Surface and Interface Science
Physics 627; Chemistry 541

Lectures 23
Nov. 18 2010

Oxide Surfaces

A) Introduction

Oxides important in a wide variety of applications

Electronic properties: Insulator; wide or narrow bandgap semiconductor; Superconductor; ferroelectric; multiferroic ; …

Focus of this lecture:

- Mainly metal oxides; perfect and defective surfaces
- Surface geometry
- Electronic structure
- Other topic: Chemisorption; Metal/oxide growth
  Phonons and vibrations; Catalysis
  DIET

B) Summary of Properties of several important oxides

Crystalline: Al_2O_3, MgO, TiO_2
Amorphous: SiO_2

B) Summary of Properties of several important oxides

Crystalline: Al_2O_3, MgO, TiO_2 ; Amorphous: SiO_2

Oxide Properties

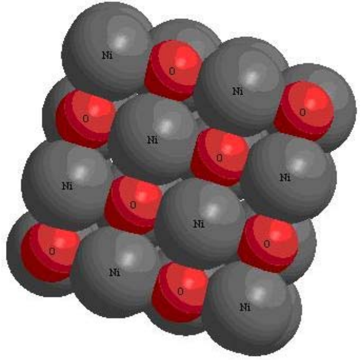
oxide	Al2O3	SiO2	TiO2	MgO
common name	saphire, alumina	glass, silica	rutile Titania	magnesia
structural name	corundum	amorph.	rutile	rocksalt
coord. no. (M:O)	6:4	4:2	6:3	6:6
lattice par.	.476nm(a) 1.299nm(c)			.421nm(a)
cleavage plane	$(10\bar{1}2)$		(110)	(100)
Energy gap	9.5eV	9.3 8.5(near interface)	3.1	7.8
Melting Temp.	2050C			2852
Dielectric Const.	4.5	3.8	14-100	3.0

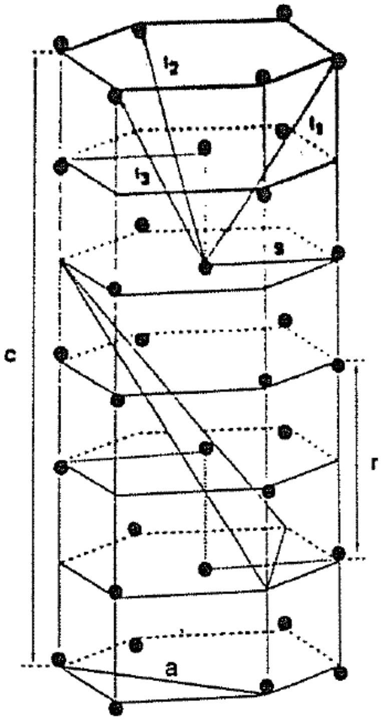
Other:
Cu - n.n. 2.56A(fcc)
Al - n.n. 2.86A(fcc)
Common Defects - Oxygen vacancies

d-Electron Configuration vs. Crystal Structure for Fourth-Period Transition-Metal Oxides

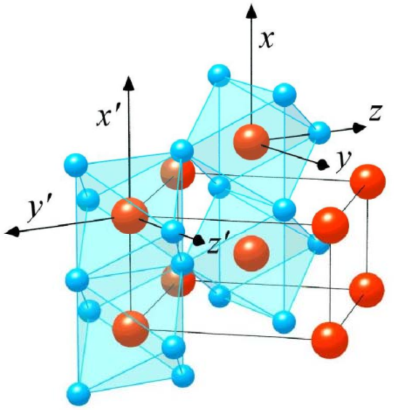
	Rutile	Corundum	Rocksalt	Spinel	Other
$3d^0$	TiO_2				Sc_2O_3 (bixbyite) TiO_2 (anatase) V_2O_5, CrO_3(orthorhombic)
$3d^1$	VO_2 (T≥340K)	Ti_2O_3			
$3d^2$	CrO_2	V_2O_3	$TiO_{X=1}$		
$3d^3$	β-MnO_2	Cr_2O_3	$VO_{X=1}$		
$3d^4$				Mn_3O_4	Mn_2O_3 (bixbyite)
$3d^5$		α-Fe_2O_3	MnO	Fe_3O_4	
$3d^6$			FeO	Co_3O_4	
$3d^7$			CoO		
$3d^8$			NiO		
$3d^9$					CuO (monoclinic)
$3d^{10}$					Cu_2O (cubic) ZnO (wurtzite)

Rock salt

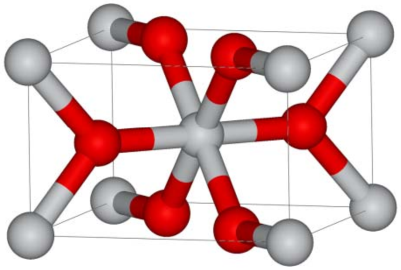




Corundum



Rutile



In ionic model:

O atoms consider to be O^{2-} with closed shell configuration

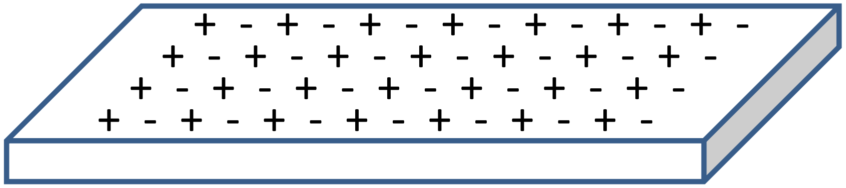
Electronic properties described as cations + ligands

Little difference between surface and bulk O^{2-}

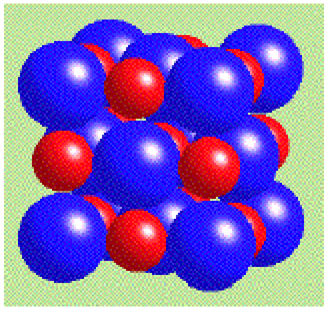
C) Surface geometry

- Most thermally stable surfaces are charge-neutral, non-polar →
  No dipole moment perpendicular to the surface; cleavage surfaces
- Potential at point external to charge-neutral sheet:

$$V(z) \sim e^{-2\pi z/a}$$



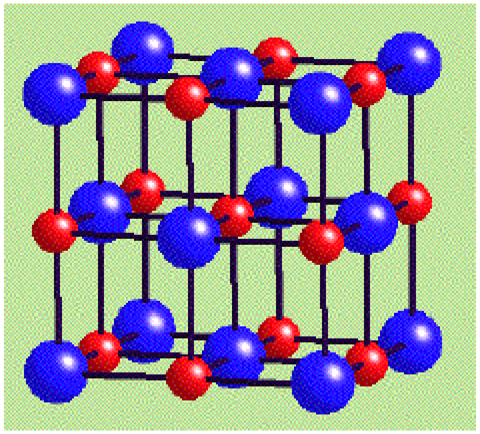
- Binding energy between charge neutral sheet is minimal
  (90% of Madelung potential at site from ions in slab, 10% from other slabs)
- Typically find nearly bulk truncation geometry for non-polar surfaces.

