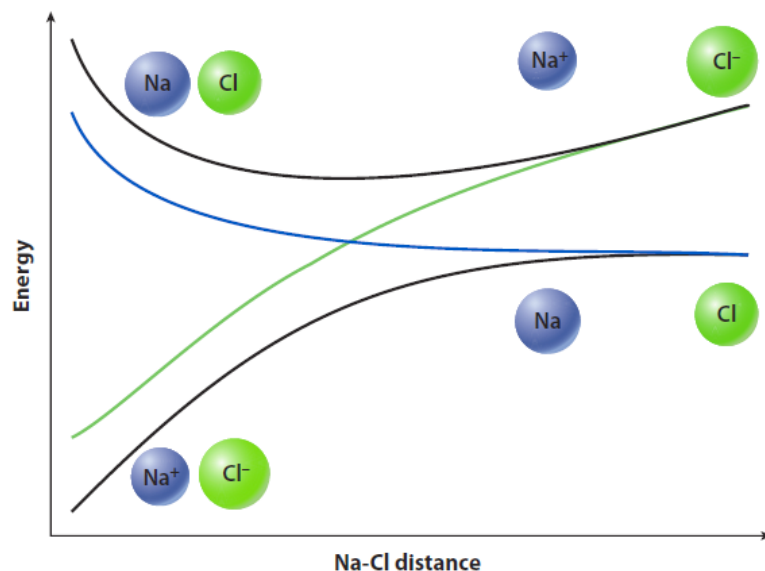
$$\Delta G^\ddagger = (\Delta G^\circ + \lambda)^2 / (4\lambda)$$

$V_{12}$  : coupling between diabatic states

# The diabatic picture of ET, reaction barriers & molecular dynamics

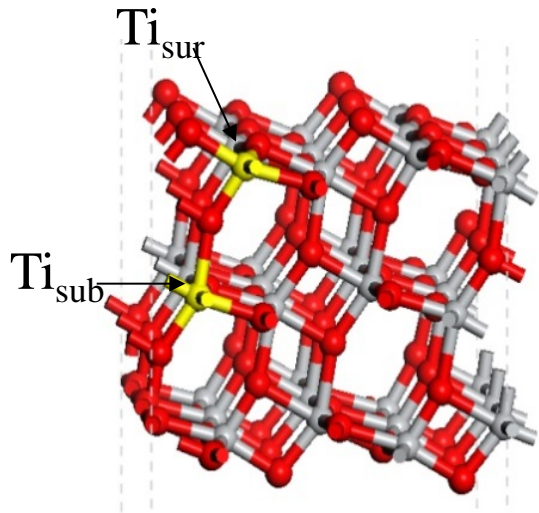
*Van Voorhis et al. Annu Rev Phys Chem 2010*

Qualitatively, a **diabatic** electronic state is one that does not change its physical character as one moves along a reaction coordinate. This is in contrast to the **adiabatic**, or Born-Oppenheimer, electronic states, which change constantly so as to remain eigenstates of the electronic Hamiltonian

