The Abdus Salam
International Centre for Theoretical Physics

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Educational, Scientific and
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1938-4

Workshop on Nanoscience for Solar Energy Conversion

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Materials-related aspects of TiO2-based photocatalysis

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Materials-related aspects in TiO_2-based photocatalysis: insights from first principles simulations

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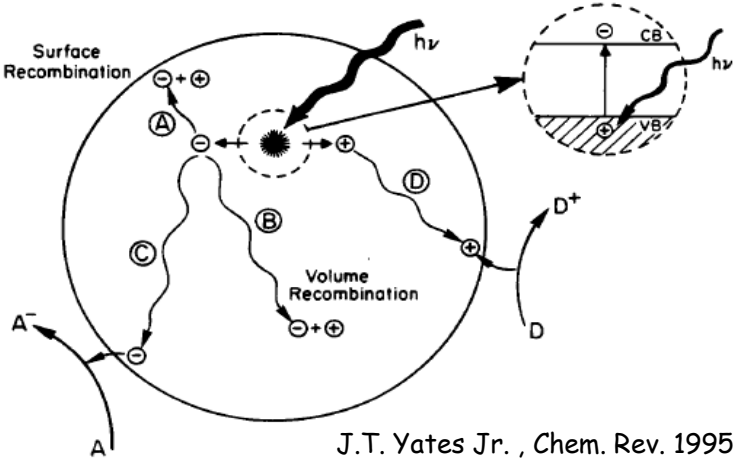
"Surface science" studies of TiO_2:

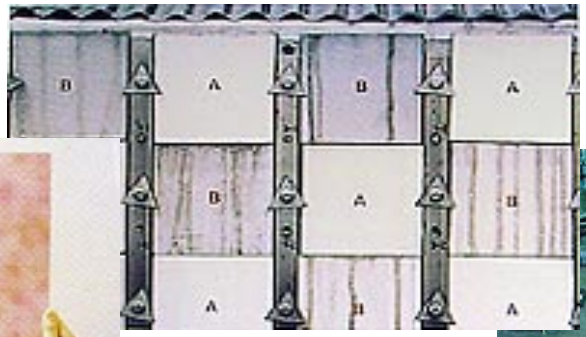
- Structure, energetics & reactivity (mostly anatase)
- Rutile vs Anatase (energies and defects)
- A model dye/TiO_2 system: catechol/R-TiO_2(110)

TiO_2:

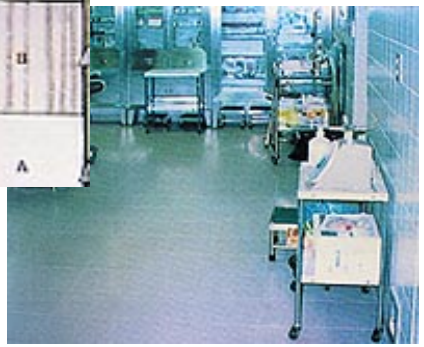
TiO_2 -based Photocatalysis: Applications and Promise



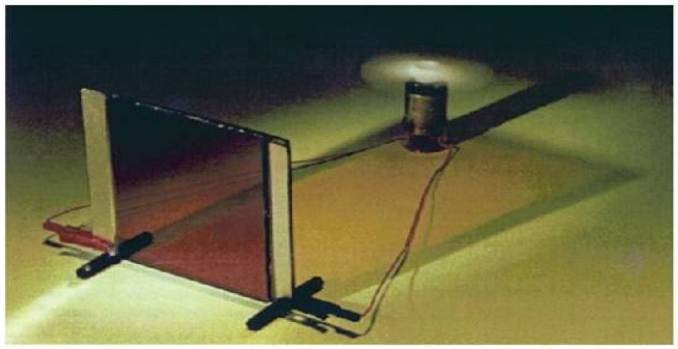
J.T. Yates Jr. , Chem. Rev. 1995

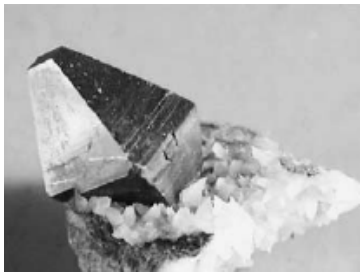


titaniumart.com



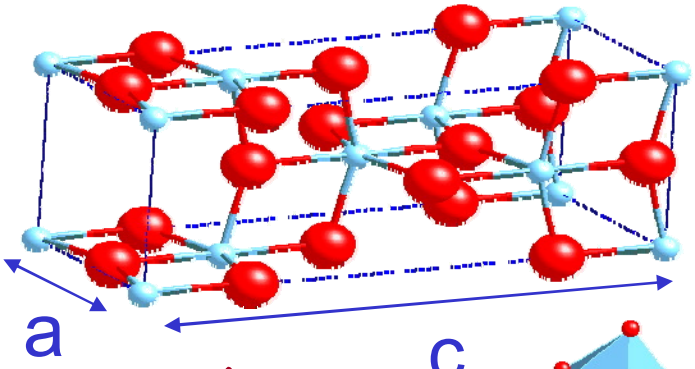
- removal of organic pollutants, purifying of water or air
- self-cleaning/desinfecting coatings (bacteria, viruses, cancer cells)
- photoelectrochemical cells, solar cells
- photocatalytic splitting of water, production of hydrogen



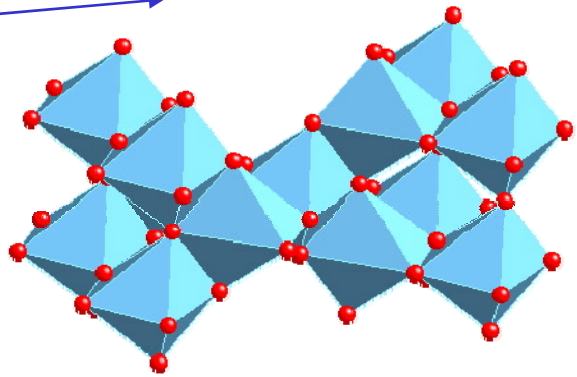


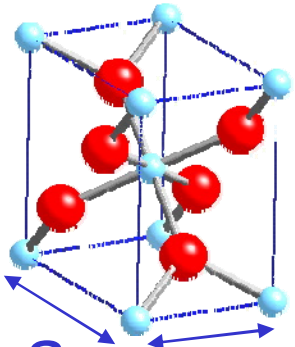
TiO_2: Anatase and Rutile

- **Rutile** is the most stable bulk phase
- **Anatase** usually more active for photocatalysis

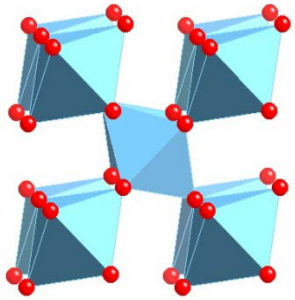


Anatase

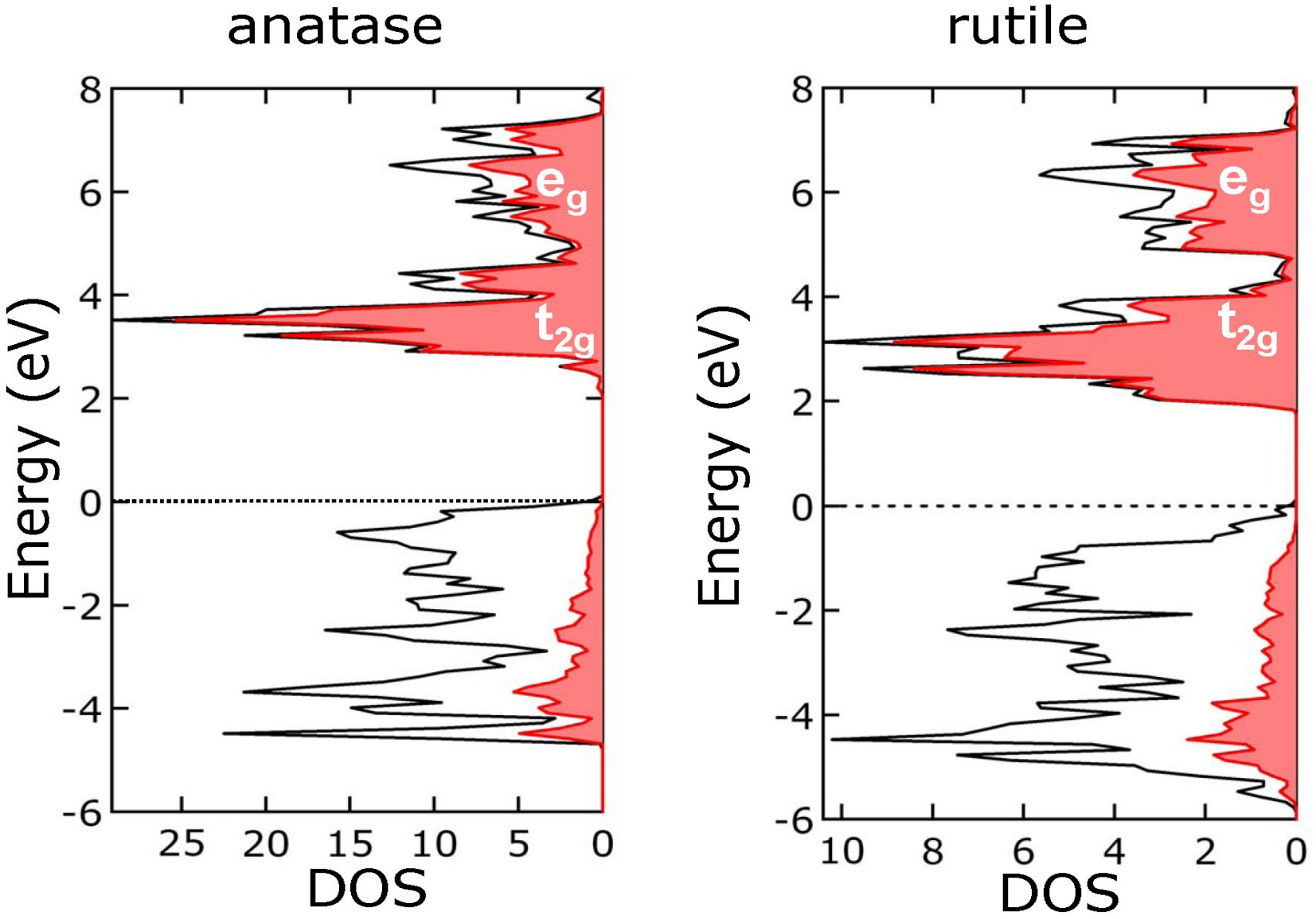




Rutile



Electronic structure: DOS (GGA-PBE)



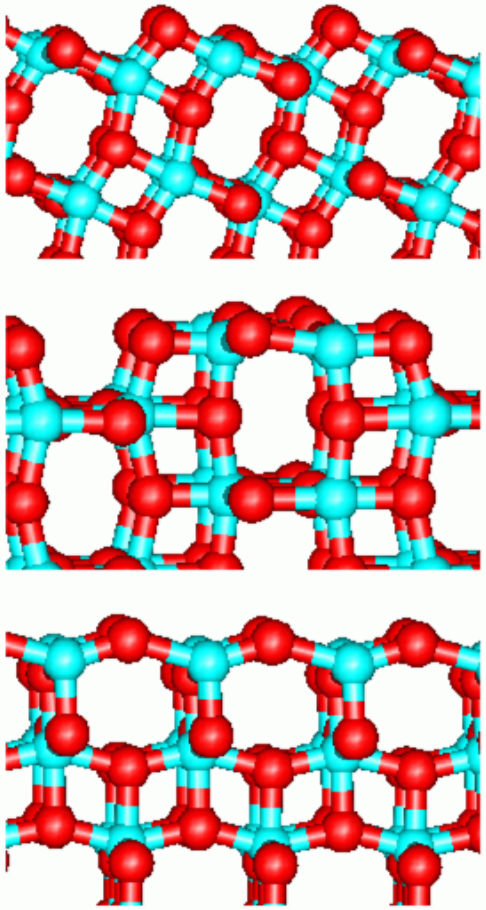
Experimental observation:

Anatase phase is most stable for **nanoparticles** up to ~ 14 nm.

