MODELLING PHOTOINDUCED REDOX PROCESSES IN THE BULK AND AT THE SURFACE OF TiO_2

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Workshop on Material Challenges in Devices for Fuel Solar Production and Employment
ICTP – TRIESTE MAY 19-23, 2014

TITANIUM DIOXIDE PHOTOINDUCED APPLICATIONS

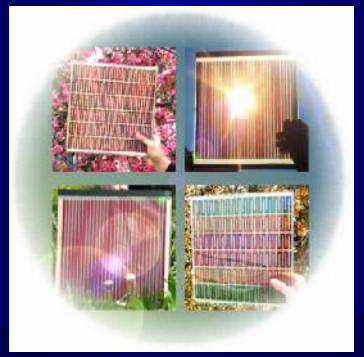
TiO_2 coating: anti-fogging

TiO_2 coating: self-cleaning glass and materials

TiO_2 coating: anti-bactirial anti-virial fungicidal

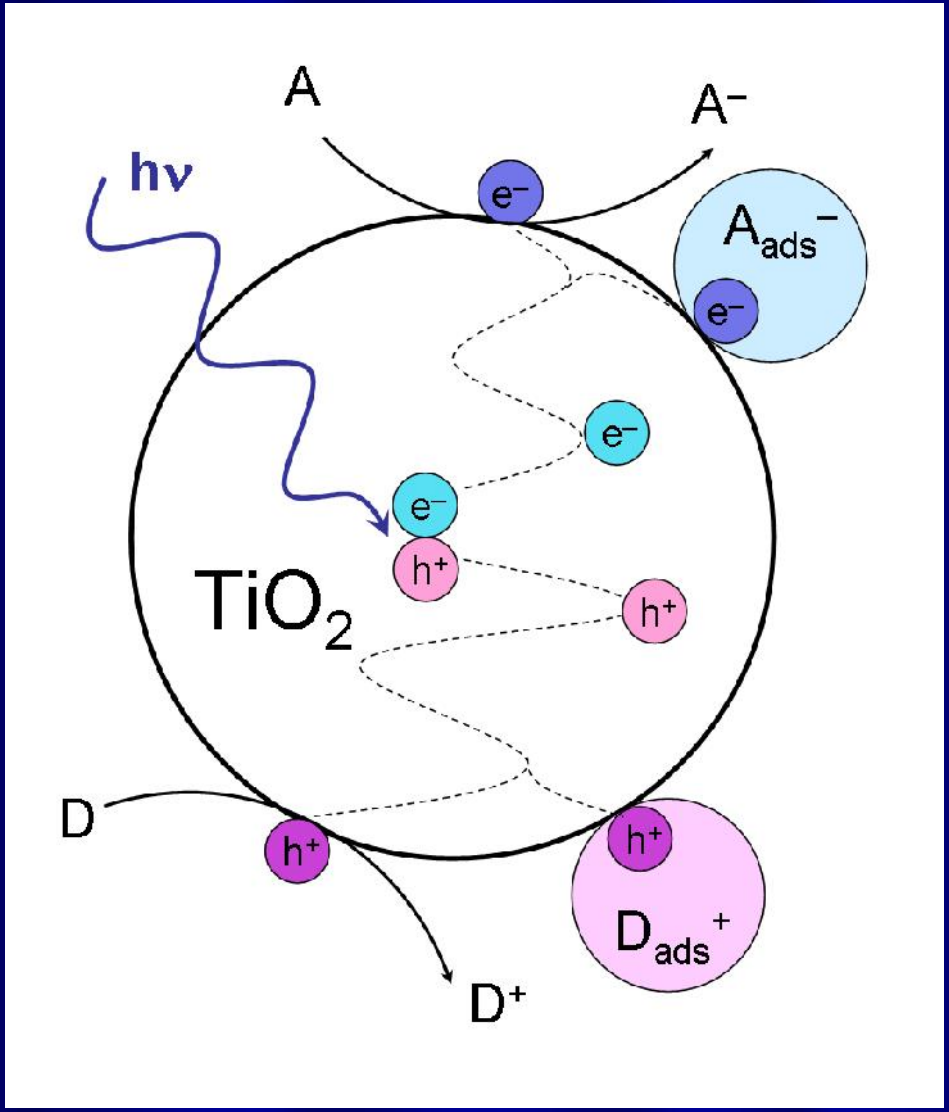
TiO_2 coating: deodorizing air-purification