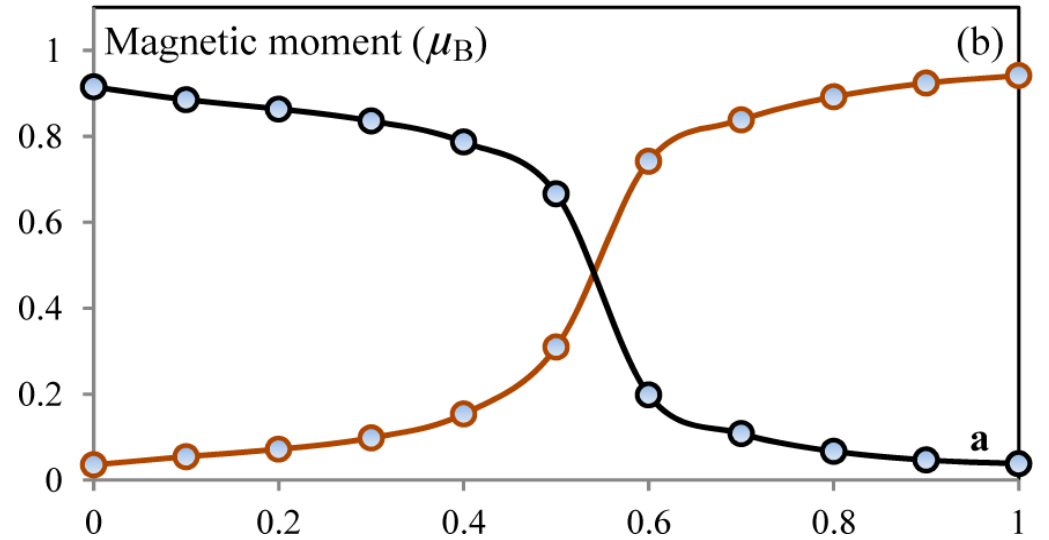
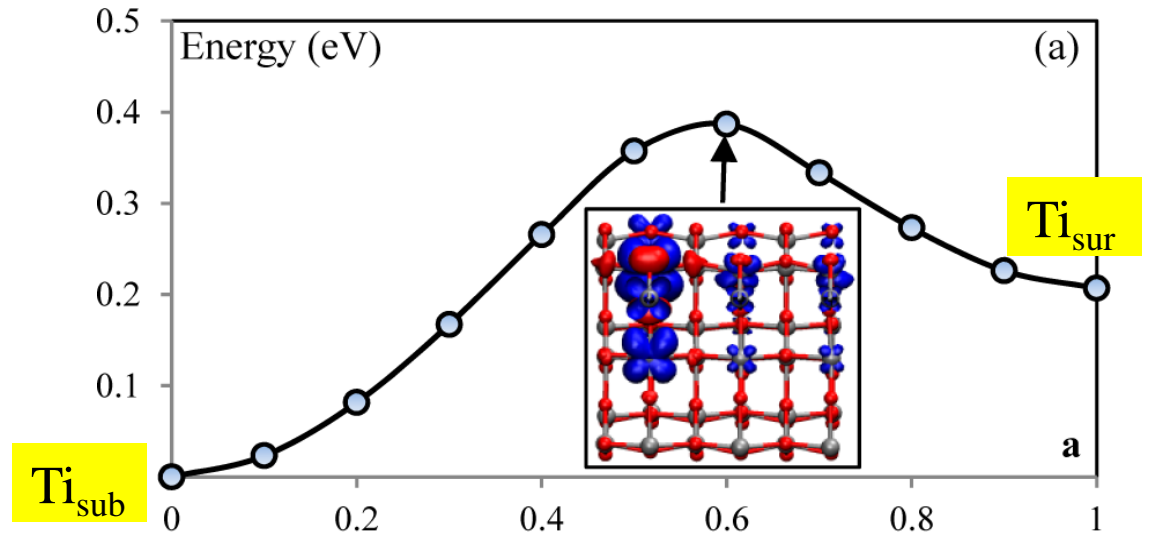


NaCl dissociation in the diabatic and adiabatic representations. The ionic (*green*) and covalent (*blue*) diabatic states maintain the same character across the potential energy surface, whereas the adiabatic states (*black*) change.

# A simple ET process: $\text{Ti}_{\text{sub}} \leftrightarrow \text{Ti}_{\text{surf}}$ electron hopping



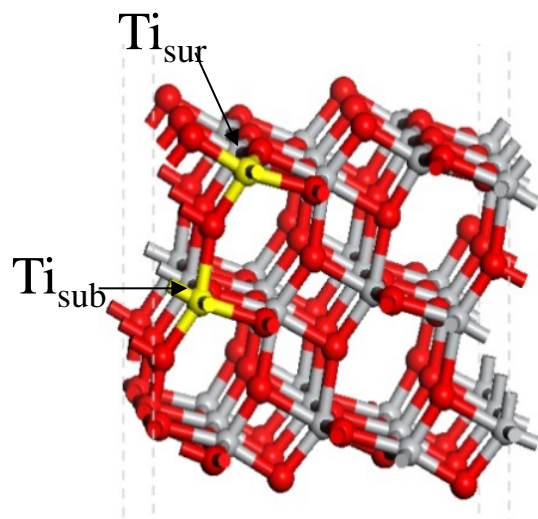
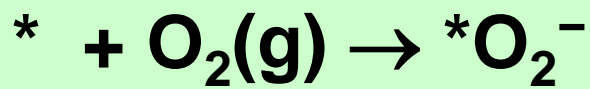
$\text{TiO}_2$  sites between which electron hops