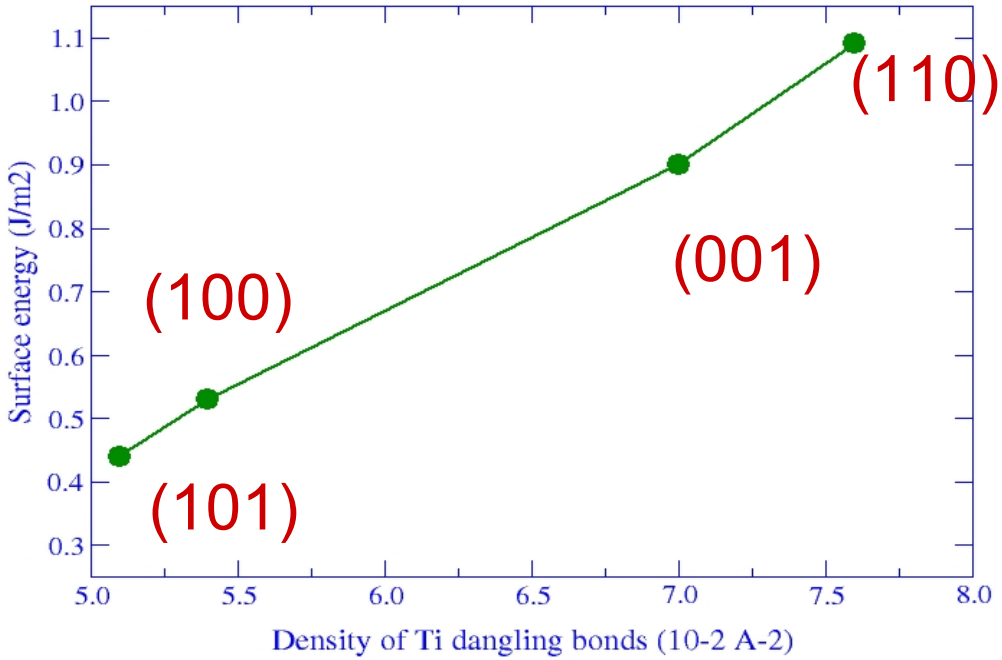
- Proposed explanation: the smaller the crystal, the larger is the fraction of surface atoms; surface energy makes the anatase phase more favorable

  [Zhang & Banfield, J. Mater. Chem. 8 (2073) 1998

Anatase stoichiometric 1 × 1 surfaces



Surface energy depends almost linearly on the density of under-coordinated Ti atoms

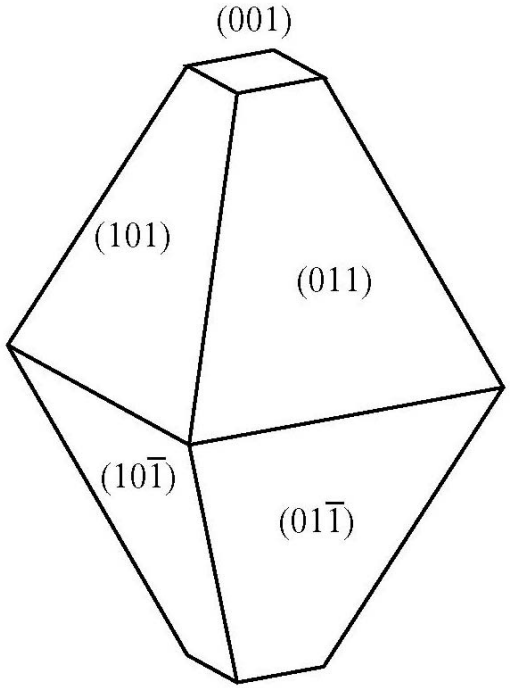


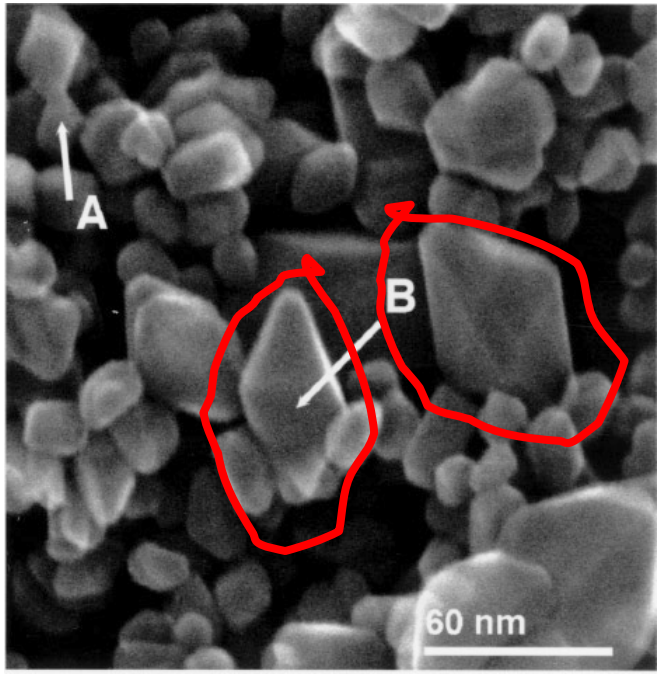
DFT claculations: PBE functional plane-waves, ultrasoft pseudopots

Quantum ESPRESSO: CP90, PWscf

http://www.democritos.it

Crystal shape: theory vs. experiment





theory

natural anatase

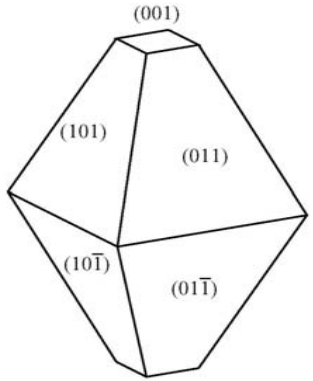
anatase nanocrystals

from: Shklover et al.
J. Sol St. Chem. 132 (1997) 60

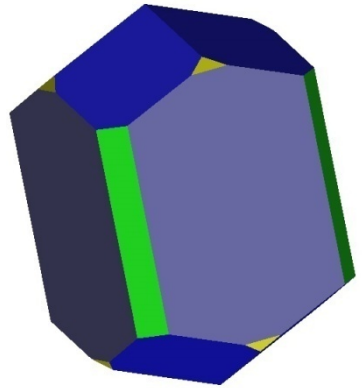
Lazzeri, Vittadini, Selloni, PRB
63 (2001) 155409.

Crystal surface energy: anatase vs. rutile

- For anatase, the most stable (101) surface constitutes 94% of the crystal surface.



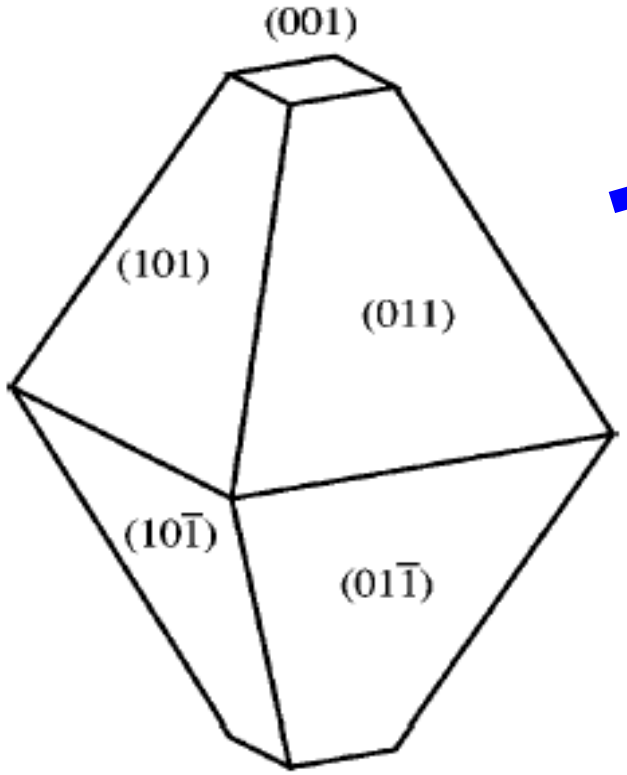
- For rutile, the most stable (110) surface constitutes only 56% of the crystal surface (Ramamoorthy et al., PRB, 1994)

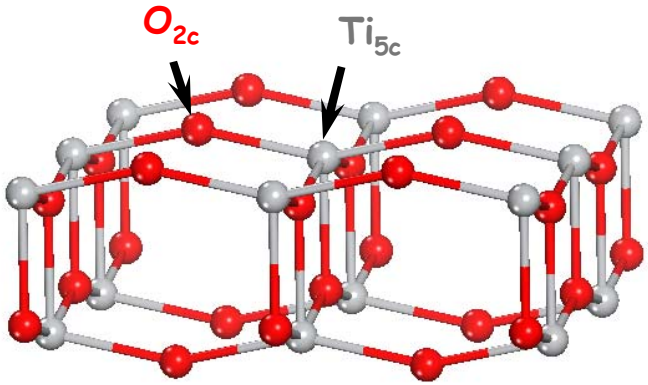


- Average surface energy (LDA):
  Rutile = 1.09 J/m^2 Anatase = 0.90 J/m^2

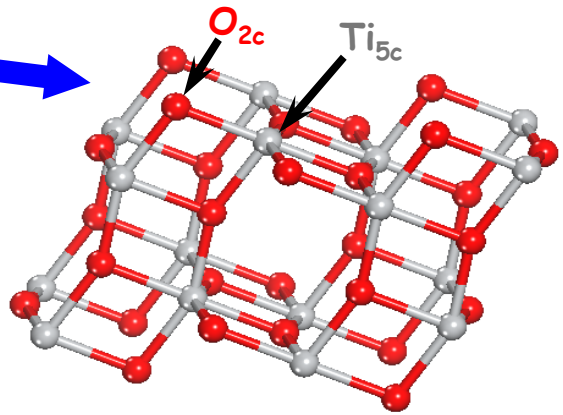
[Zhang & Banfield, J. Mater. Chem. 8 (2073) 1998]

Anatase TiO_2





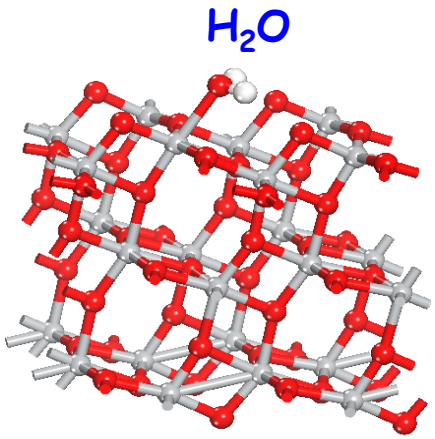
Minority $TiO_2(001)$

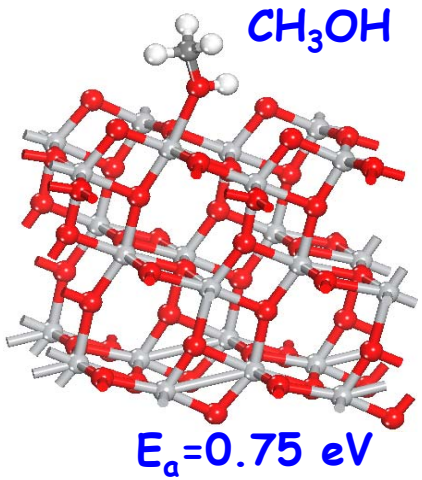


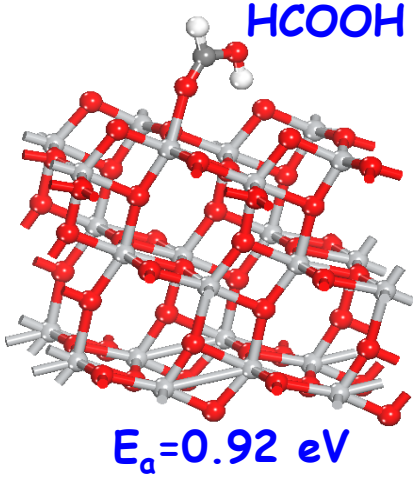
Majority $TiO_2(101)$

(Lazzeri, Vittadini, Selloni, PRB *63*, 155409, 2001)

Adsorption of small probe molecules: majority anatase TiO_2(101)