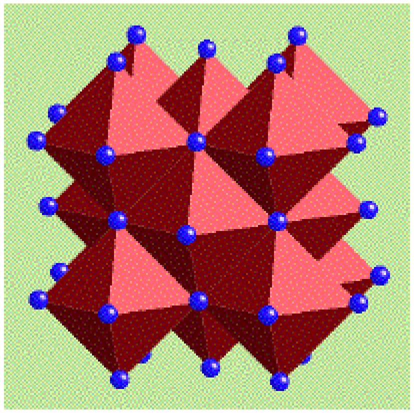


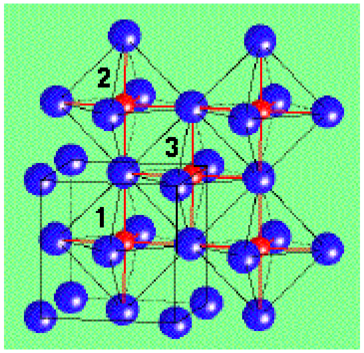
MgO

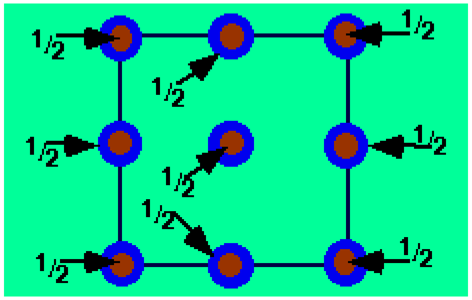
Rock Salt

(Halite)

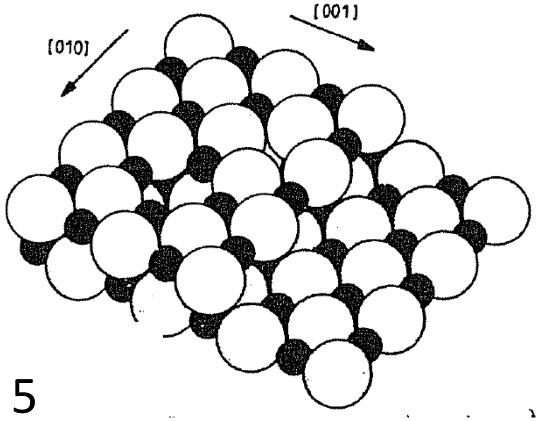




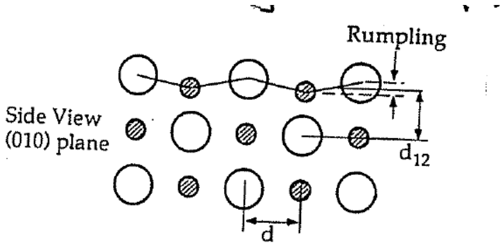




a) Rocksalt



1. fcc lattice, M^{2+} cation surrounded by 6 O^{2-} anions in regular octahedral arrangement
2. O^{2-} almost always larger than M^{2+} (e.g. $r_{O--} \sim 2r_{Mg++}$)
3. Extremely stable. Melting pt of MgO ~ 3100K
4. (100) cleavage plane.
    - Reduction in coordination of M^{2+} and O^{2-} from 6 to 5
    - LEED of NiO, CaO, MgO → nearly bulk truncation
    - LEIS of MgO(100) → ~ 1% relaxation, 0.5% rumpling



5. Role of point defects

   O^{2-} vacancies cause reduction in cation screening (important for electronic structure, reactivity)
6. Steps, kinks: theory predicts atomic displacements

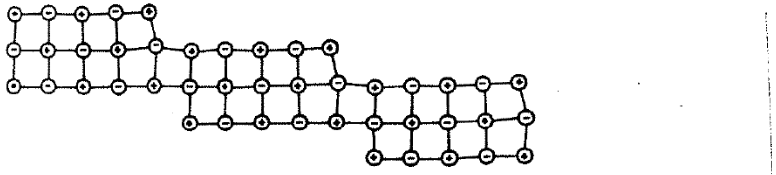
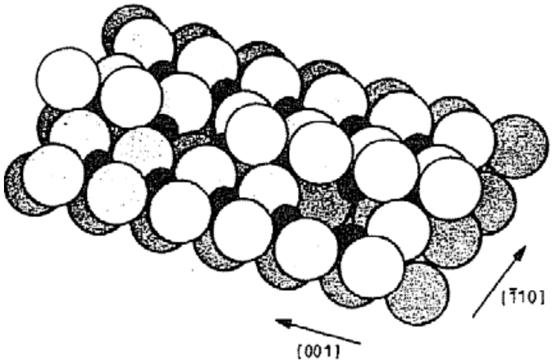
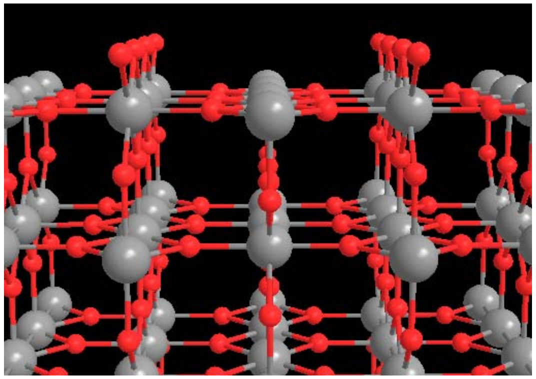


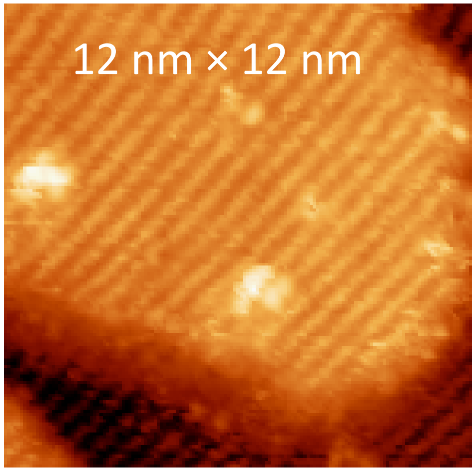
Fig. 7. Atomic displacements around the step on a (105) MgO surface drawn to scale.

b) Rutile

1. MO_2: Cations in body-centered tetragonal structure
   cations surrounded by 6 anions: TiO_2, SnO_2, RuO_2, …
2. Rutile does not cleave well,, but (110) plane most stable
   - 5-fold and 6-fold coordinated Ti^{4+}
   - Bridge and in-plane oxygen
   - (1 x 1) LEED pattern, STM
   - Rumpling and relaxation



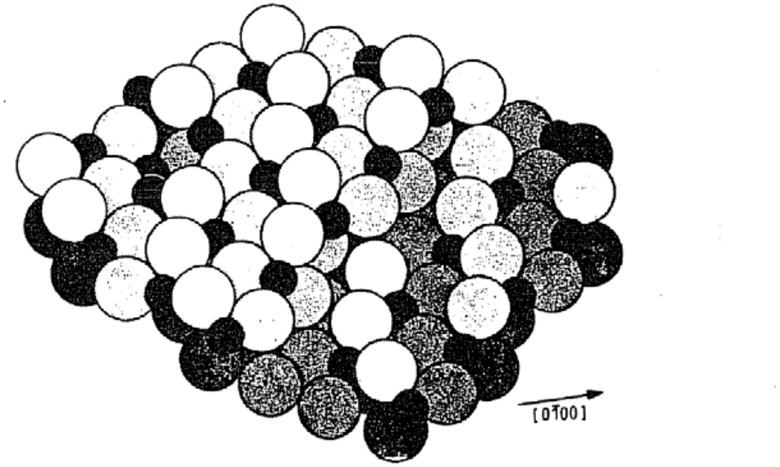




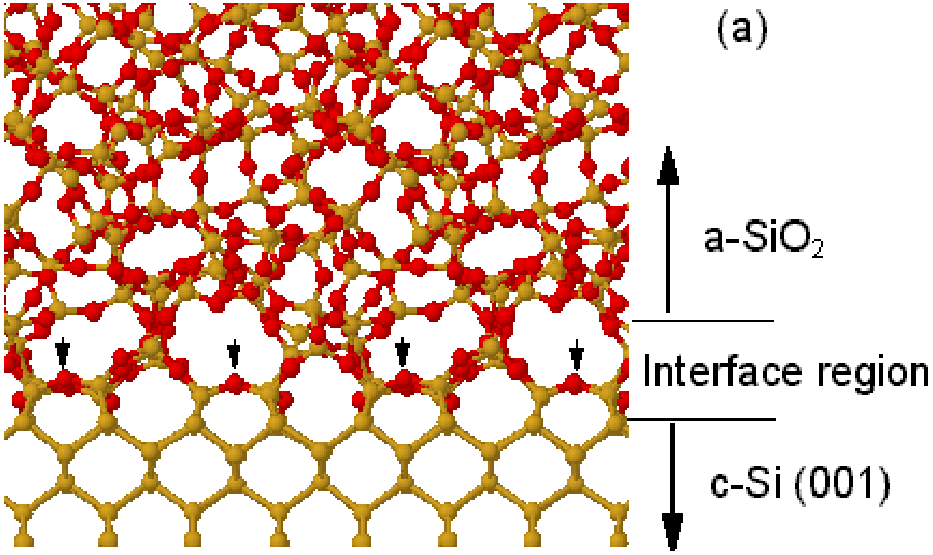
3. Role of point defects: produced by ion bombardment, thermal, e-bombard.
4. O^{2-} vacancies cause reduction in cation screening
5. Thermally annealed (001) surface forms facets of (110) and (114)