TiO_2 based photo electrochemical water splitting



Grätzel cells

PHOTOINDUCED PROCESSES ON TITANIUM DIOXIDE



PEOPLE GENERICALLY TALK OF:
RECOMBINATION
OR
CHARGE TRAPPING

BUT WHAT ARE THEY?
STILL MANY OPEN QUESTIONS:

FOCUS OF OUR WORK

- **PHOTOINDUCED EXCITONS**
- **CHARGE SEPARATION**
- **ELECTRON-HOLE PAIR**
- **SELF-TRAPPING**
- **CHARGE MIGRATION**
- **ROLE OF INTRINSIC OR EXTRINSIC DEFECTS**
- **CHARGE TRAPPING AT SURFACE**
- **SCAVENGERS**
- **REDOX PROCESSES**

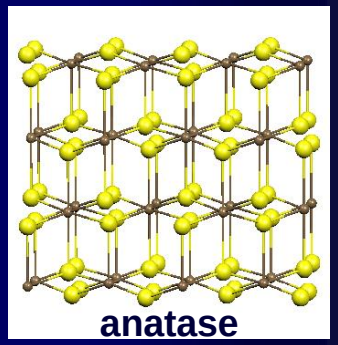
OUTLINE

- computational info
- photoexcited TiO_2:
  - bulk excitons
  - electron and hole polarons in bulk
  - electron and hole polarons on clean or OH surface
- photoreduction and photooxidation at TiO_2 surface
  - molecular oxygen as an electron scavenger
  - organic molecules as hole scavengers
    - (formic acid, methanol, iso-propanol,
    - tert-butanol, glycerol and catechol)
- anatase vs rutile
- conclusions

COMPUTATIONAL APPROACH

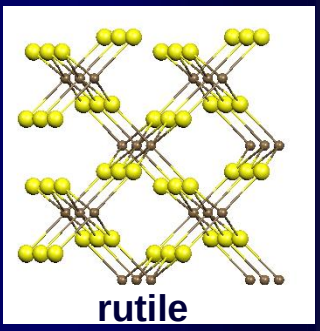
CRYSTAL09 (hybrid DFT)

atomic gaussian basis set and PBC (3D and 2D)
Hybrid DFT functionals – spin polarized calculation
hyperfine coupling constants (EPR)


anatase

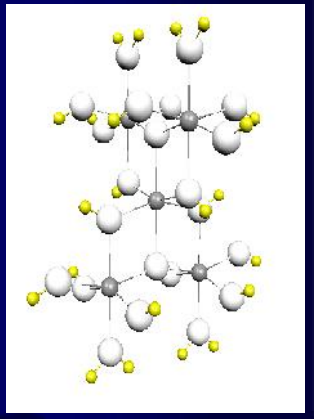
QUANTUM EXPRESSO (standard DFT and DFT+U)

PWSCF: plane-wave-pseudopotential and PBC (3D)
PBE functional – spin polarized calculations
CAR-PARRINELLO molecular dynamics simulations


rutile

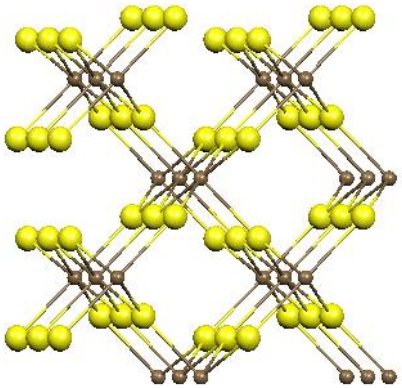
GAUSSIAN09 (hybrid DFT)

atomic gaussian basis set and embedded cluster approach
Hybrid DFT functionals – spin polarized calculation
hyperfine coupling constants and g-tensors (EPR)
TD time dependent calculations