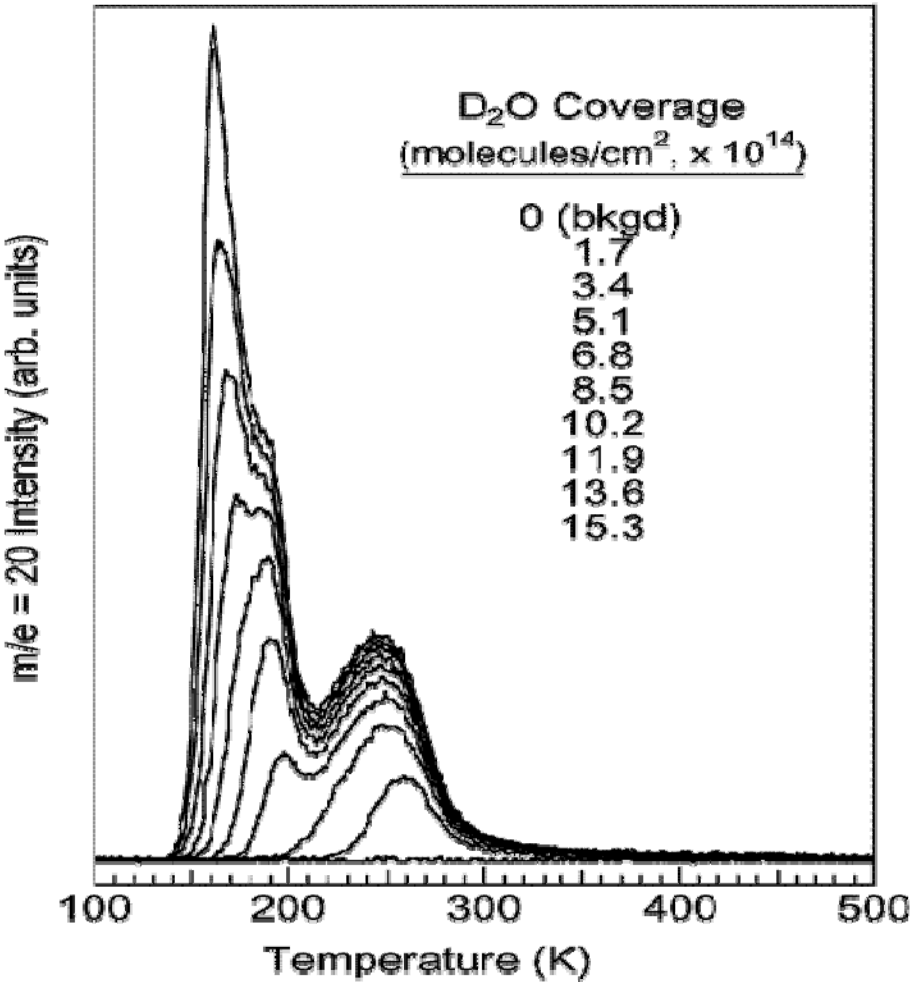
Molecular adsorption only (MD, 300K)

Weak molecular adsorption ⇒low reactivity, in line with the low surface energy of anatase (101)

(Vittadini *et al*, PRL *81*, 2954, 1998; JPC-B *104*, 1300, 2000)
(Tilocca and Selloni, JPC-B 108, 19314, 2004)

Water on anatase TiO_2(101)

TPD spectrum



250 K: H_2O-Ti_{5c}

190 K: H_2O-O_{2c}

160 K: multilayer H_2O

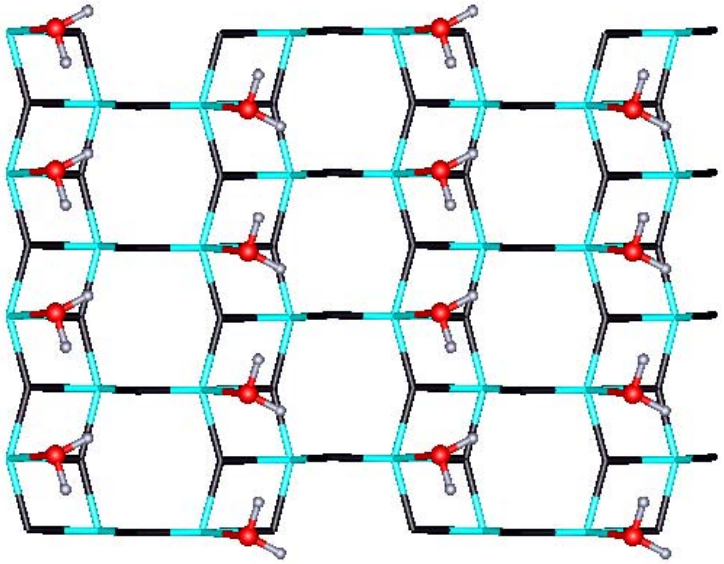
No dissociated H_2O

CH_3OH: **Molecular Adsorption**
(tiny amount of dissociation)

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

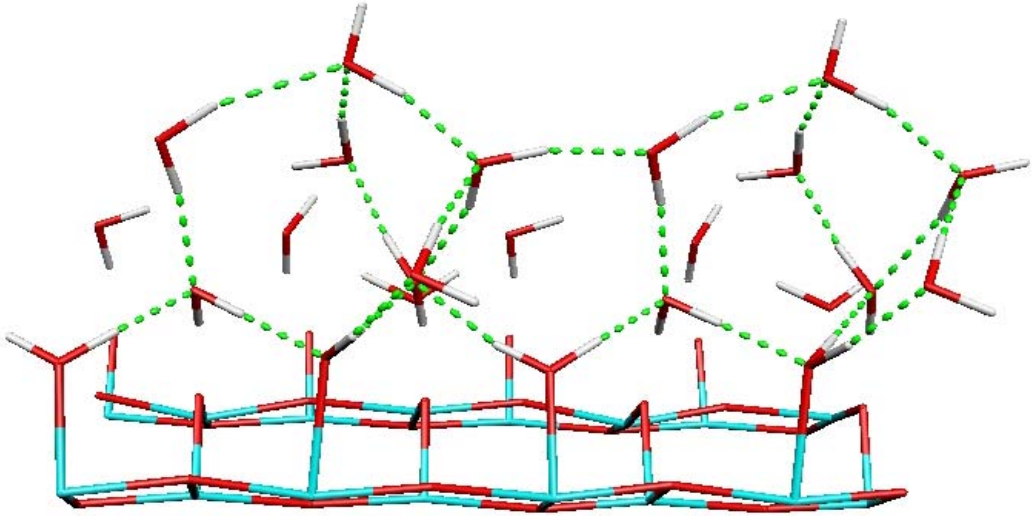
H_2O on anatase (101)

A. Tilocca, A. Selloni: JCP 119, 74445 (2003); JPCB 108, 4743 (2004);
Langmuir 20, 8379 (2004); JPCB 108, 19314 (2004)



1 ML

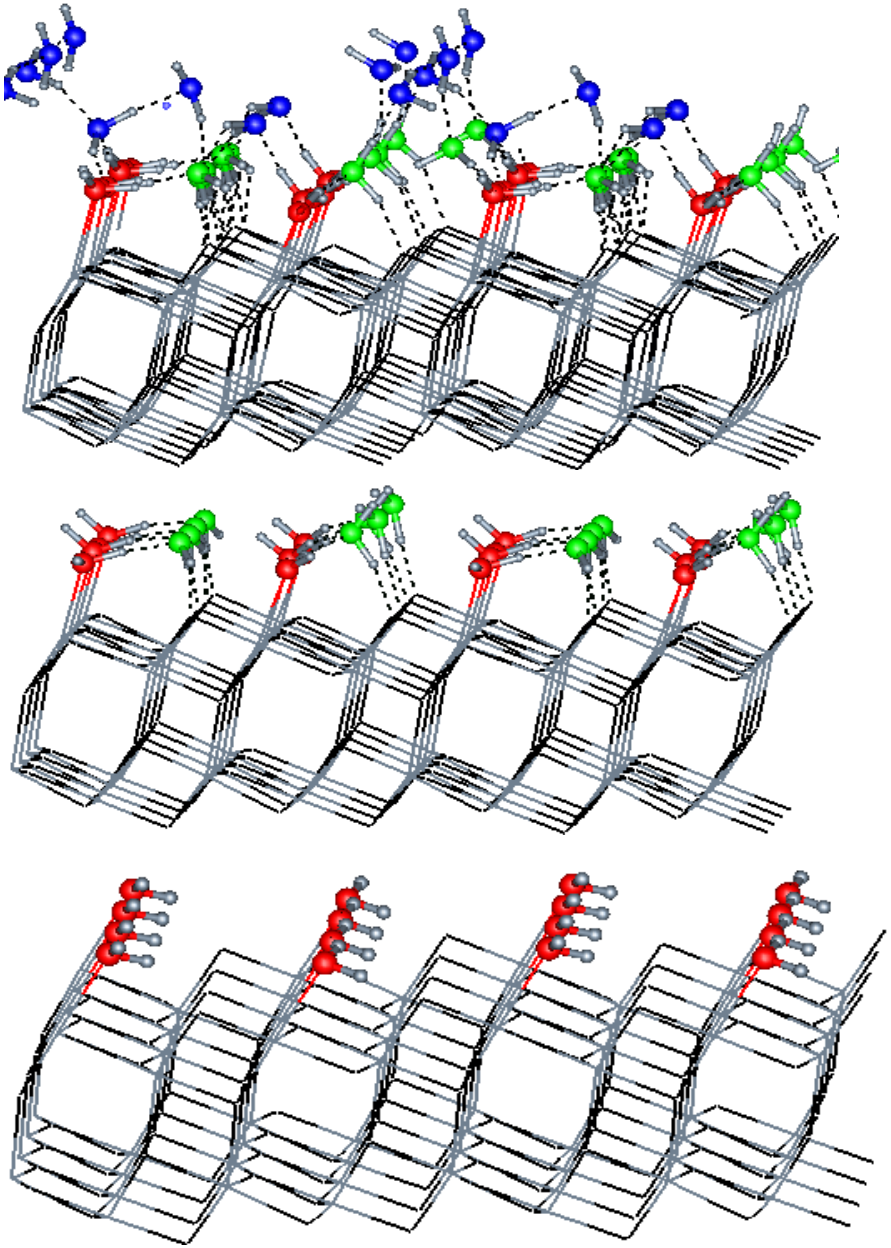
E_{ads} = 0.69 eV / molecule

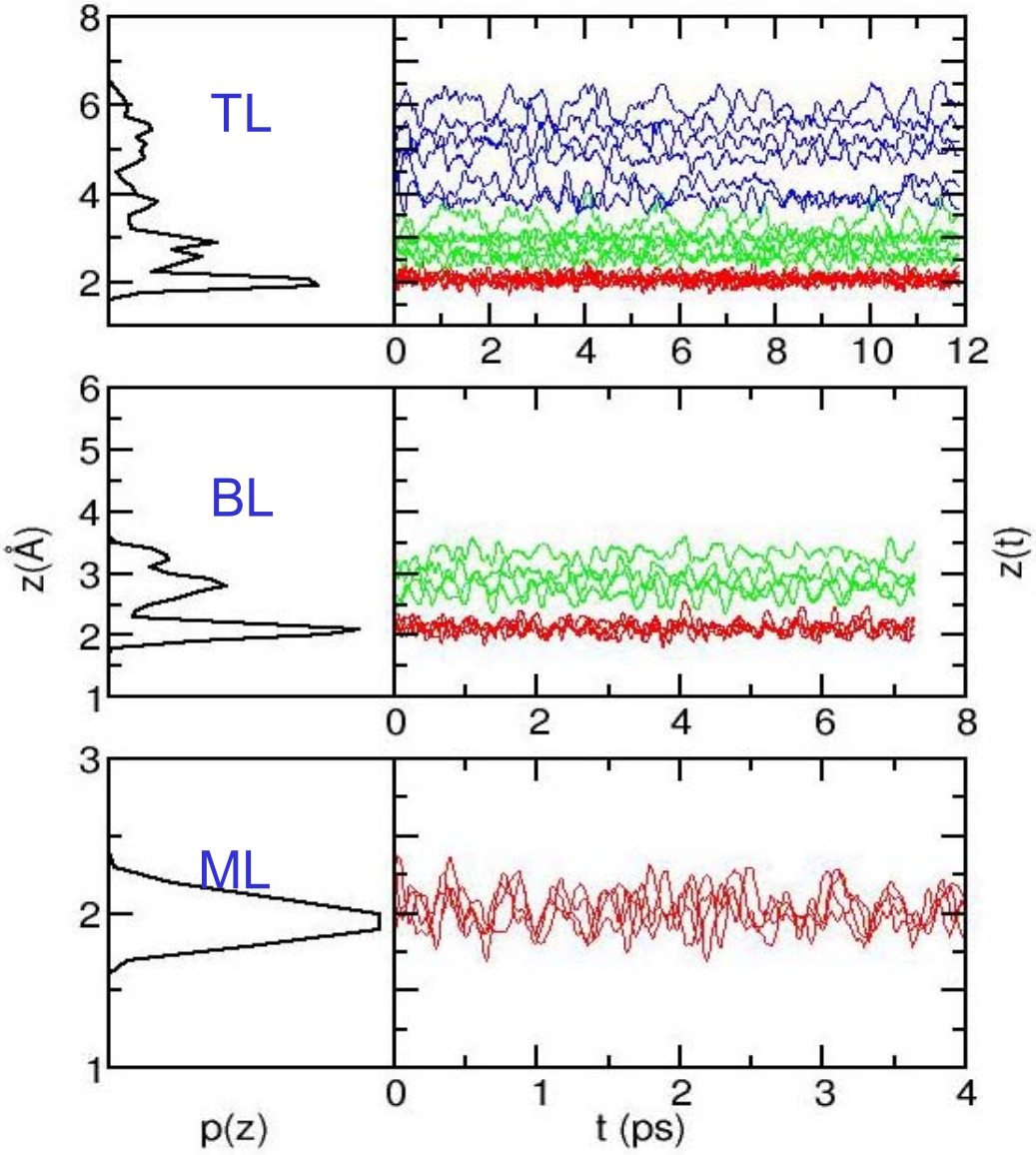


3 ML (TL)

(ice-like structure)