c) Corundum

1. M_2O_3: trigonal; M^{3+} is formal cation valence
   cations surrounded by 6 anions: Ti_2O_3, V_2O_3, Al_2O_3, …
2. Cleavage plane is (10-12) for Ti_2O_3, V_2O_3; Al_2O_3 does not cleave



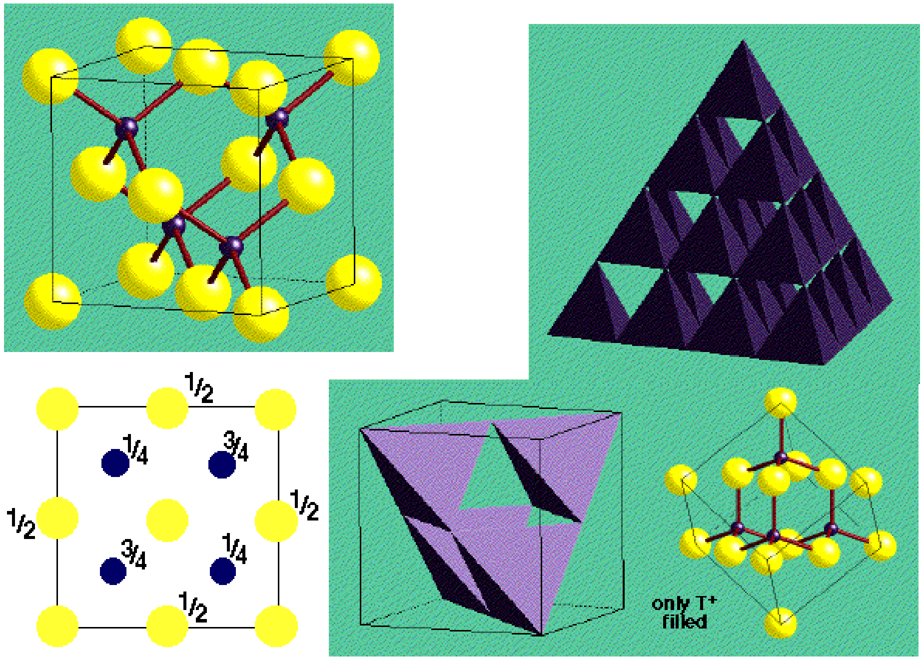
l of the corundum $(10\bar{1}2)$ surface. A $\{10\bar{1}2\}$ step to another $(10\bar{1}2)$ terrace and an O-vacancy

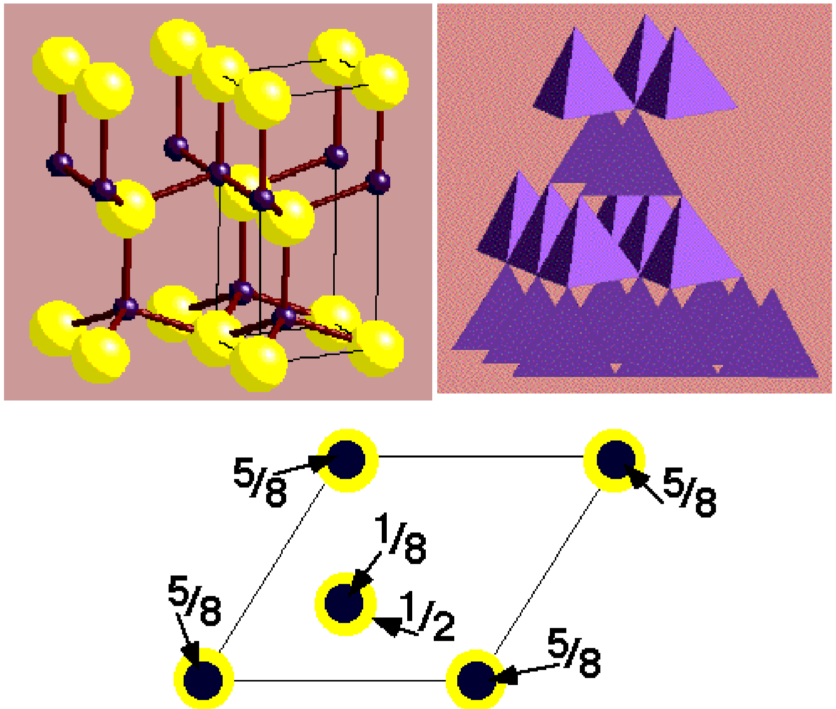


d) SiO_2

2. Amorphous
3. Dominated by 6-member rings, but some 5-member
4. Range of bond angles around 104 deg
5. Bridging and non-bridging oxygens, channels

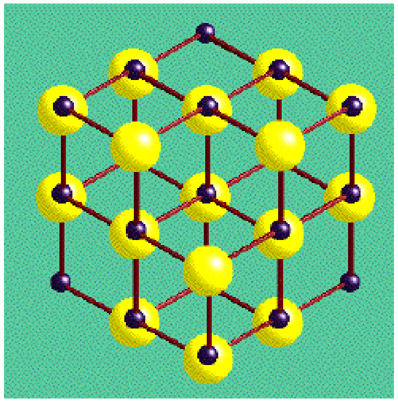
e) Zincblend (GaAs), Wurtzite (ZnO)





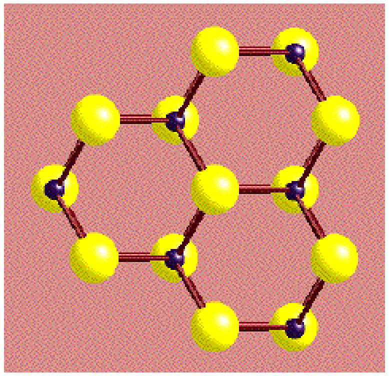
1. Cations tetrahedrally coordinated
2. Dipole layer causes field along (0001), get anion-rich and cation-rich polar faces
3. Reconstruction, facetting common, neutralizaion produced by vacancies