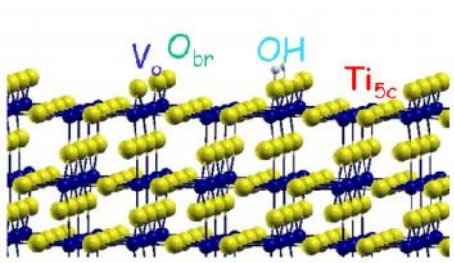


TiO_2 MODELS

RUTILE

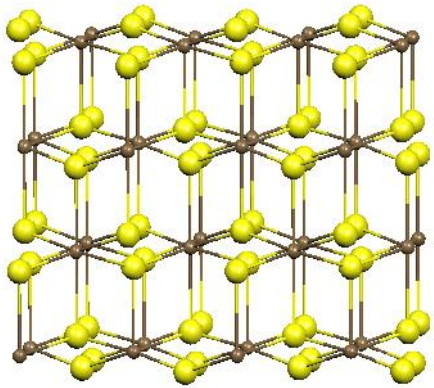


rutile bulk

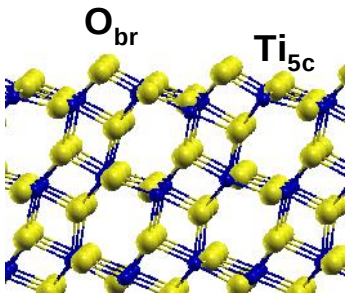


rutile 110 surface

ANATASE



anatase bulk

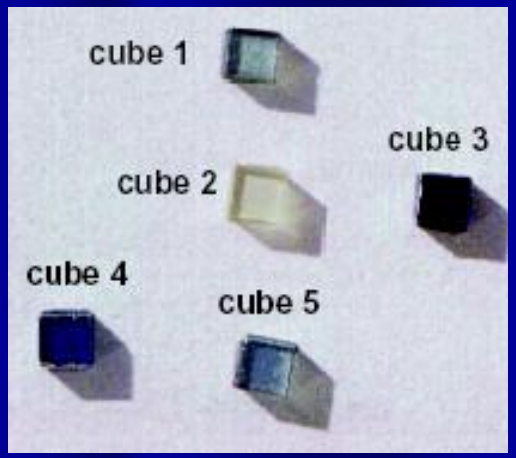


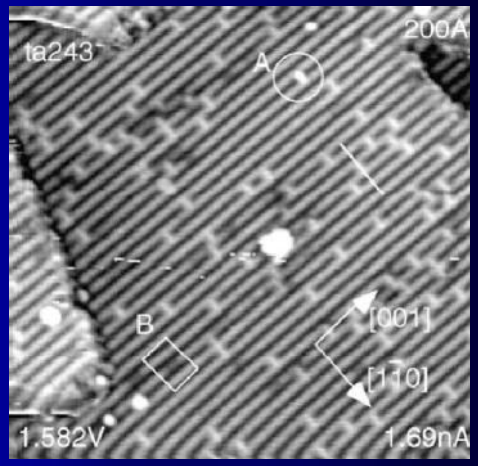
anatase 101 surface

TiO_2: VERY IMPORTANT ROLE OF DEFECTS

COLOR CHANGE IN TiO_2 SAMPLES INDUCED BY INCREASING OXYGEN SUB-STOICHIOMETRY

DEFECTS CHANGE ELECTRONIC AND OPTICAL PROPERTIES OF THE MATERIAL





U. Diebold, Surf. Sci. Reports, 2003, 48, 53

TiO_{2-x}	$Ti_{1+x}O_2$
O VACANCIES	Ti INTERSTITIALS

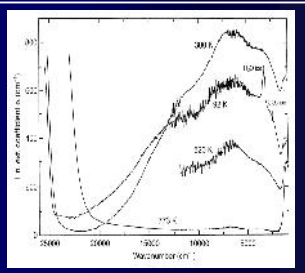
V. Ganduglia-Pirovano et al.
Surf. Sci. Rep. **62**, 219 (2007)