Vertical order: layering

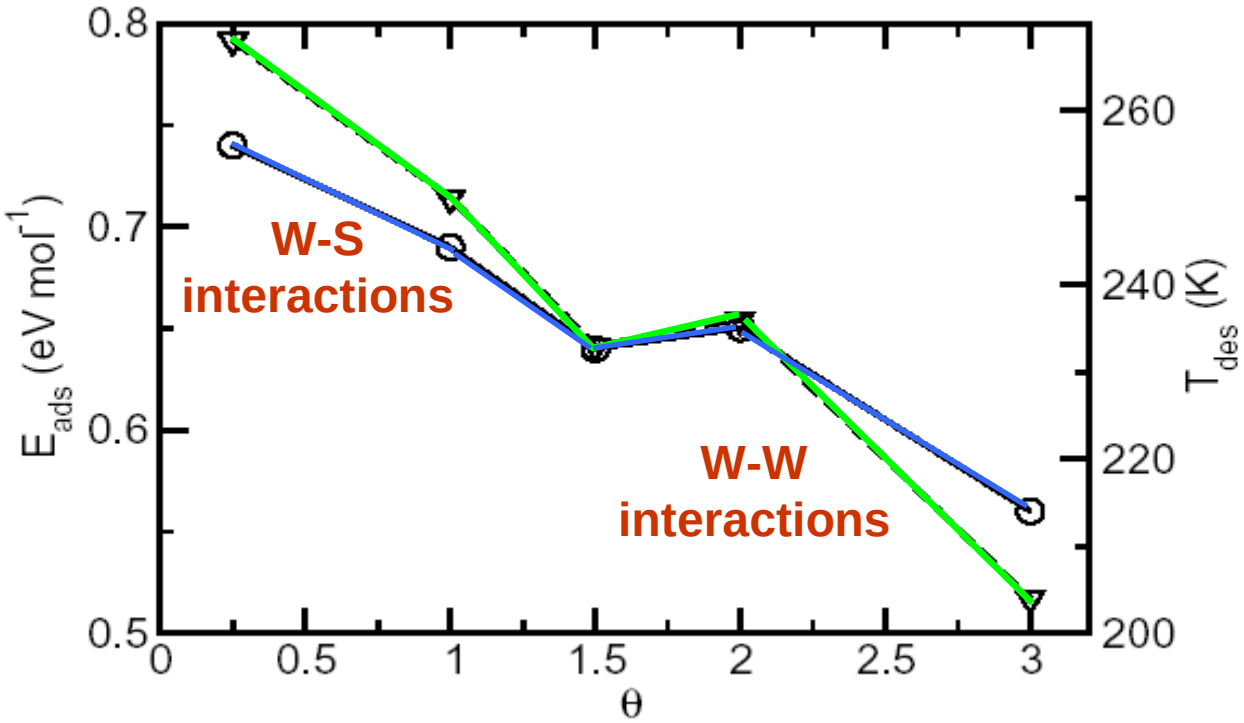




Water multilayer: adsorption energies

A.Tilocca & A. Selloni, Langmuir (2004)

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



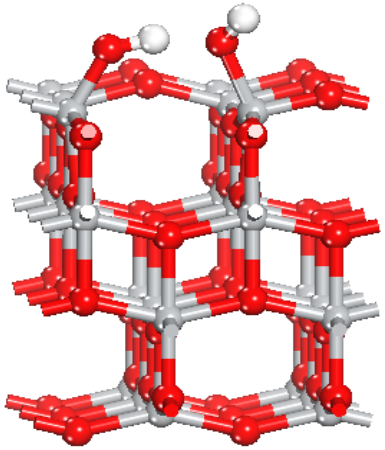
T_{des} from Redhead's equation

$E_{ads/mol}$

Trend in estimated desorption T in agreement with TPD experiments

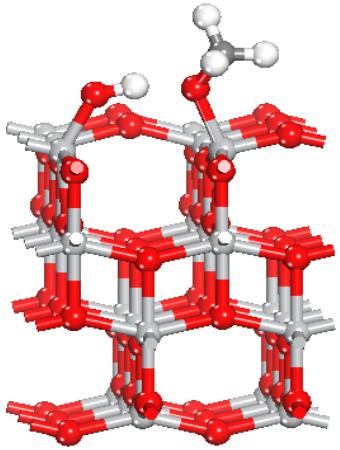
Adsorption of small probe molecules: minority anatase TiO_2(001)

H_2O



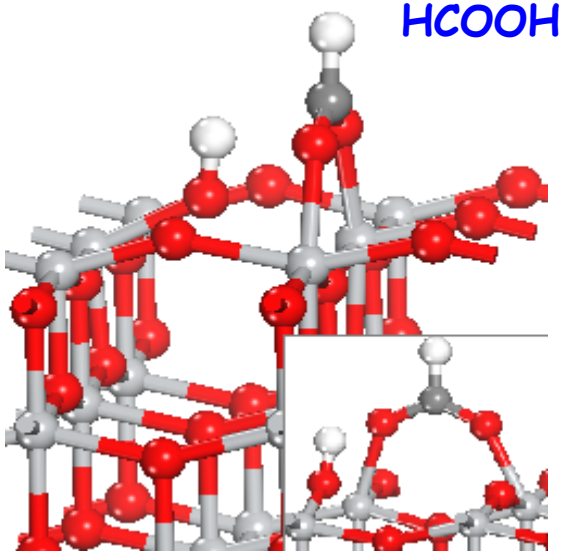
E_a=1.25 eV

CH_3OH



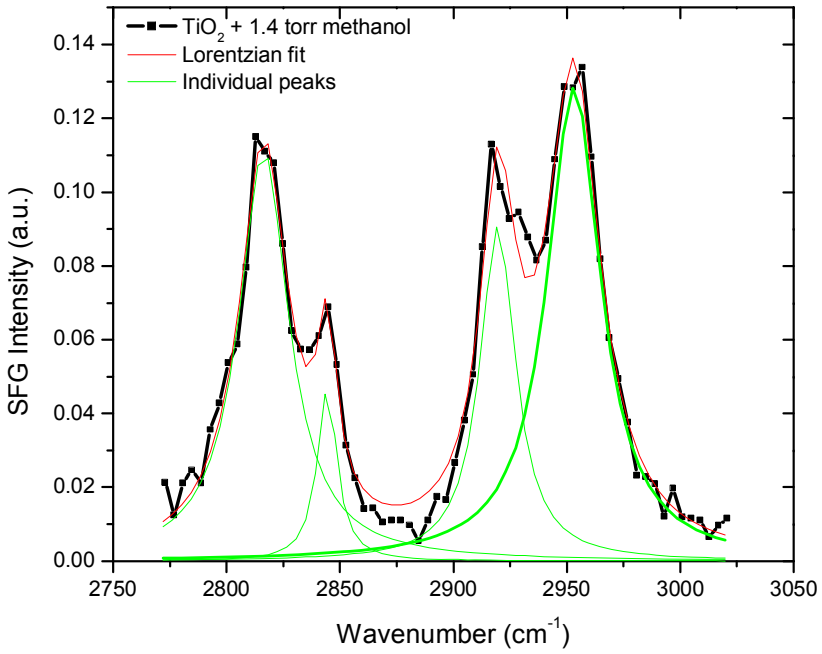
E_a=1.36 eV

HCOOH



E_a=1.54 eV

Dissociative adsorption ⇒ high reactivity, in line with the high surface energy of anatase (001)



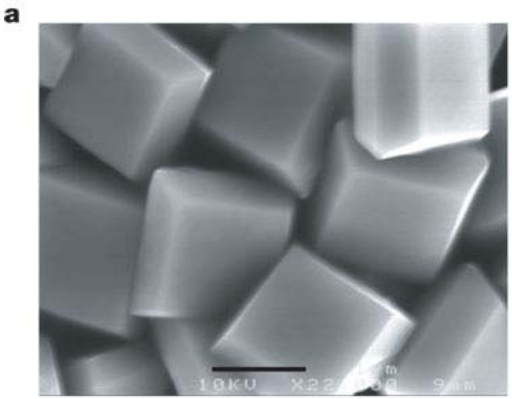
~50% of dissociated MeOH & H_2O on ~2nm anatase nanoparticles inferred from SFG intensities

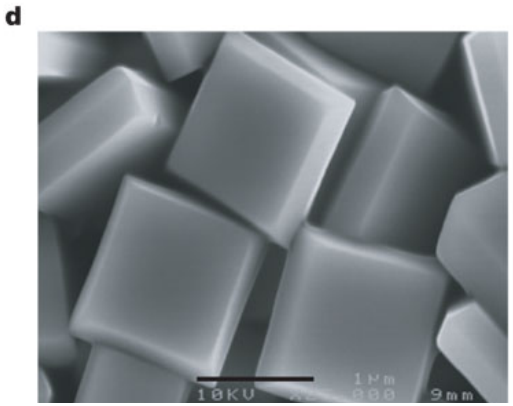
SFG: Wang, Groenzin, Shultz JACS 2004, 2005

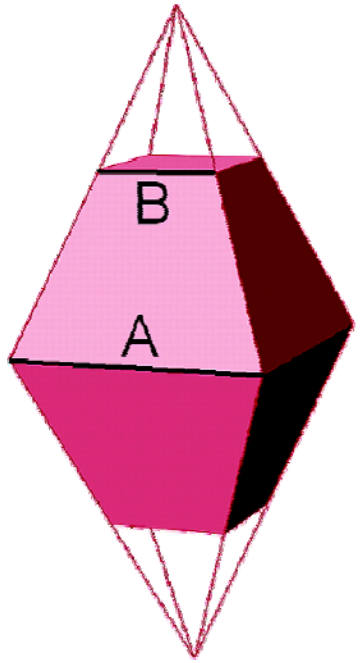
SFG spectrum of methanol on thin, nanoparticulate film of TiO_2.
Peaks at 2844 & 2953 cm^{-1} → symmetric and antisymmetric vibrational modes of molecular methanol.
Peaks at 2816 & 2919 cm^{-1} → symmetric and antisymmetric modes of adsorbed methoxy CH_3 groups.