PLAN VIEWS



Zinc Blende

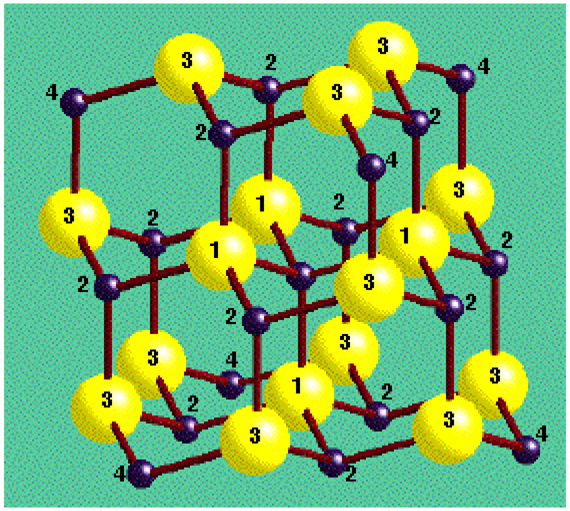
CCP ABC repeat



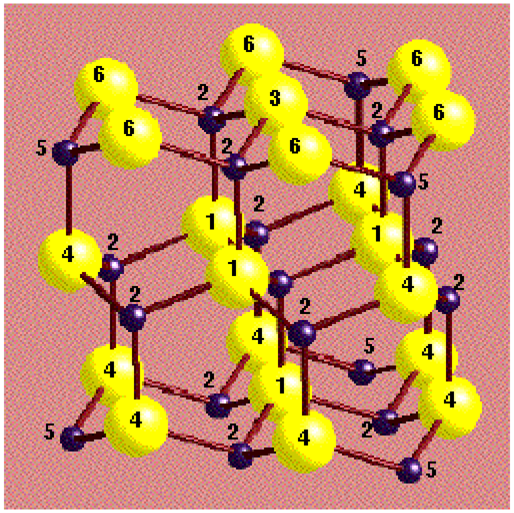
Wurtzite

HCP AB repeat

COORDINATION ENVIRONMENTS



Zinc Blende



Wurtzite

4 Nearest Neighbours (***Tetrahedral***)

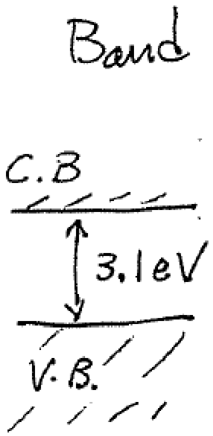
12 Next-Nearest Neighbours

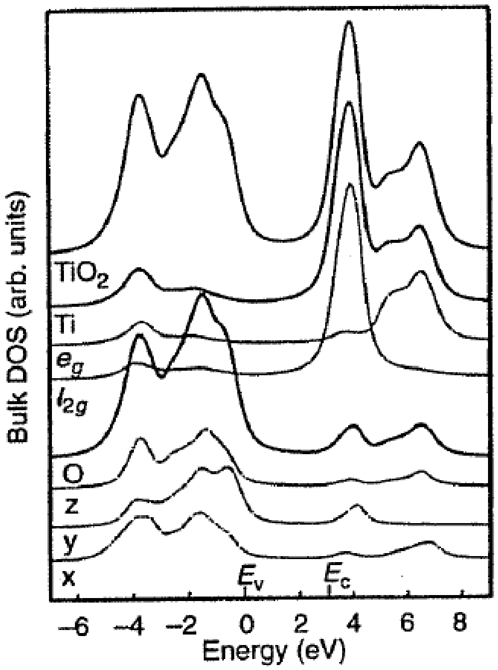
Cuboctahedral ← → ***Anti-Cuboctahedral***

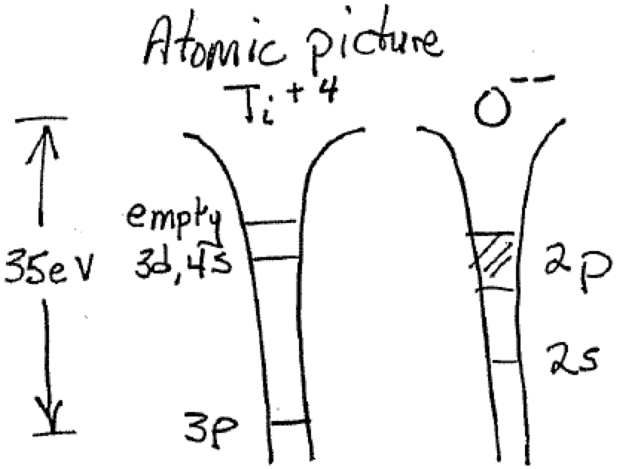
Very different Next, Next-Nearest Neighbour Coordinations & beyond

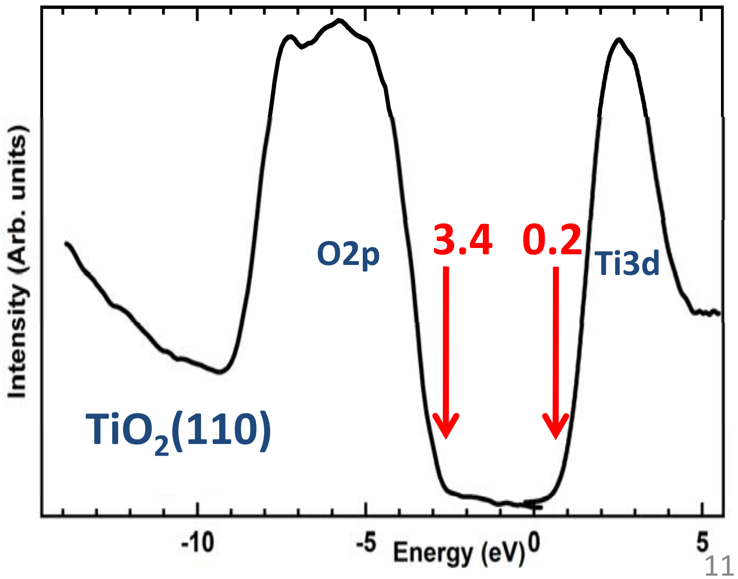
D) Electronic Structure

- Focus on TiO_2
- For insulating oxides, charging is a problem for electron spectroscopies
- TiO_2 partially reduced by heating making it n n-type semiconductor



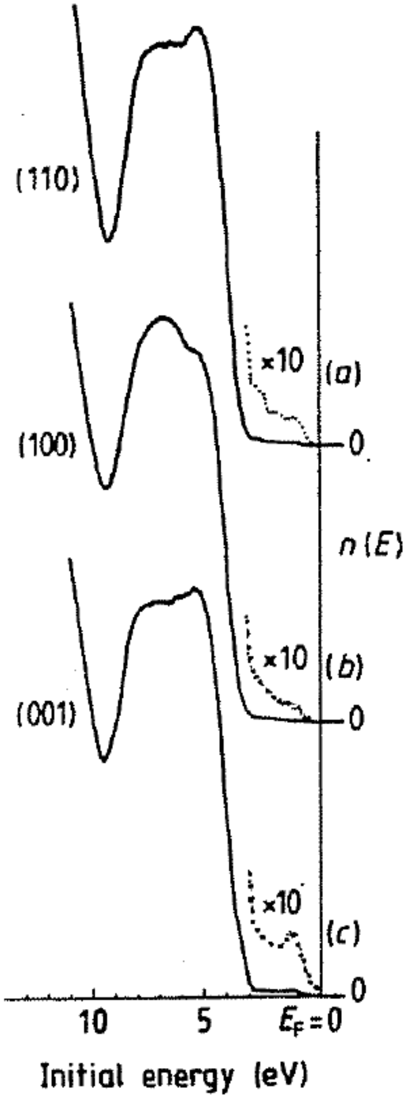






UPS spectra from 3 vacuum-cleaved TiO_2 surfaces:

- Different surfaces exhibit similar electronic structure despite different geometries
- I mplies that reduction of ligand coordination by itself is not sufficient to significantly alter electronic structure
- Band gap emission implies different defect structures on different surfaces