M. A. Henderson Surf. Sci. **419**, 174 (1999)
S. Wendt et al. Science **320**, 1755 (2008)

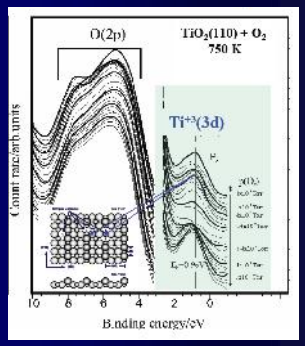
IN REDUCED TITANIA Ti ATOMS ALWAYS EXCEED O ATOMS RESULTING IN THE FORMATION OF Ti^{3+} SPECIES

REDUCED TITANIA: Ti^{3+} SPECIES

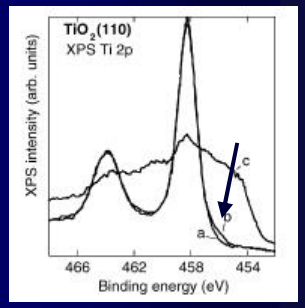
- **UV-vis** — (1) absorption bands in the visible region responsible for the change in color (assigned to d-d transitions)



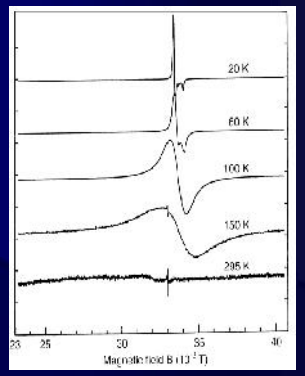
- **UPS/EELS** — (2) occurrence of a new state in the gap at about 0.8-0.9 eV below the conduction band attributed to the reduced Ti^{3+} ions



- **XPS** — (3) shift in the core level binding energies of the reduced Ti atoms from X-ray photoemission



- **EPR** — (4) presence of more than one EPR signal associated to various kinds of paramagnetic Ti^{3+} ions in the lattice