Reaction coordinate

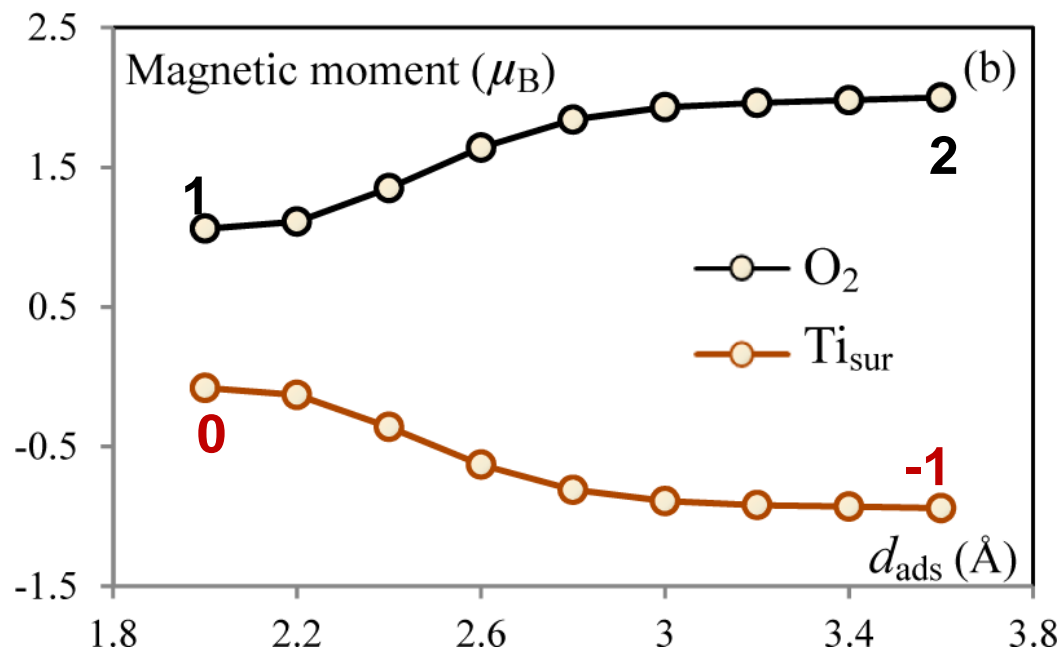
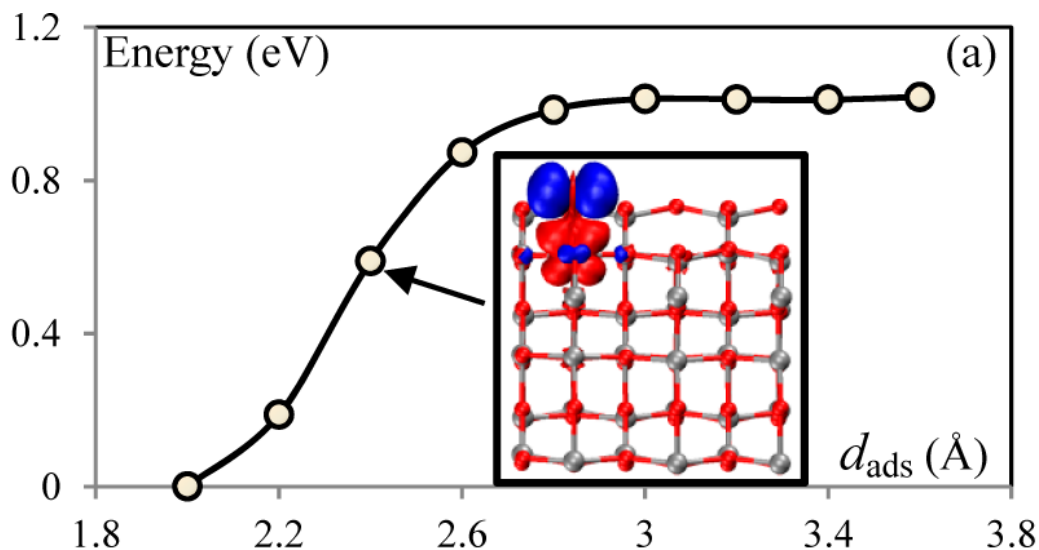
$$X(a) = a \cdot X(A) + (1 - a) \cdot X(B)$$