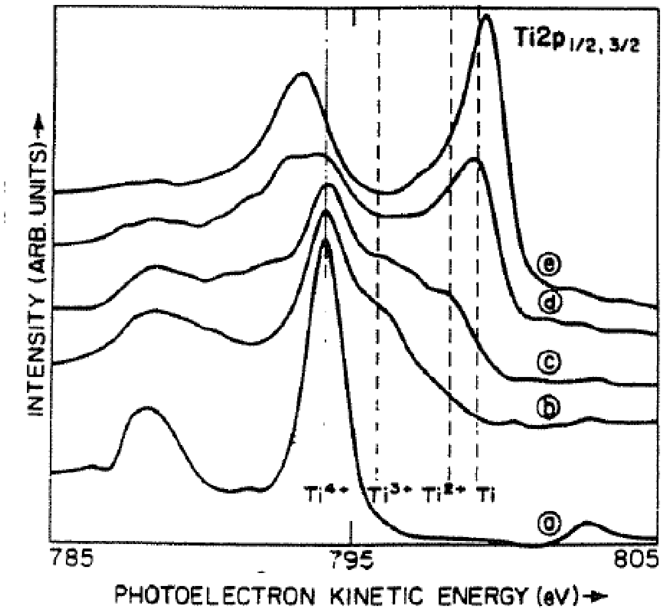
Defects on TiO_2 surfaces:

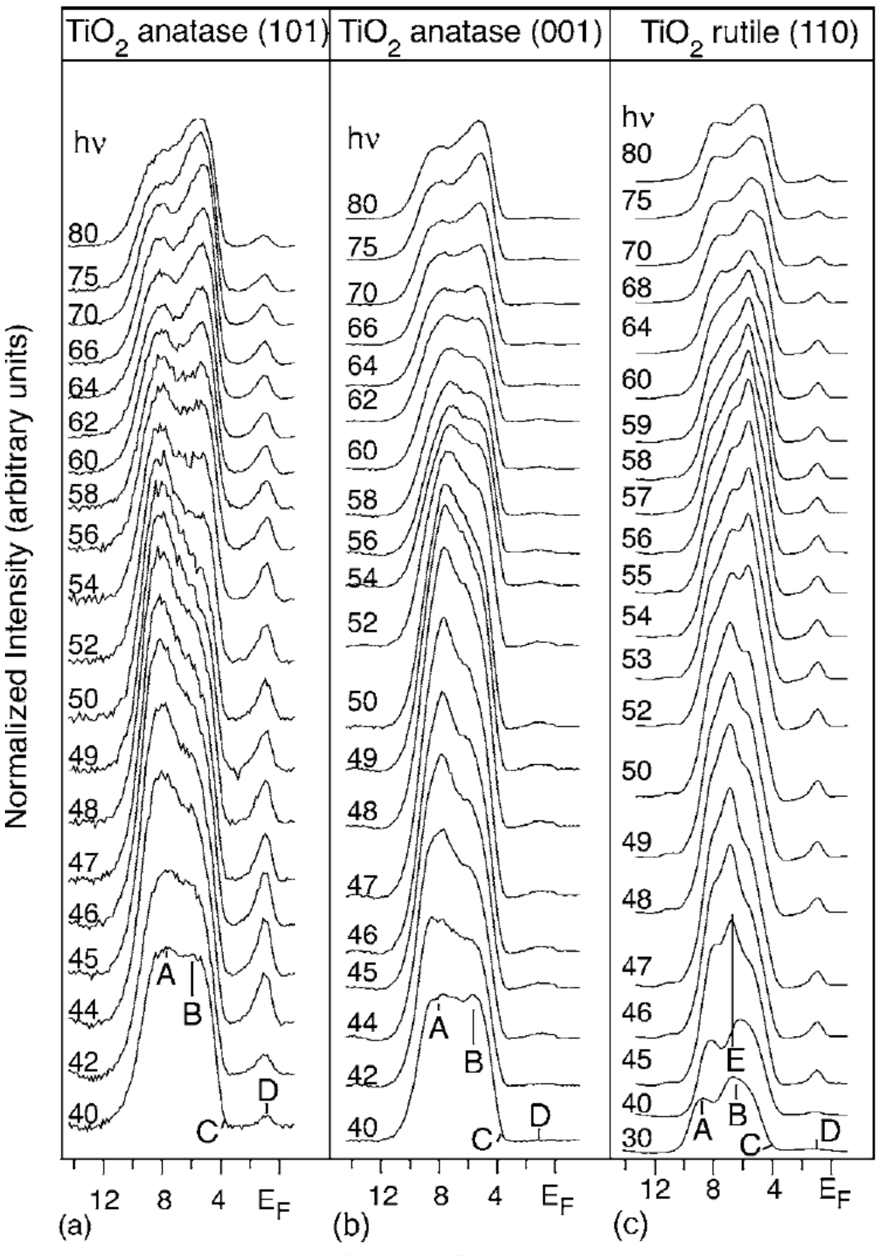
- Dominant defect is oxygen vacancy

Ti^{4+} O^{2-} Ti^{4+} → Ti^{3+} X Ti^{3+}

- O^{2-} vacancy leaves neighboring Ti ions in Ti^{3+} oxidation state

- Resonant photoemission indicated Ti 3d nature of defect-induced gap state

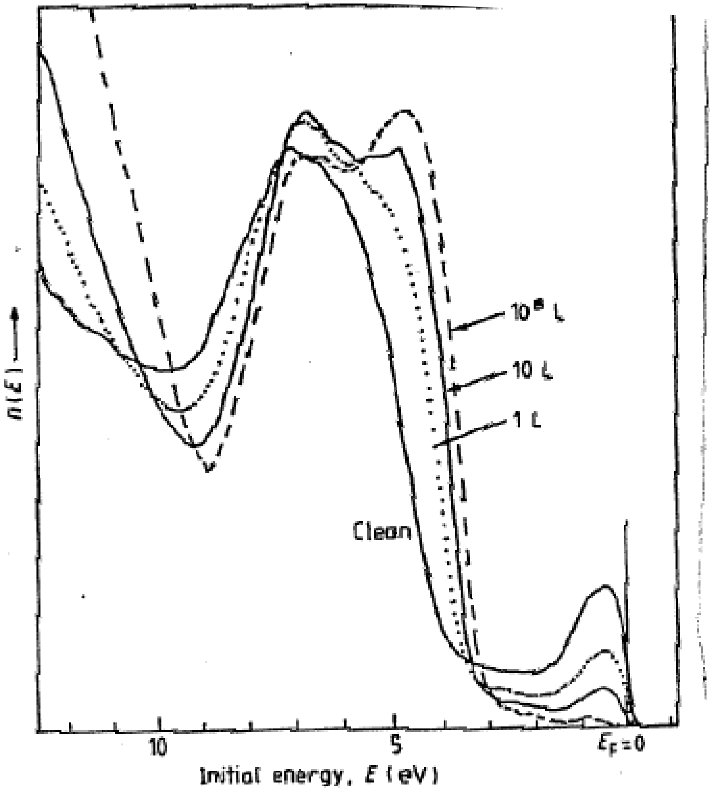


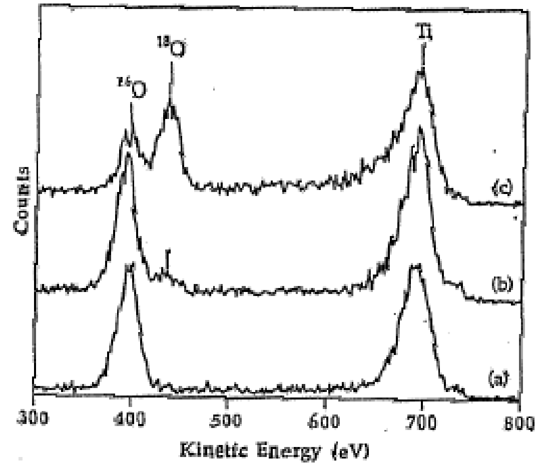


- Stoichiometric TiO_2 surface inert to O_2

- Defective TiO_2 surfaces oxygen deficient

- Sputtered TiO_2, TiO_x, will adsorb oxygen





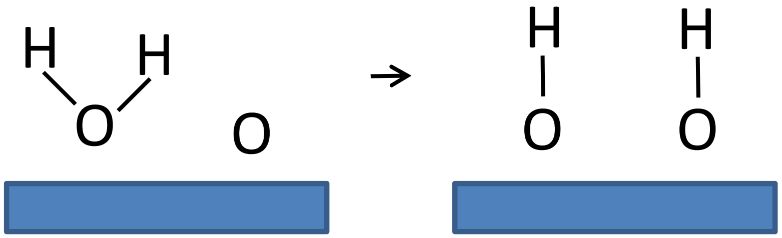
500 L $^{18}O_2$ exposure

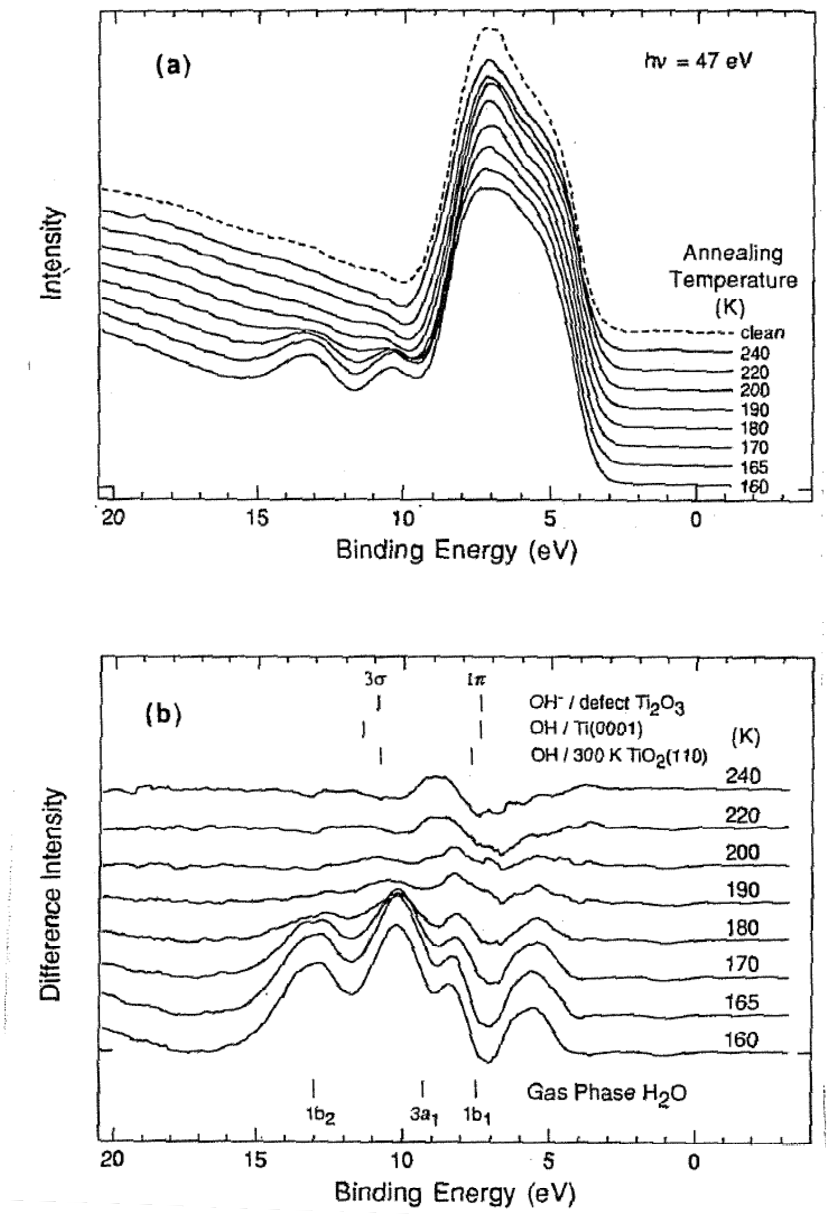
Water adsorption on stoichiometric TiO_2

Expect strong interaction between cation and dipole of H_2O

Screening by anions, molecular rotation weakens effect.

Adsorption of OH- stable at 300K



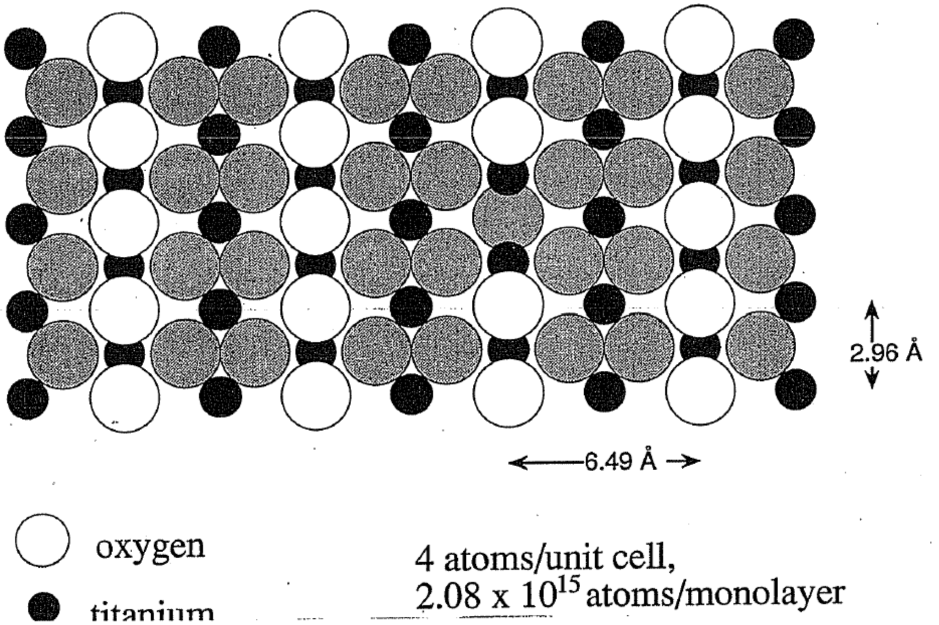


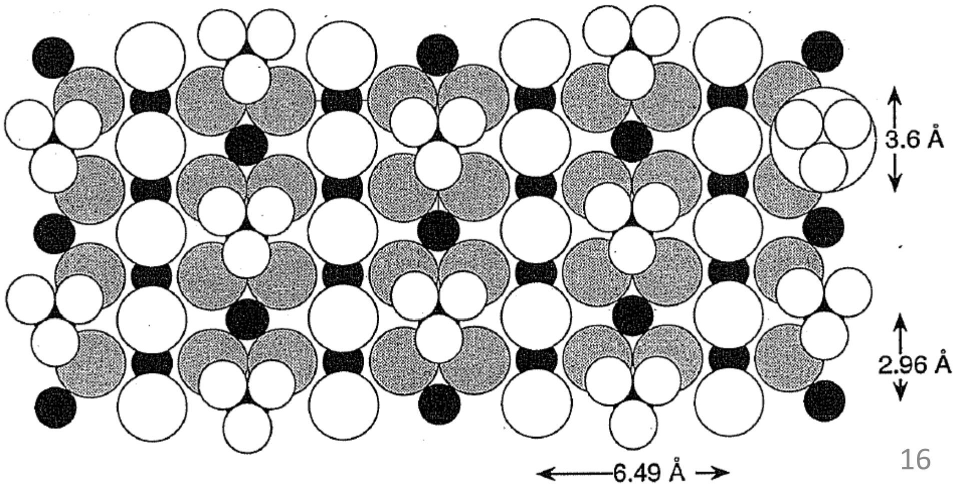
NH_3 adsorption on oxides

NH_3 used to titrate acid sites (exposed cations)