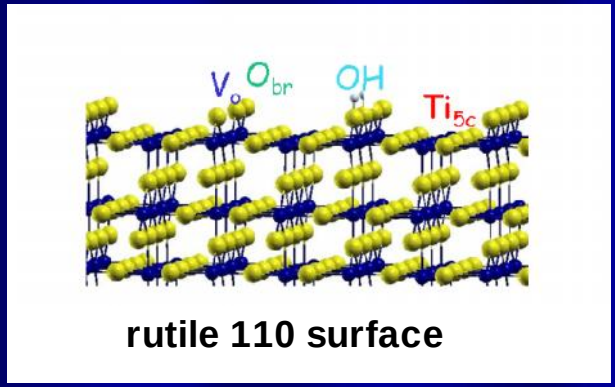


REDUCED TITANIA: Surface Oxygen Vacancy

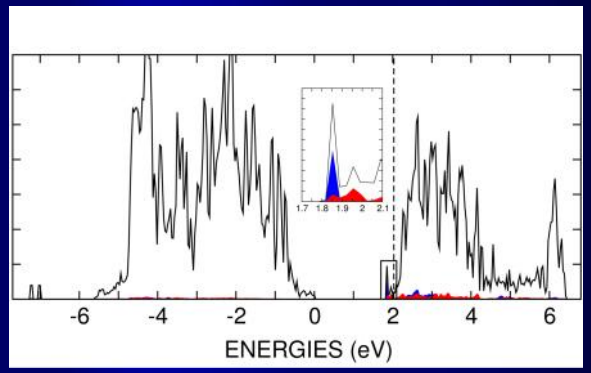
PBE vs B3LYP

RUTILE (110) SURFACE

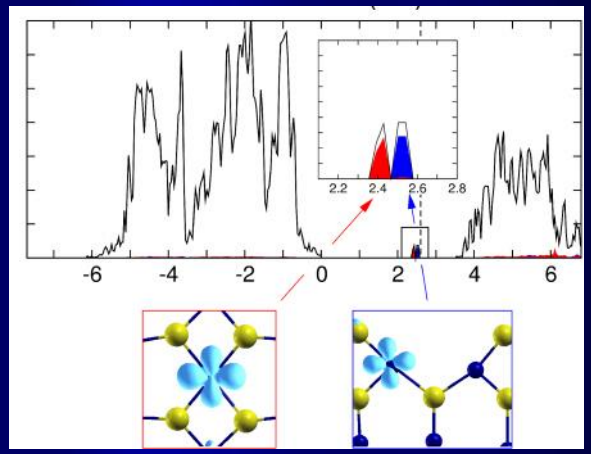
CDV, Pacchioni, Selloni PRL 97 (2006) 166803