Anatase TiO2 single crystals with a large percentage of reactive facets

H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng & G. Q. Lu, Nature 453, 638 (2008)



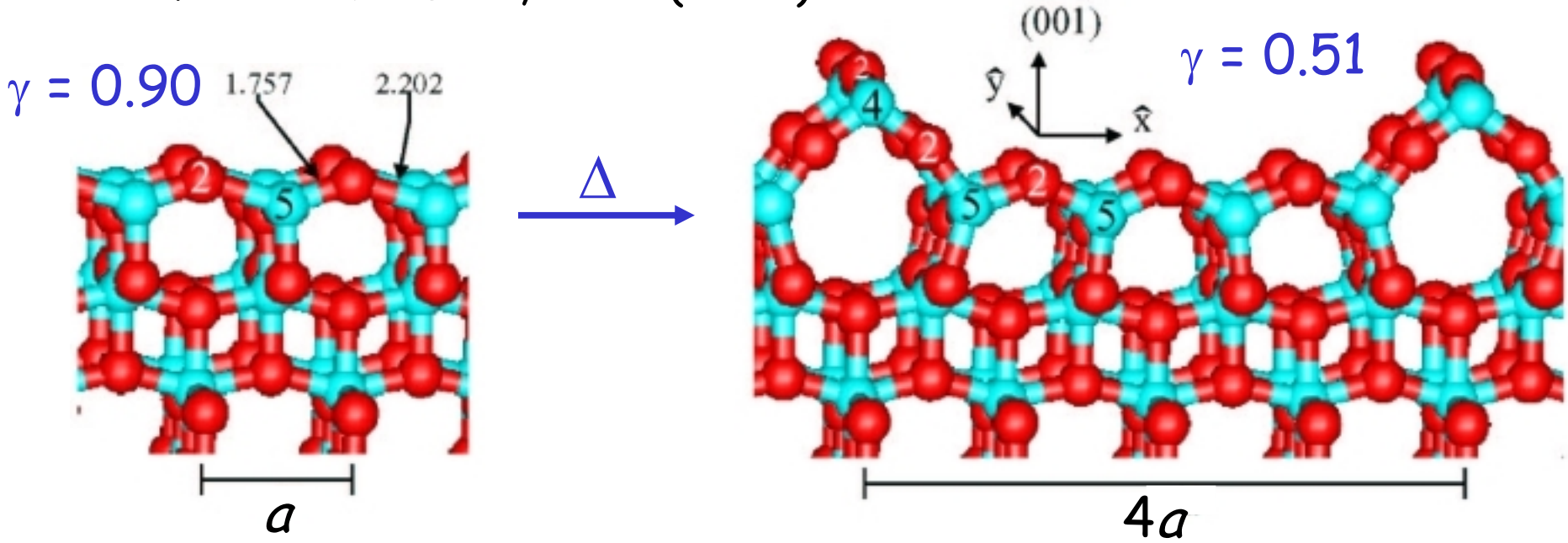




See also: A.Selloni, Nature Materials 7, 613 (2008)

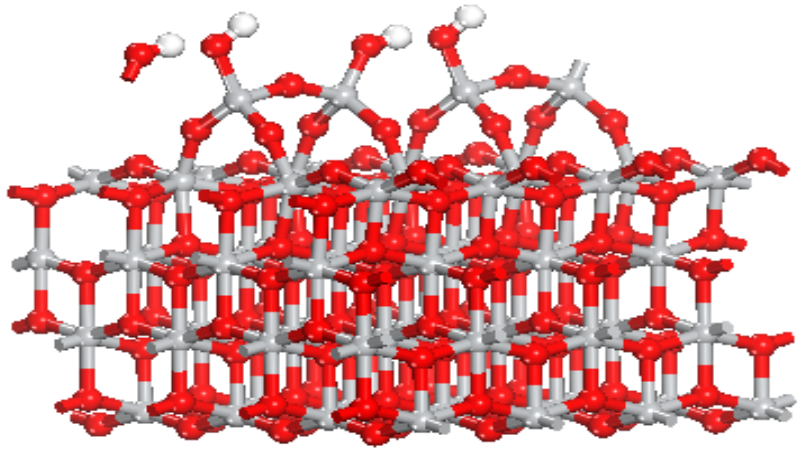
Anatase (001): (1x4) reconstruction

- Clean anatase (001) is actually reconstructed!
  Herman et al. PRL 84, 3354 (2000)



- Most favorable model imply the formation of a polymer of TiO_2 units adsorbed on the surface.
  This lowers the surface energy from 0.90 to 0.51 J/m^2
  (Lazzeri & Selloni, PRL 87 (2001) 266105)

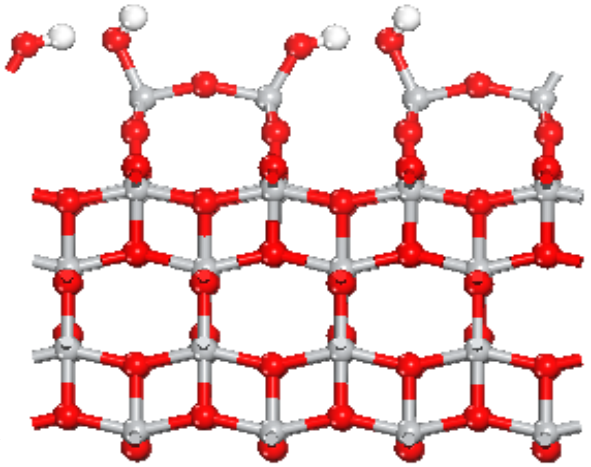
Water on anatase TiO_2(001)-1×4



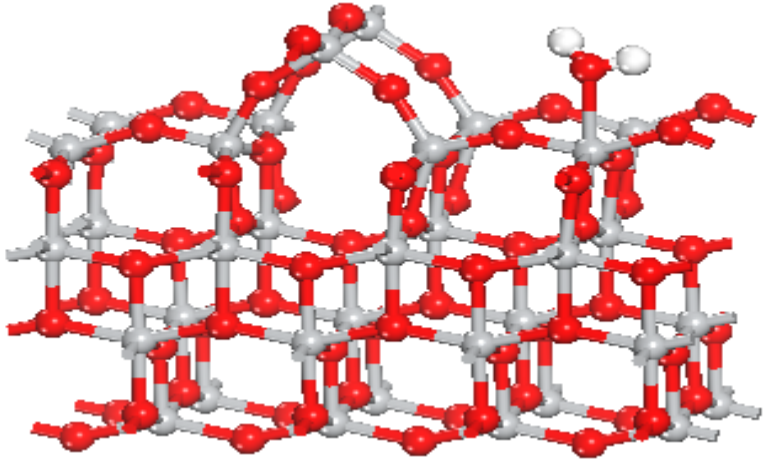
On hill

side view

two unit cells



- Eads = 1.82 eV



On terrace

- Eads = 1.18 eV (molecular, weaker than on 1x1)

Gong et al., JCPB 110, 2804(2006)

Can the surface be functionalized before reconstructing?

Anatase vs Rutile: point defects

…much of the surface chemistry of metal oxide is defect-driven…

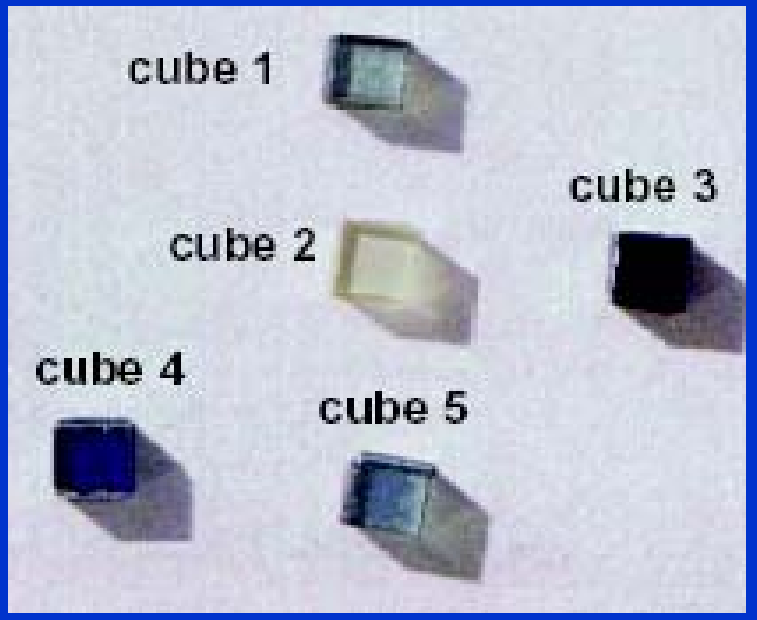
V. Henrich, P.A. Cox, "The Surface Science of Metal Oxides" Cambridge University Press 1994

Step edges:

- Very common at crystal surfaces .
- Key role in roughening, faceting, growth…
- On nanocrystals, a large fraction of atoms are at steps

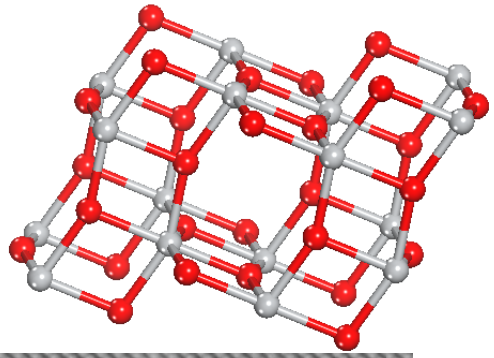
Color change in TiO_2 samples induced by increasing level of oxygen vacancies

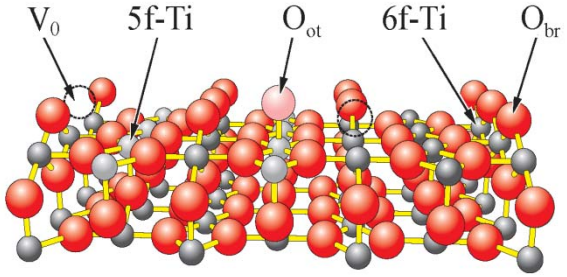
Defects change electronic properties of the material



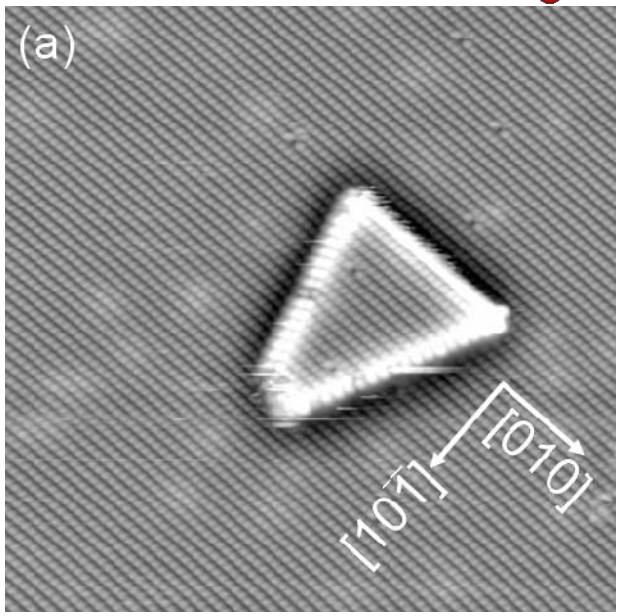
Structure and STM images

Anatase (101)



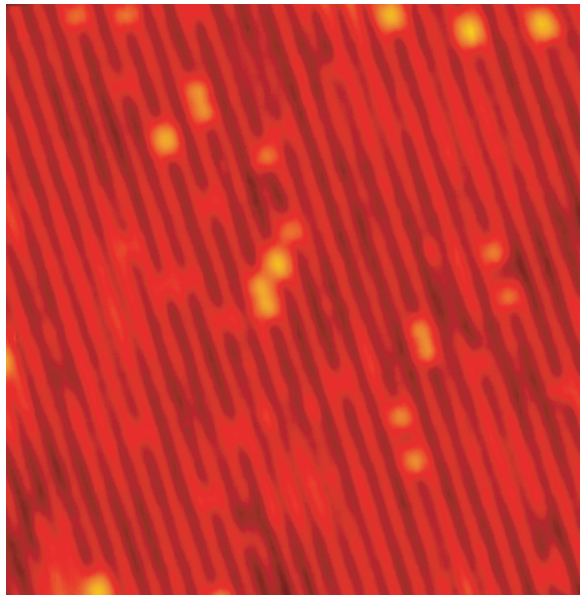


Rutile (110)



Empty state STM image of anatase (101)

Diebold & co. (2008)



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

Besenbacher & co. Surf. Sci. (2005)