Strong point charge – dipole interaction

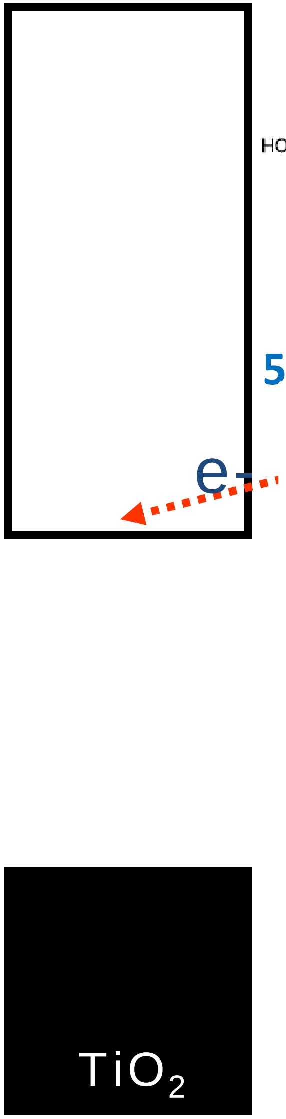
NH_3/TiO_2:
Saturation coverage: 0.125 ML
Experimental: ~ 0.16 ML


"perfect" $TiO_2(110)$


Ammonia on $TiO_2(110)$

Energetics: N3 molecule on TiO_2

P. Persson and M. Lundqvist,
J. Phys. Chem. B 2005, *109,* 11918-11924



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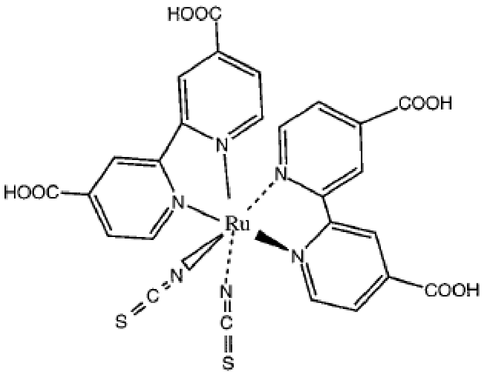
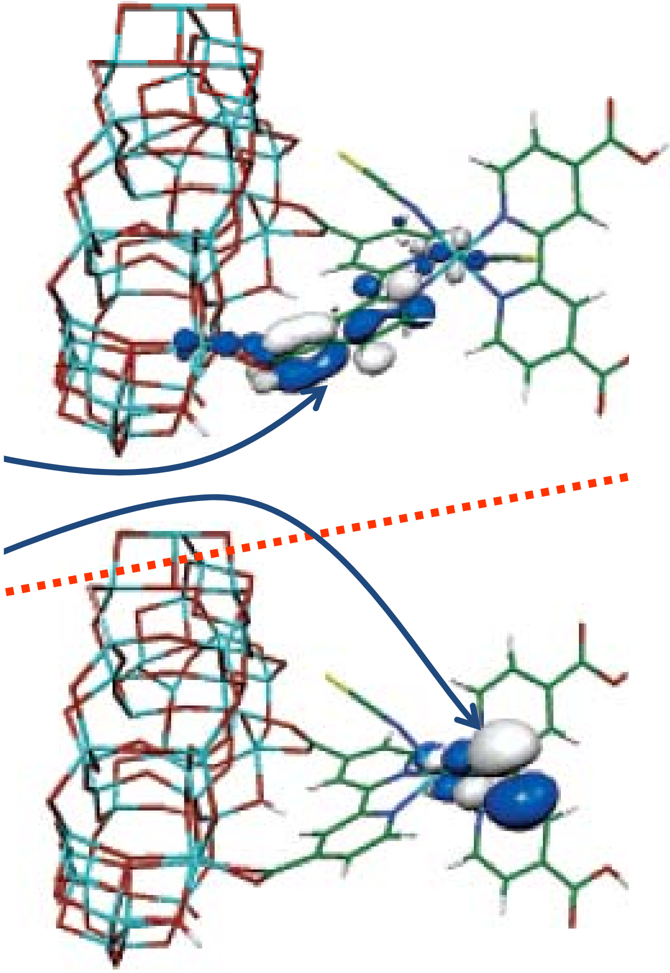
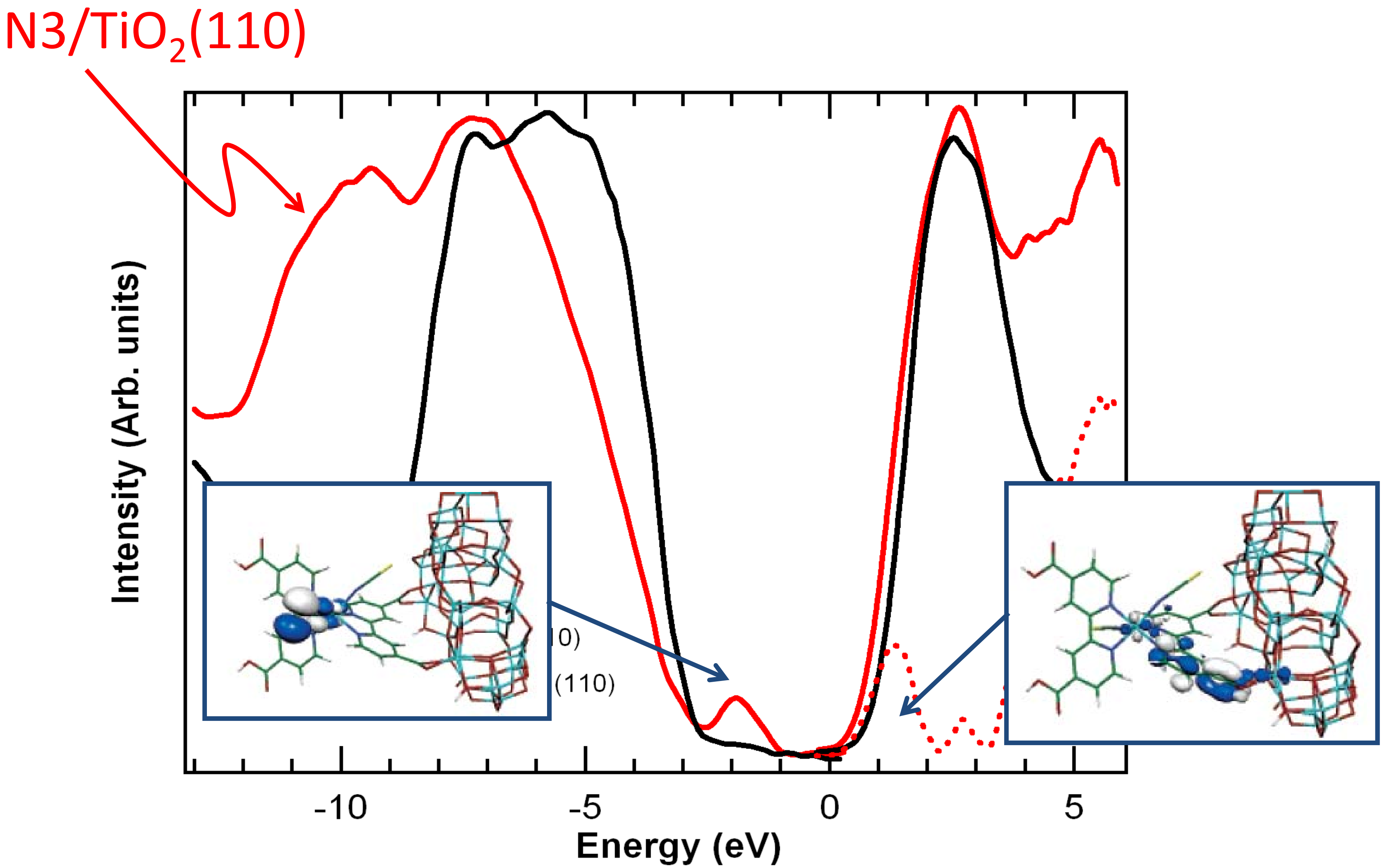