rutile 110 surface

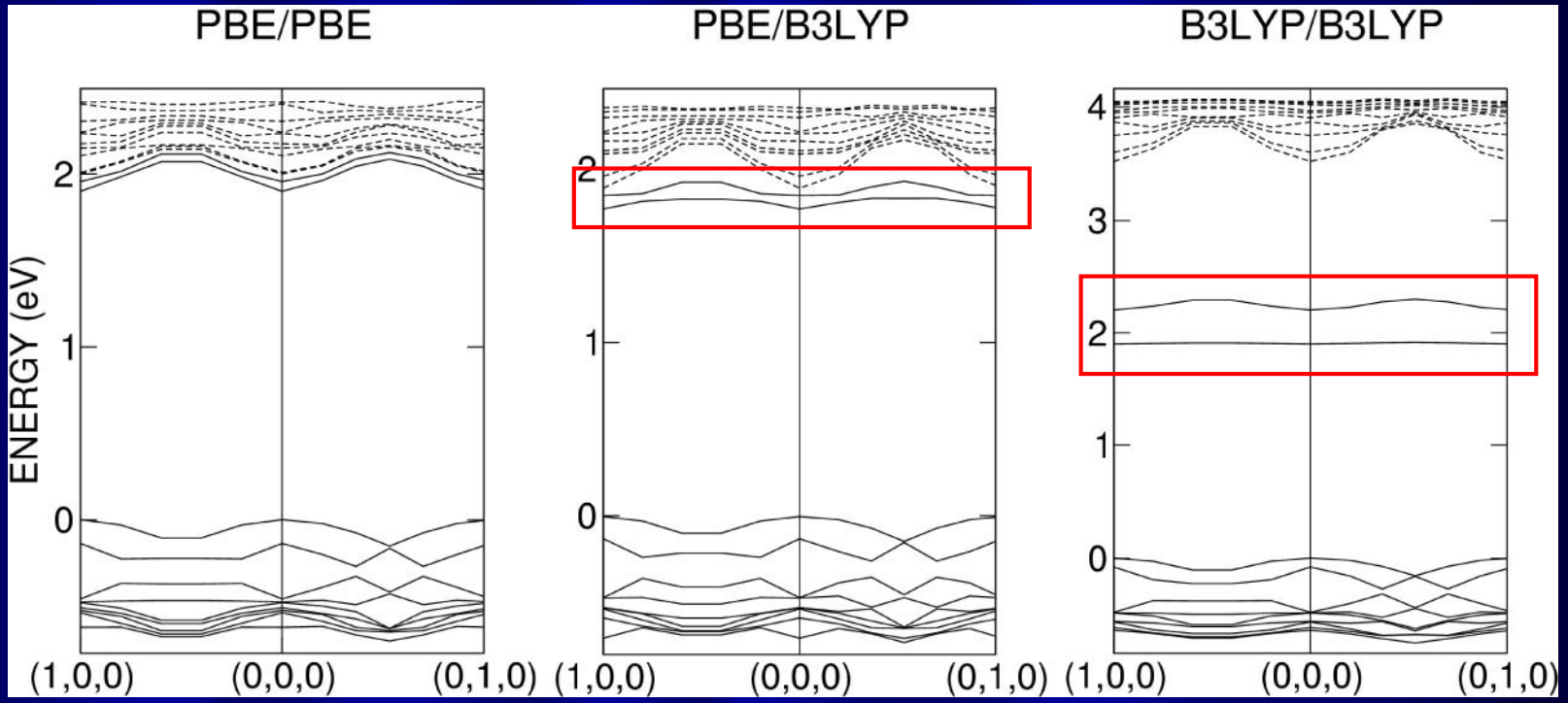


- pure DFT functionals (PBE): band gap underestimated
- O vacancy induced states are at the bottom of conduction band (not 0.8 eV below as in exp.)
- states delocalized, not localized as shown by EPR (Ti^{3+})



POLARONIC NATURE OF OXYGEN VACANCY

OXYGEN DEFICIENT RUTILE (110) SURFACE



PBE ON DISTORTED B3LYP GEOMETRY LEADS TO LOCALIZATION!

PRAGMATIC WAYS TO IMPROVE THE MODEL

Hybrid functionals

Use of hybrid functionals where HF-like exchange is mixed in with the DFT exchange:
B3LYP (20%), H&H LYP (50%)

$$E_{xc}^{B3LYP} = a\,E_x^{LSDA} + (1-a)\,E_x^{HF} + b\,\Delta E_x^{Becke} + (1-c)\,E_c^{LSDA} + c\,E_c^{LYP}$$

Becke J. Chem. Phys. 98, 5648 (1993)

DFT+U methods

Systems where atomic-like features are persistent in the solid:
explicit description of on-site Coulomb interaction
for a few selected localized orbitals
Add a Hubbard-like E_{Hub} term to the standard functional:

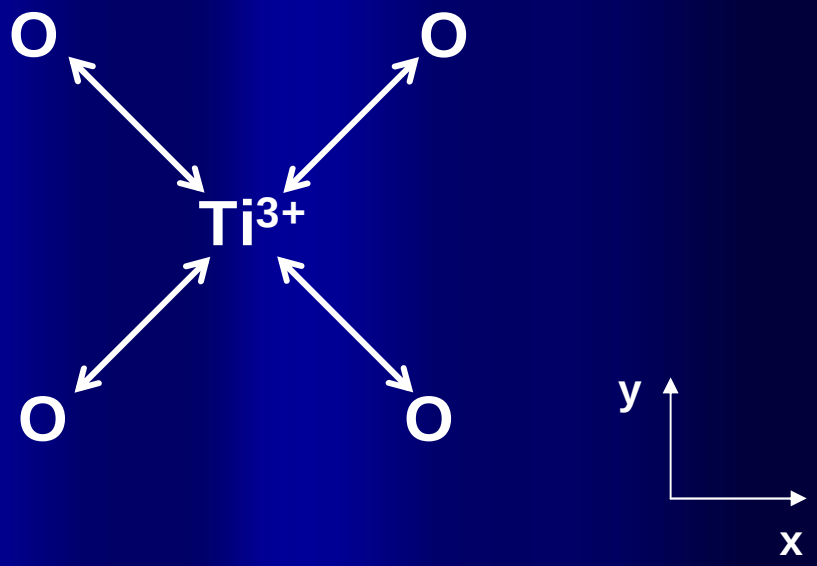
$$E_{LDA+U}[n(r)] = E_{LDA}[n(r)] + E_{HUB}[\{n_m^{l\sigma}\}] - E_{DC}[\{n_m^{l\sigma}\}]$$