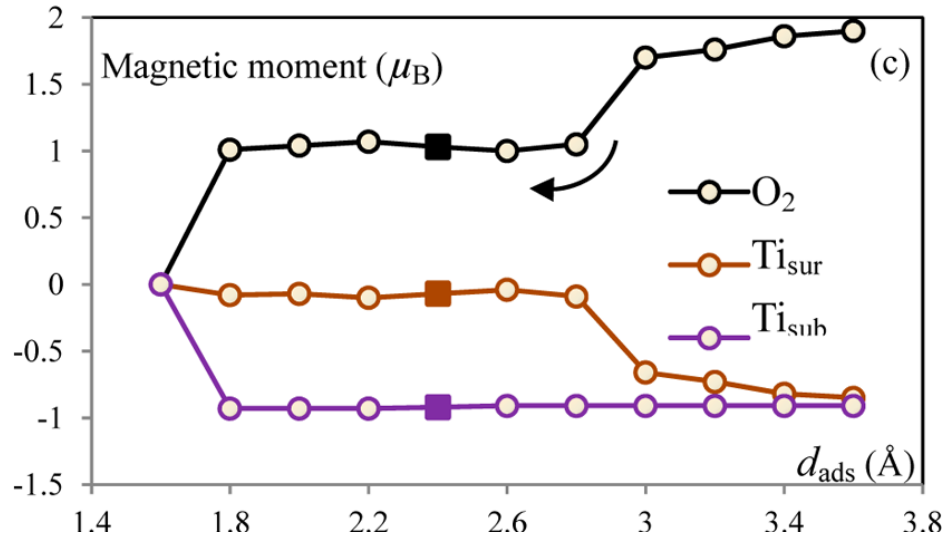
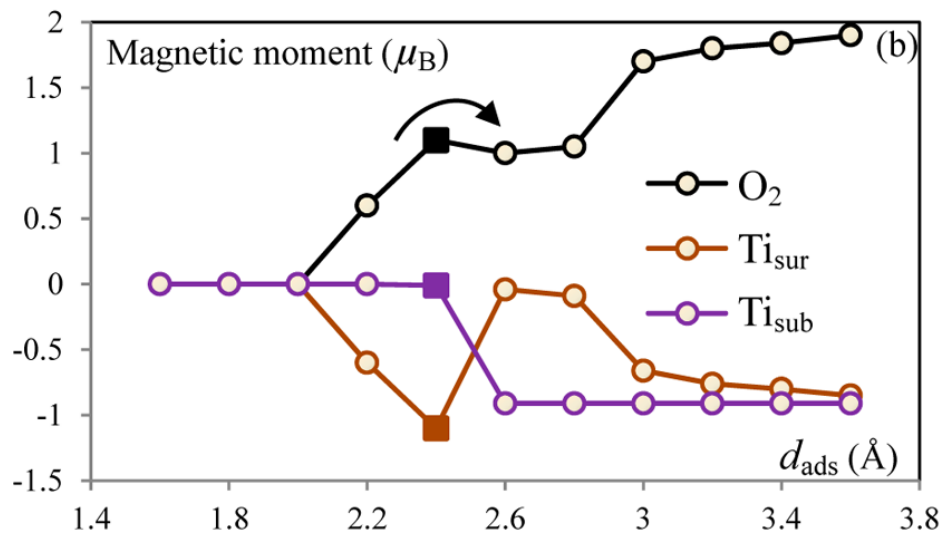
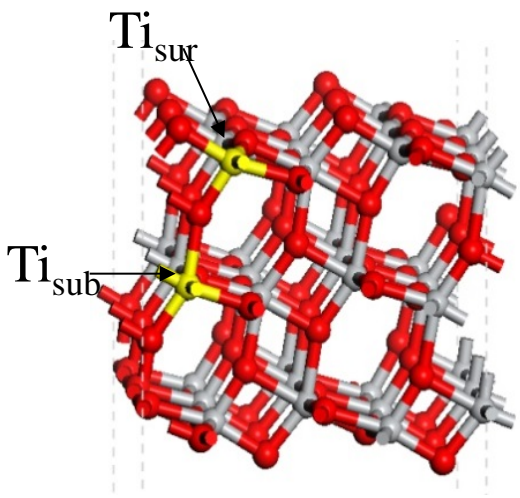