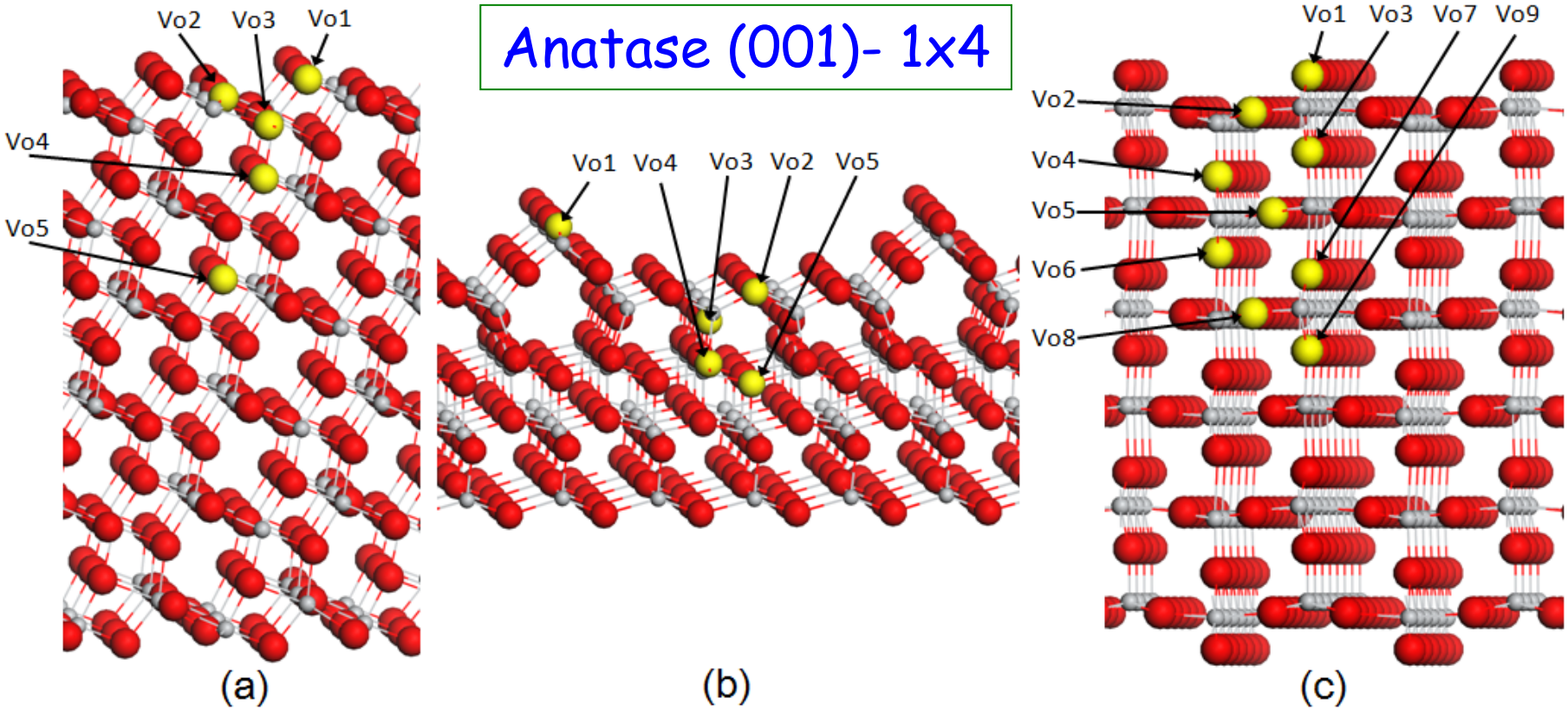
Much fewer point defects point defects on anatase (101) vs rutile (110) under similar preparation conditions!

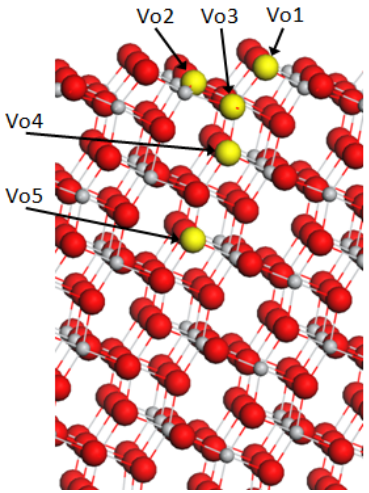
Comparing O-vacancy formation energies

Anatase (101)

Anatase (001)- 1x4

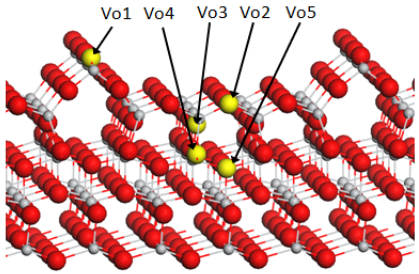
Rutile (110)





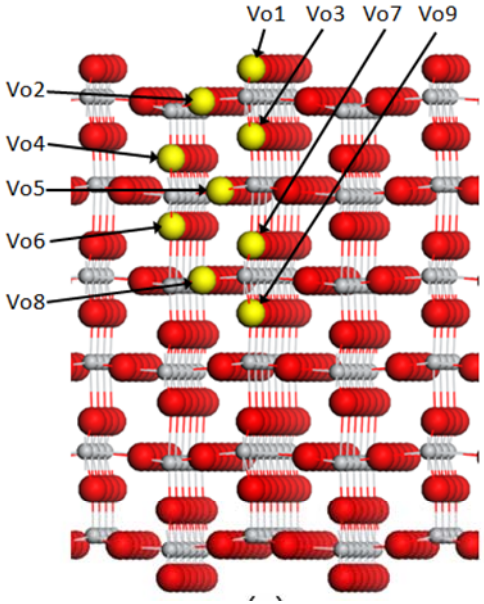
Anatase (101)

Vo1	Vo2	Vo3	Vo4	Vo5
4.15	(5.40)	(4.73)	3.69	3.65



Anatase(001)-1x4

Vo1	Vo2	Vo3	Vo4	Vo5
4.57	5.17	4.29	4.78	4.10



Rutile(110)

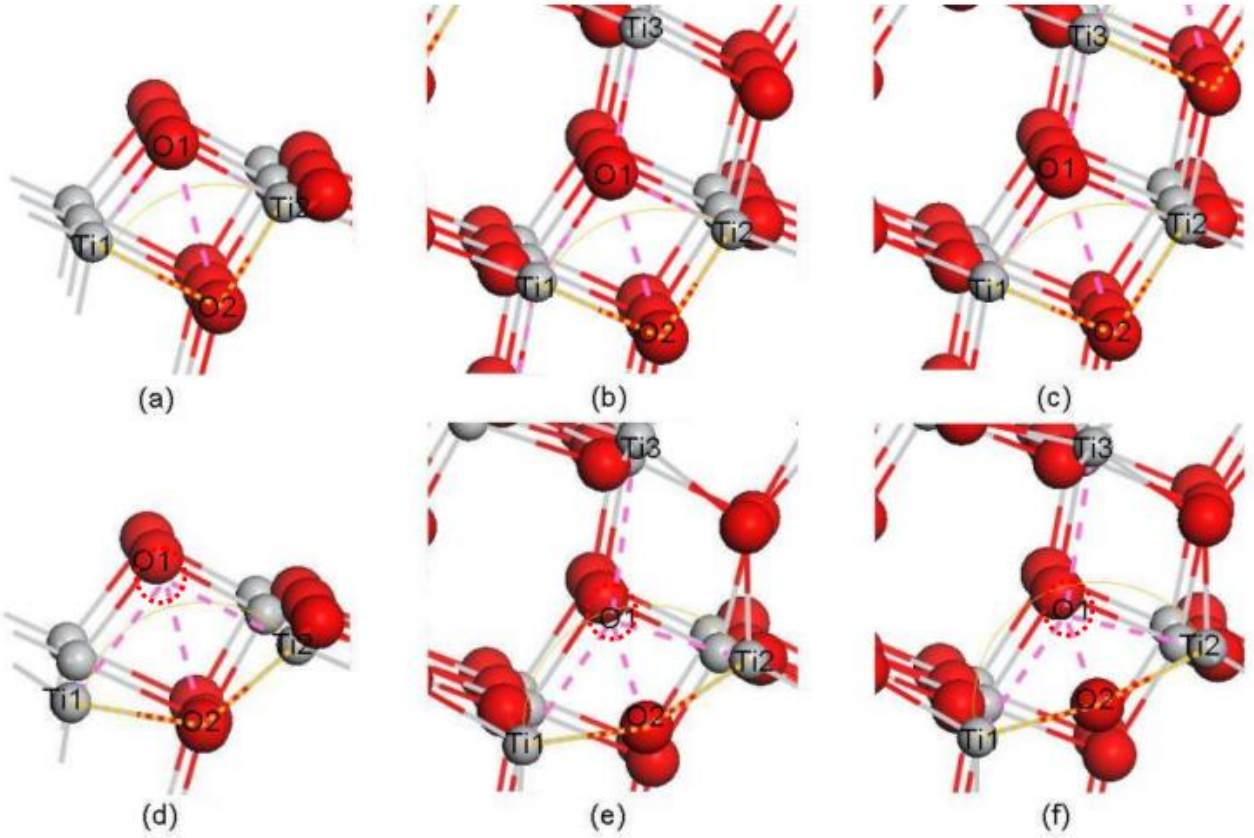
Vo1	Vo2	Vo3	Vo4	Vo5	Vo6	Vo7	Vo8	Vo9
3.68	4.50	3.99	5.23	4.73	5.28	4.46	4.67	4.38

Prediction

- **Anatase**: O-vacancies prefer **subsurface** rather than surface sites.
- **Rutile**: surface O-bridging and sub-bridging sites are favored with respect to subsurface and bulk sites

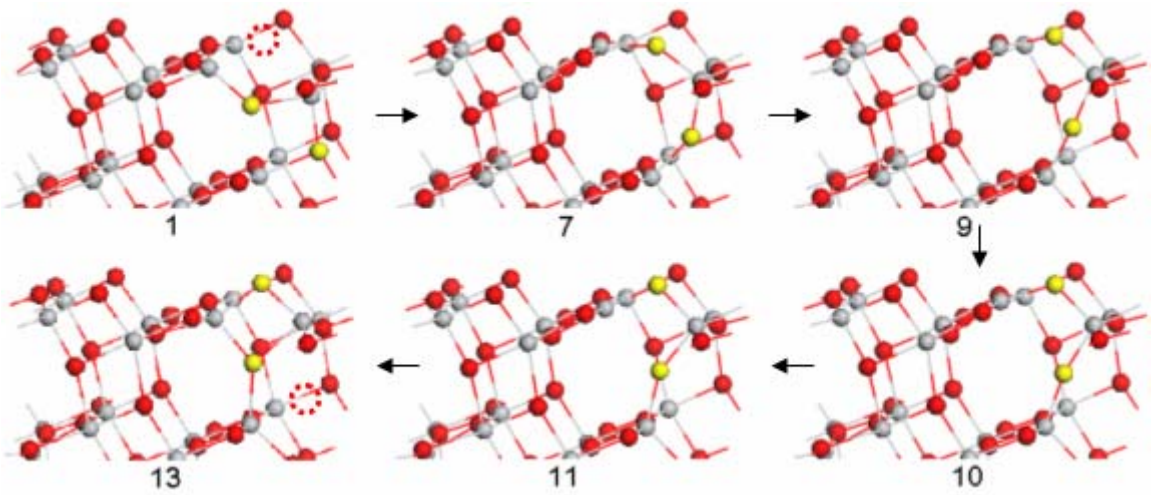
agrees also with resonant photoemission data (Thomas, Flavell & co, PRB 75, 035105 (2007))

…analyze relaxation at surface & subsurface sites

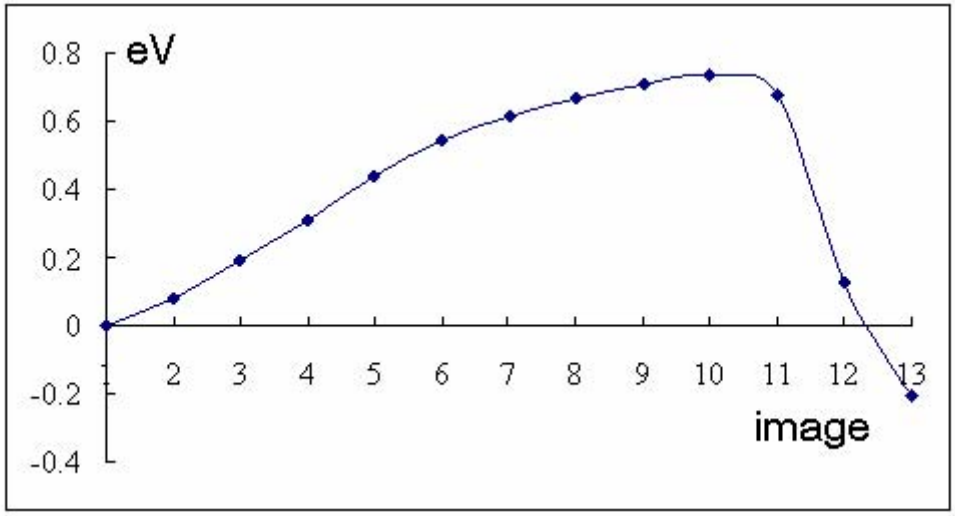


Relaxed atomic structure before (upper row) and after (lower row) creation of an O-vacancy at surface and subsurface sites of the anatase(101) surface: (a,d) Vo1; (b,e) Vo4; (c,f) Vo5. ⇒ Relaxation is more important at subsurface sites, surface is more "rigid"

Facile O-vacancy diffusion from surface to subsurface



Selected configurations along MEP



Potential energy profile along MEP: barrier = 0.74 eV

Summary

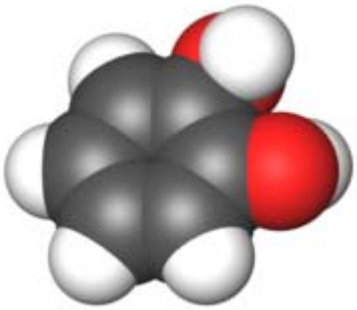
Surface vs subsurface distribution of O-vacancies in anatase is different from that in rutile.