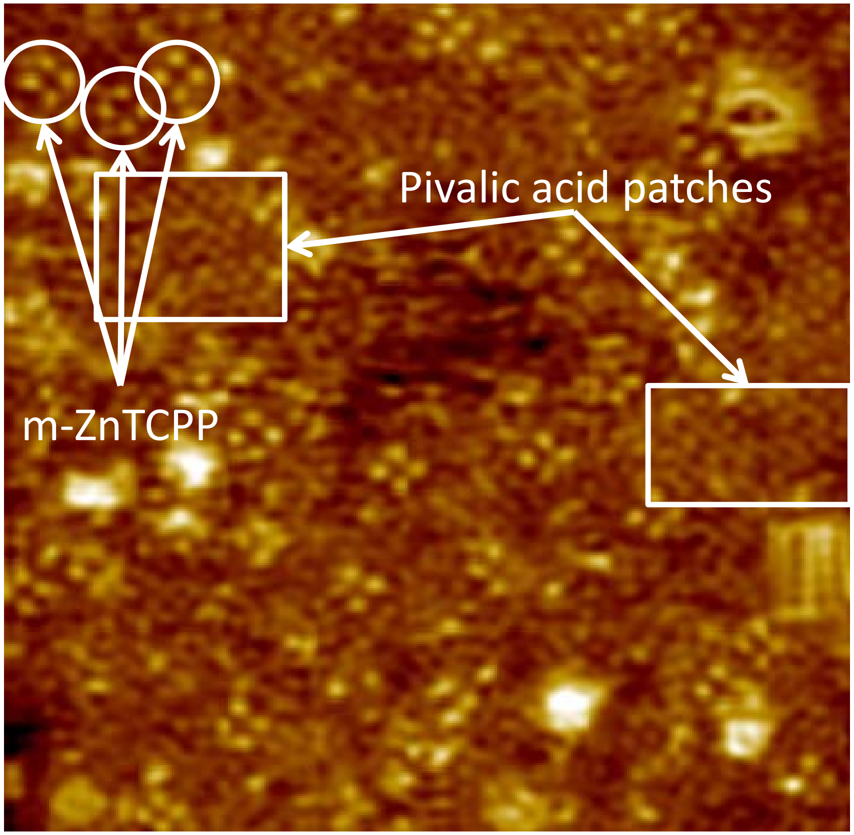
N3

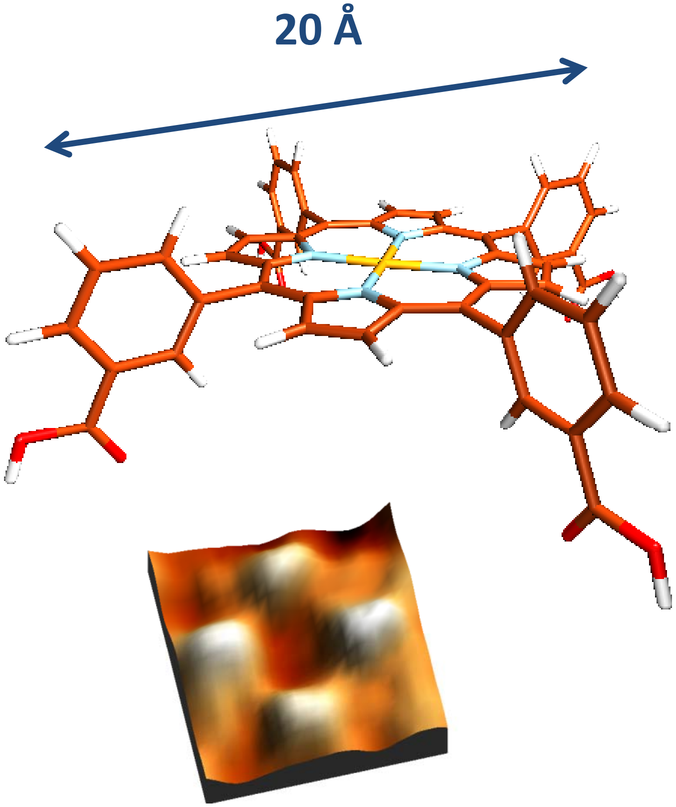


N3 on TiO_2 (110)


N3/TiO_2(110)

m-ZnTCPP adsorption



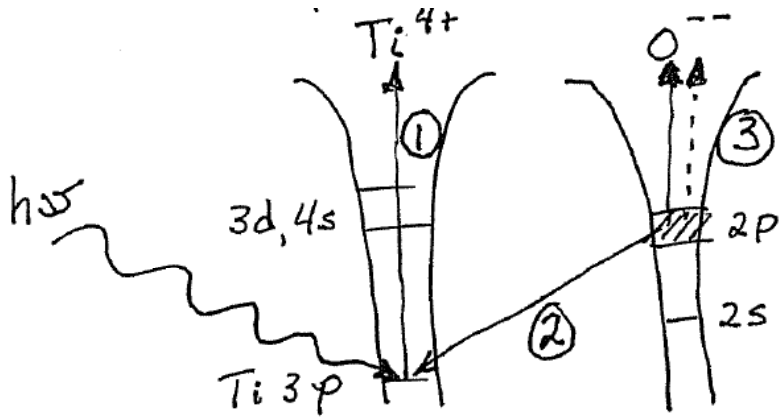


DIET from oxides

Desorption Induced by Electronic Transitions

For maximum valency oxides:
Knotek-Feibelman mechanism

"Interatomic Auger process results in O^+ that experiences a reverse Madelung potential



$O^{--} \rightarrow O^{+}$

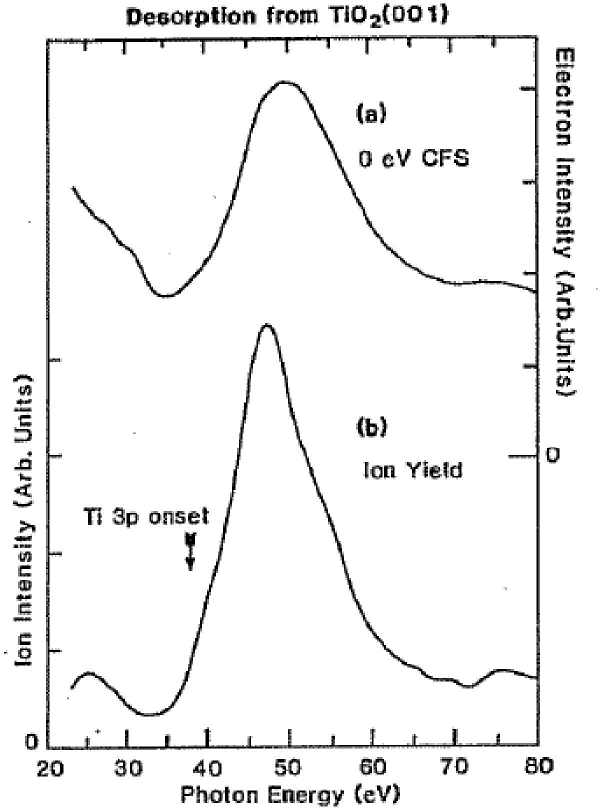


Fig. 1. Photon energy dependence of the 0 eV CFS spectrum (photoabsorption), upper curve, and the total ion yield, lower curve, from annealed TiO_2 (001) measured with a double-pass CMA. The shapes of the curves are similar for the (110) surface and for sputtered TiO_2 surfaces although absolute magnitudes vary.