Anisimov et al., Phys. Rev. B 44, 943 (1991)

POLARONIC NATURE OF Ti^{3+} CENTERS

B3LYP AND PBE+U

POLARONIC NATURE:
distortion around the defect Ti^{3+}



ELONGATION OF EQUATORIAL Ti-O BONDS OF ABOUT 0.1 - 0.15 Å

DESCRIPTION OF OXYGEN VACANCY IN TiO_2

HYBRID FUNCTIONALS and DFT+U VS STANDARDS GGA METHODS

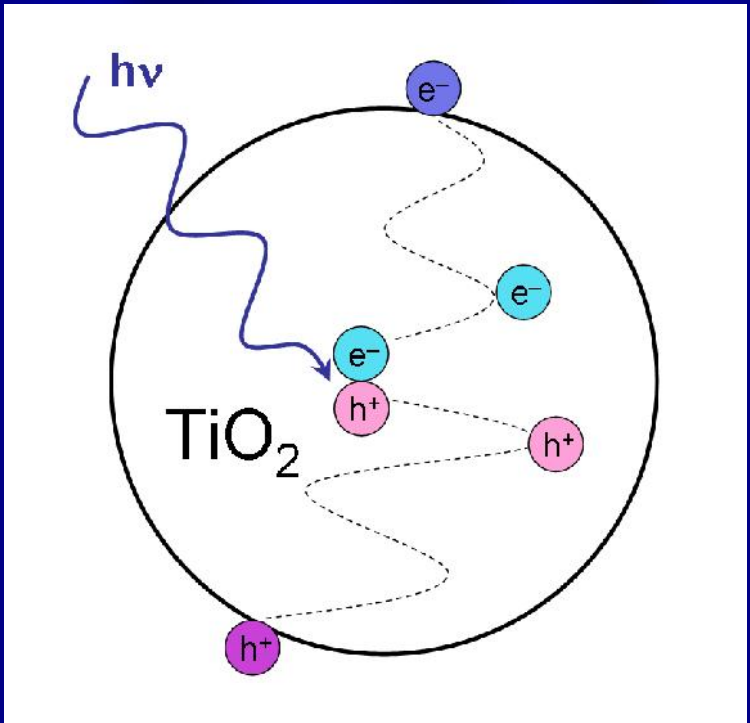
Di Valentin C., Pacchioni G., Selloni A. PRL 97 (2006) 166803

Morgan B. J., Watson G. W. Surf. Sci. 601 (2007) 5034

Calzado C. J., Hernandez N. C., Sanz J. F. PRB 77 (2008) 045118

Mattioli G., Filippone F., Alippi P., Amore Bonapasta A. PRB 78 (2008) 241201

PHOTOEXCITED ANATASE TiO_2



PHOTOGENERATED CHARGES ARE PROBED BY:

- **IR**
- **EPR**
- **PHOTOLUMINESCENCE**
- **O_2 PHOTODESORPTION**

- **PHOTOEXCITATION**
- **BULK EXCITONS**
- **CHARGE CARRIERS SEPARATION**
- **ELECTRON AND HOLE POLARONS TRAPPING IN BULK**
- **MIGRATION TO THE SURFACE**
- **TRAPPING AT CLEAN AND OH SURFACE**