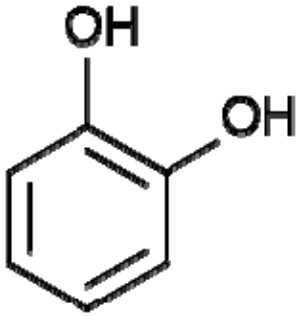
O-vacancies are most likely to occur on the surface in rutile.

In anatase, a relatively defect-free surface is predicted, i.e. defects are mainly confined in the subsurface region.

Adsorption of catechol on TiO_2(110)

(collaboration with U. Diebold, Tulane)





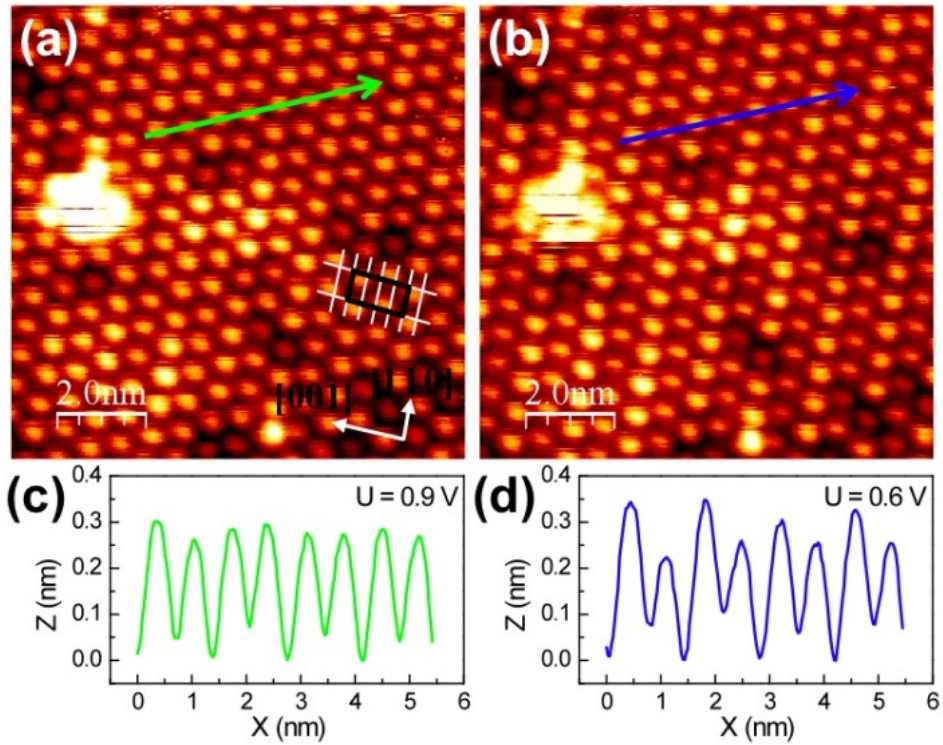
1,2 benzenediol

Motivation:

- Model dye/TiO_2 semiconductor system
- Model 'sticky molecule' for photocatalytic cleaning of TiO_2 coatings (on EUV mirrors)

Step1 (expt) –

STM measurements show the formation of a well-ordered superstructure with a 4 × 1 periodicity at saturation coverage

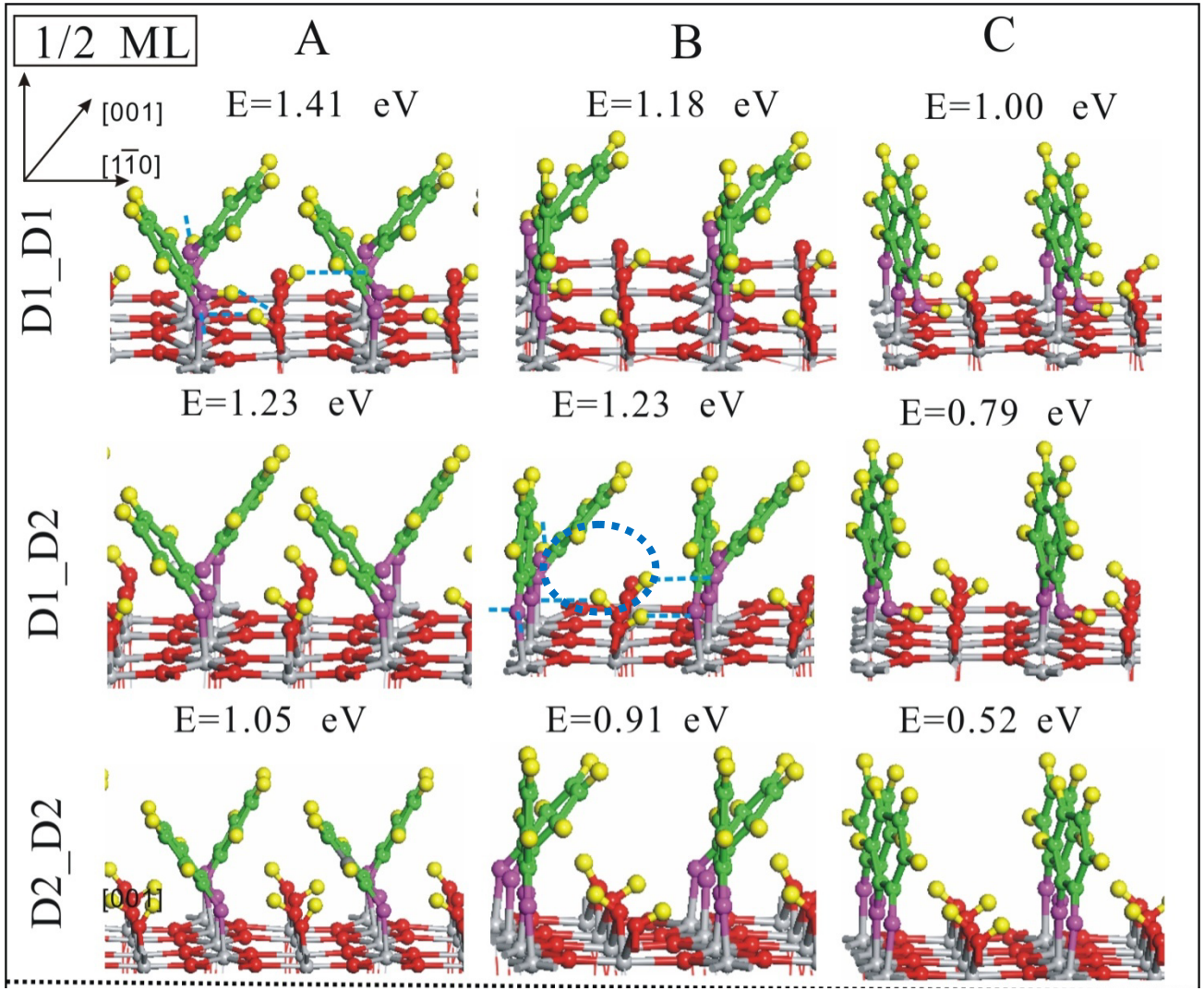


STM images (10 x 10 nm^2) of a TiO_2(110) surface covered with a 4 × 1 overlayer of catechol, recorded on the same area with sample bias voltages of (a) +0.9 V and (b) +0.6 V and a tunneling current of ~0.03 nA.

Step 2 (calc) -Adsorption structures of 0.5 ML catechol on TiO_2(110) from DFT (2 mol/(4x1) cell)