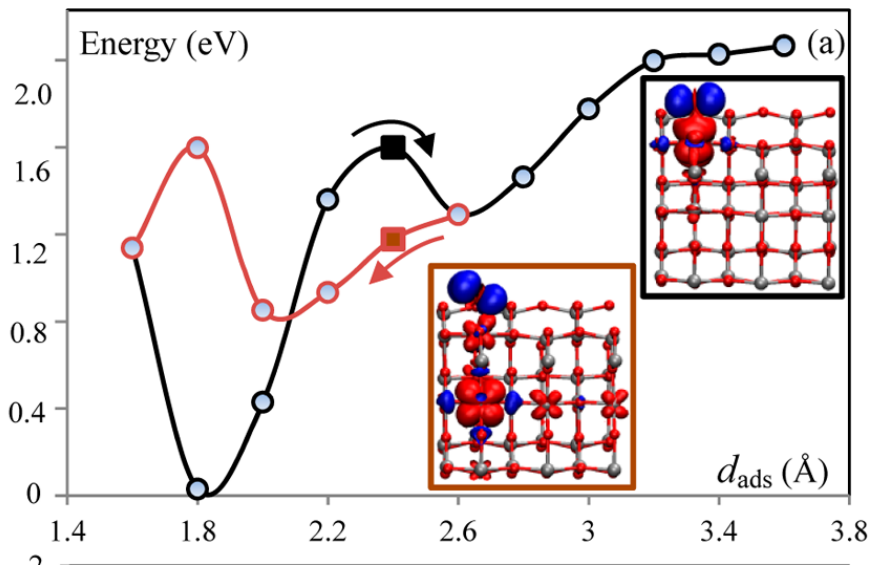
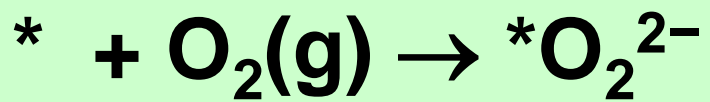