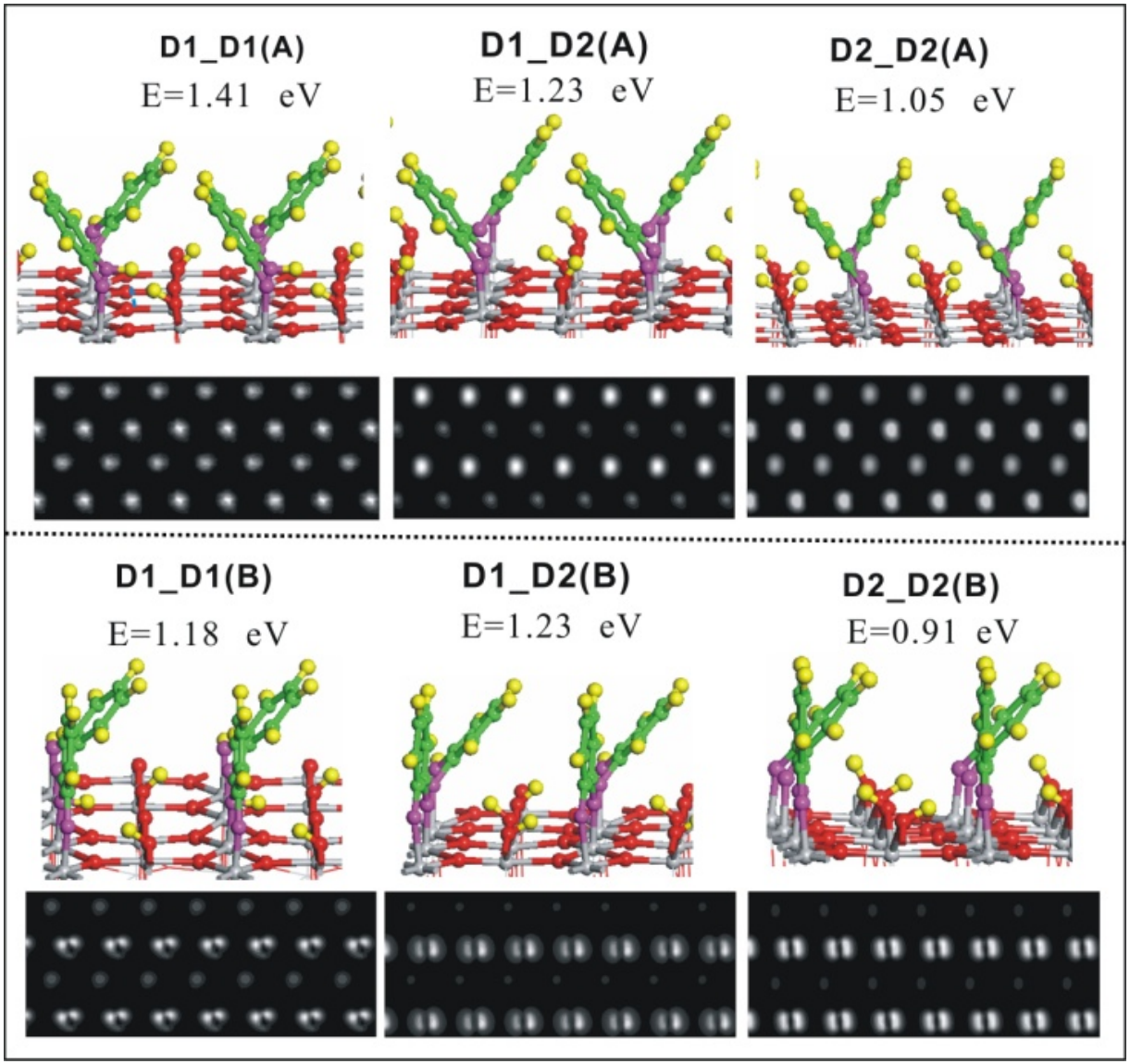
D1 = mono-dentate

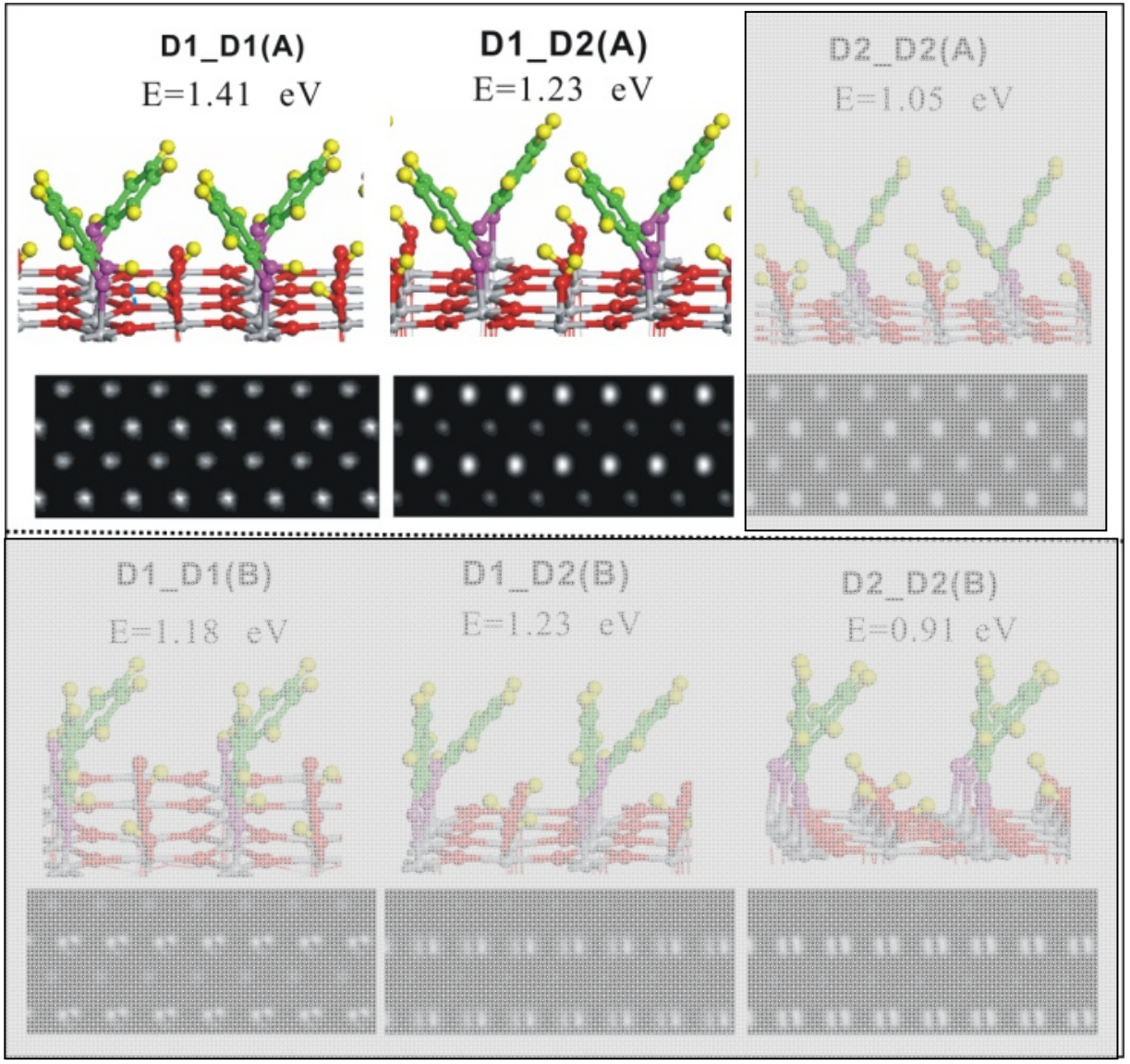
D2 = bi-dentate



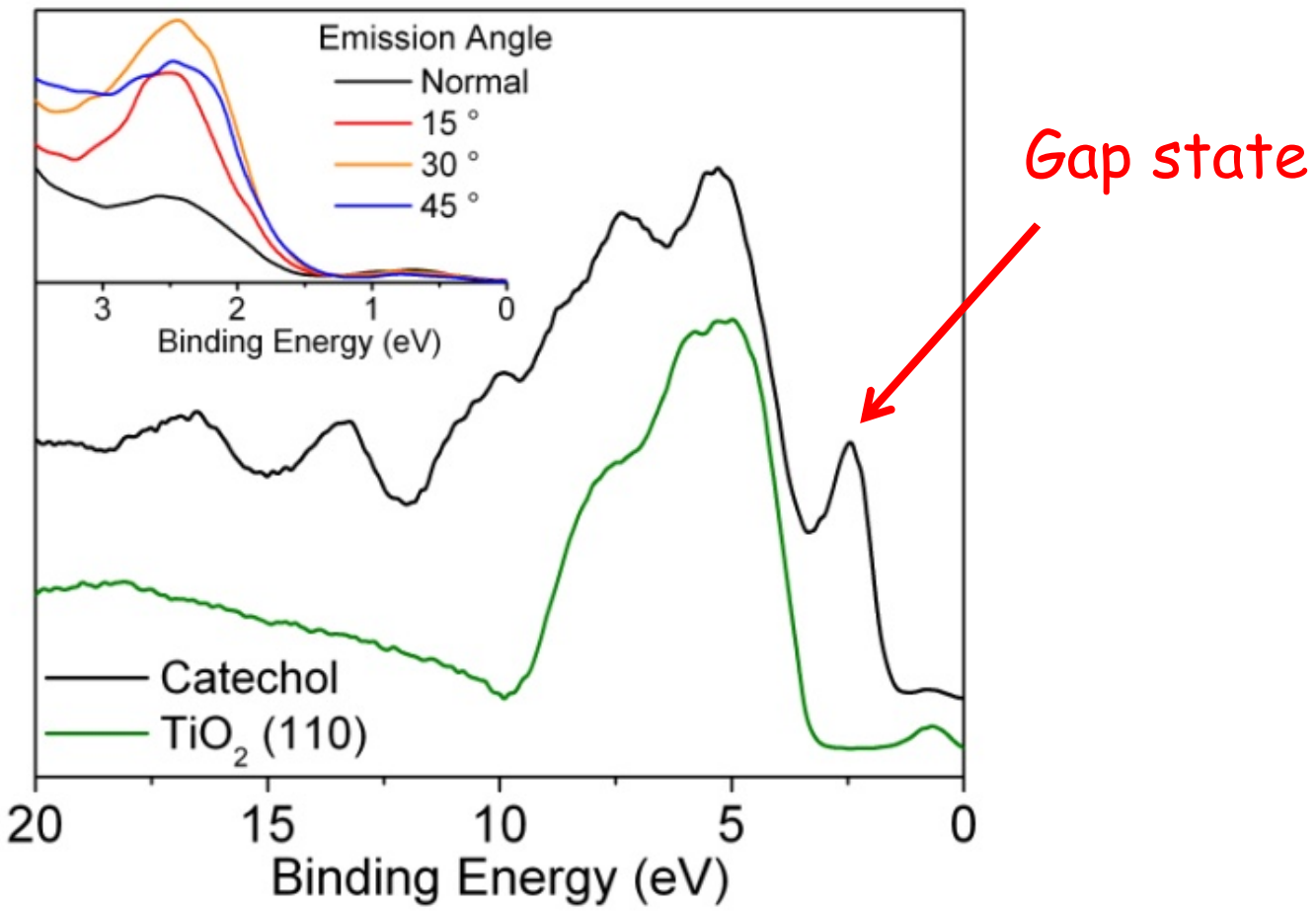
Tilted molecules favored b/c of reduced repulsion
H-bonding favors tilted D1 structures

Adsorption structures & simulated STM images of 4x1 ML catechol on TiO_2(110) from DFT calcs




D1_D1(A)
E=1.41 eV
D1_D2(A)
E=1.23 eV
D2_D2(A)
E=1.05 eV
D1_D1(B)
E=1.18 eV
D1_D2(B)
E=1.23 eV
D2_D2(B)
E=0.91 eV

Step 3 (expt)



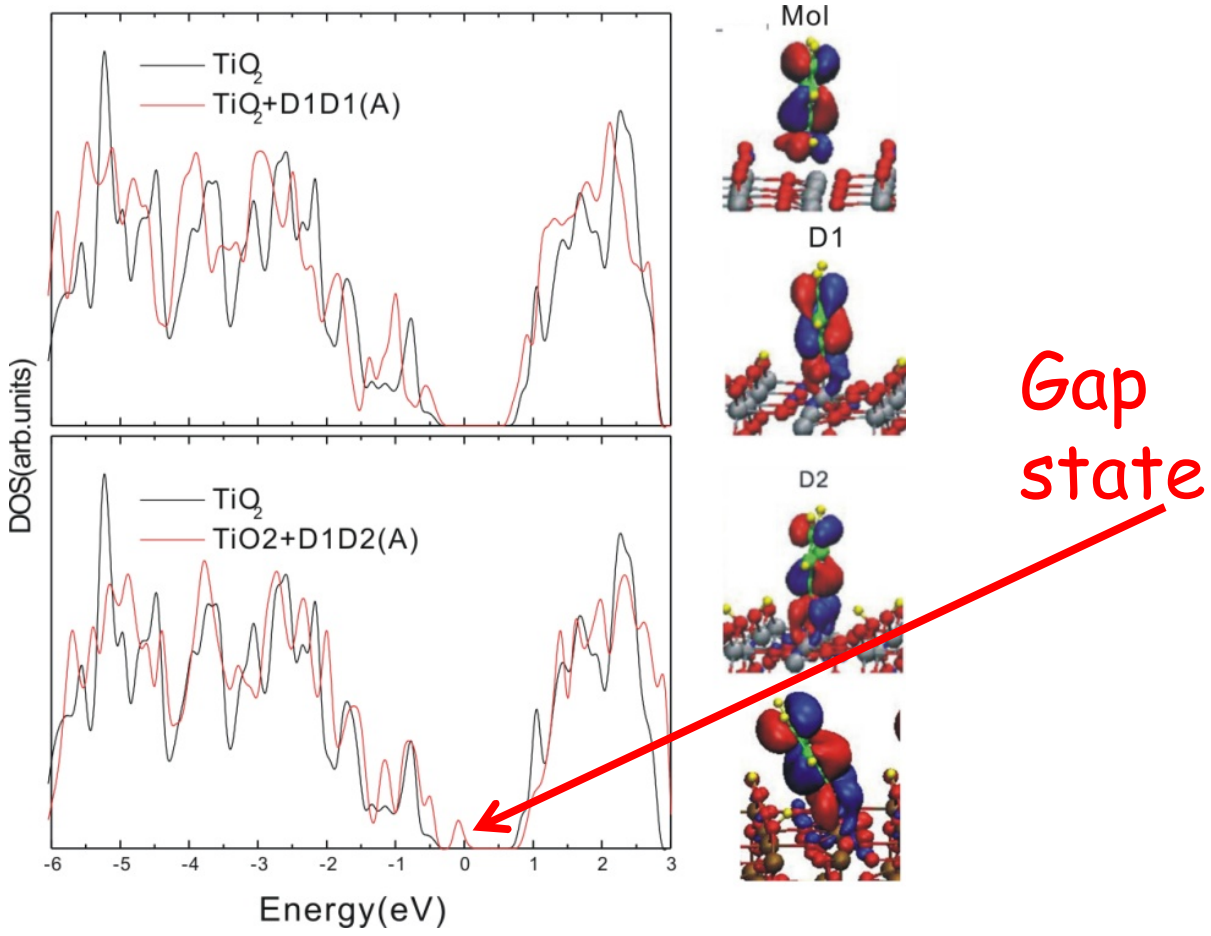
UPS valence band spectra (hv = 40 eV), from a clean TiO_2(110) surface and after exposure to a saturation coverage of catechol at RT. The inset shows the intensity variation of these states with the analyzer take-off angle.

Step 4 (th)

Total DOS of 4 × 1 ML catechol/TiO_2 (110) + DOS for the clean surface (back curve). Energy zero = theor Fermi energy.

D1-D1

D1-D2



Only bidentate (D2) molecules introduce states in the gap (increased mixing with Ti conduction band states)

SUMMARY & CONCLUSIONS

Catechol / TiO_2(110) forms two full coverage H-bonded structures, D1-D1 and D1-D2. These two structures can easily convert from one into the other via proton exchange between the surface and the adsorbed catechol.

Strong correlation between electronic structure & adsorption geometry.

Occupied states in the TiO_2 band gap are traps for photo-generated holes $\Rightarrow$ D2 catechol more easily photo-oxidized than D1 catechol.

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