$\text{O}_2$  adsorbs on  
/desorbs from  $\text{Ti}_{\text{sur}}$

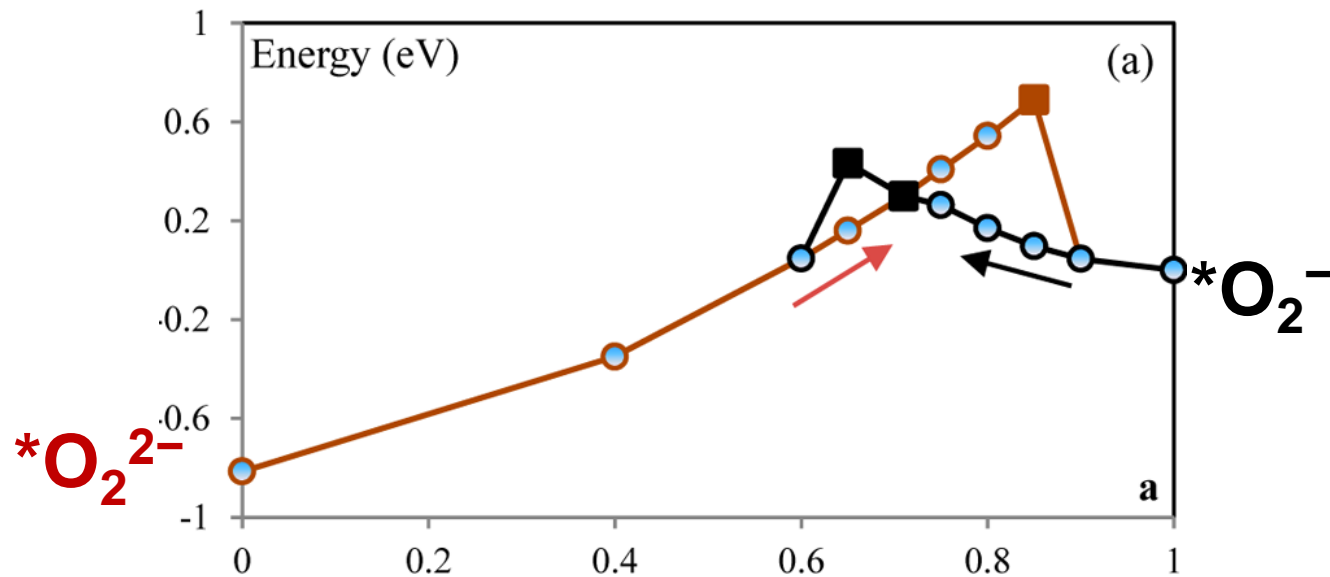
Adsorption/desorption  
are reversible



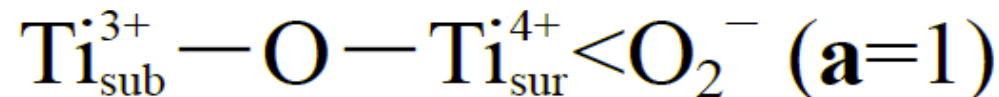
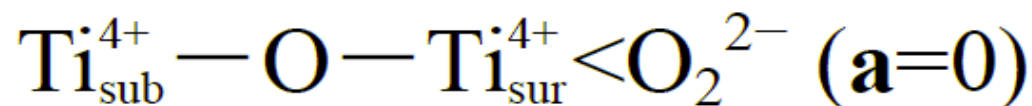
Reaction coordinate:  $d_{\text{ads}} = [d(\text{Ti}_{\text{sur}}-\text{O}_a) + d(\text{Ti}_{\text{sur}}-\text{O}_b)]/2$



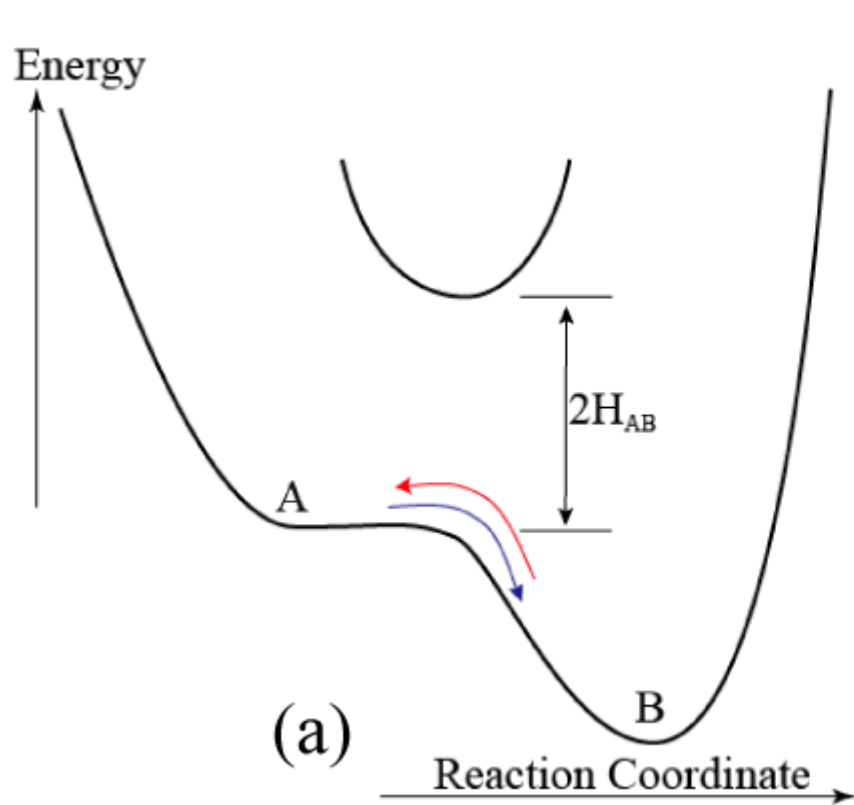
# Electron transfer between $*\text{O}_2^-$ and $*\text{O}_2^{2-}$ states



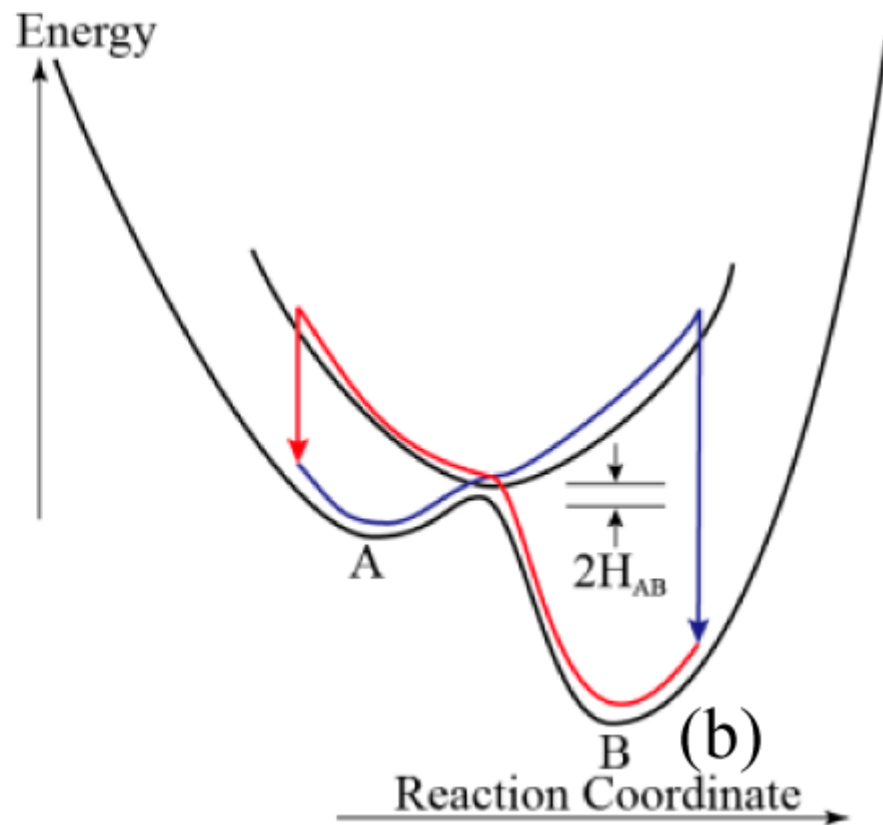
$$X(\mathbf{a}) = a \cdot X(\text{A}) + (1 - a) \cdot X(\text{B})$$



# Adiabatic vs non-adiabatic ET



Strong coupling  $\rightarrow$  adiabatic  $\rightarrow$   
Reversible energy profile



Weak coupling  $\rightarrow$  non-adiabatic

## Some conclusions

- Electron transfer from reduced  $\text{TiO}_2$  surface to approaching  $\text{O}_2$  studied by PBE0 calcs.
- Formation of adsorbed superoxide,  $^*\text{O}_2^-$ , is barrierless
- Transfer of second electron to transform superoxo into adsorbed peroxide, i.e.  $^*\text{O}_2^- + e^- \rightarrow ^*\text{O}_2^{2-}$ , is nonadiabatic with a barrier of 0.3eV.
- Nonadiabaticity originates from instability of intermediate with second electron localized at superoxo adsorption site

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- National Energy Research Scientific Computing Center
- PICSciE-OIT High Performance Computing Center and Visualization Laboratory.