PHOTOEXCITED ANATASE TiO_2

ELECTRONIC GAP

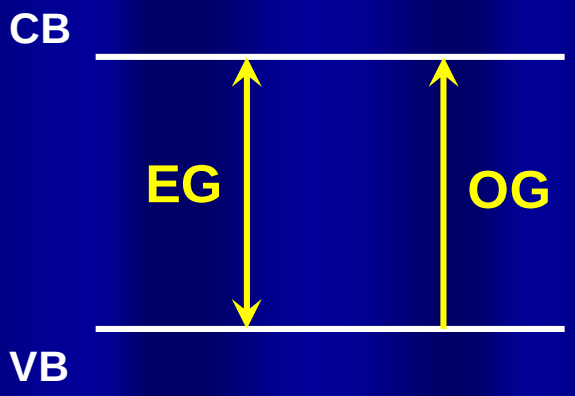
PHOTOEMISSION EXPERIMENTS

DFT or MANY BODY CALCULATIONS

OPTICAL GAP

LIGHT ABSORPTION EXPERIMENTS

TD-DFT or BSE CALCULATIONS INCLUDING EXCITONIC EFFECTS



BUT:

ELECTRON-PHONON COUPLING and SELF_TRAPPING ENERGY (REORGANIZATION ENERGY - LOCAL RELAXATION EFFECTS)

NOT EASELY INCLUDED!

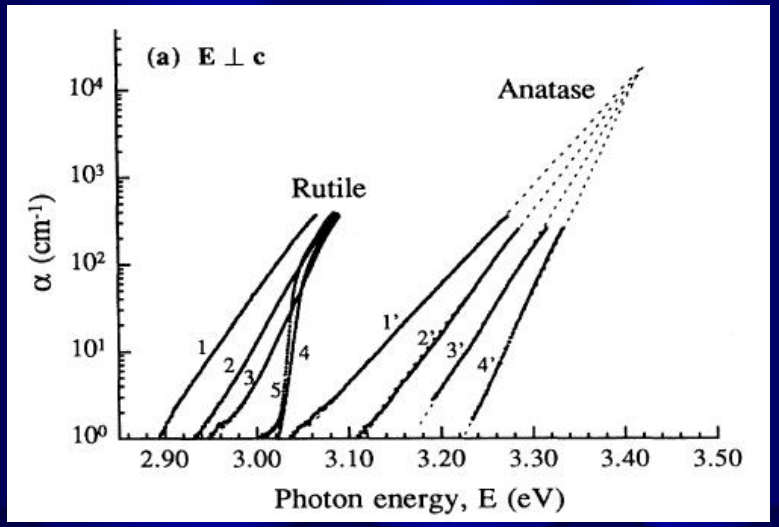
PHOTOEXCITED ANATASE TiO_2: EXCITONS FORMATION

PHYSICAL REVIEW B VOLUME 52, NUMBER 11 15 SEPTEMBER 1995-I

Urbach tail of anatase TiO_2

H. Tang, F. Lévy, H. Berger, and P. E. Schmid
Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
(Received 17 January 1995; revised manuscript received 7 April 1995)

The fundamental absorption edge of the anatase phase of TiO_2 has been studied by performing polarized optical transmission measurements on single crystals at temperatures ranging from 4.2 to 300 K. An Urbach tail has been found that shows an exponential spectral dependence down to liquid-helium temperature. The optical gap of anatase has been estimated to be 3.420 eV in polarization E⊥c, and 3.460 eV in polarization E∥c. Our experimental results can be accounted for in terms of the theory of Toyozawa and co-workers, which ascribes the Urbach tail to the momentary localization of excitons due to phonon interaction. Comparing, in this case, the measured abosrption spectra of anatase and rutile, we conclude that the excitons in anatase are self-trapped while those in rutile are free. This opposite nature of exciton states in anatase and rutile is consistent with the results of previous photoluminescence studies.



URBACH TAIL DEPENDENCE WITH T INDICATES A SELF-TRAPPED EXCITON FOR ANATASE NOT FOR RUTILE

PHOTOEXCITED ANATASE TiO_2: EXCITONS FORMATION

Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Luminescence 112 (2005) 88–91
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Time-resolved study of self-trapped exciton luminescence in anatase TiO_2 under two-photon excitation

M. Watanabe*, T. Hayashi

Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

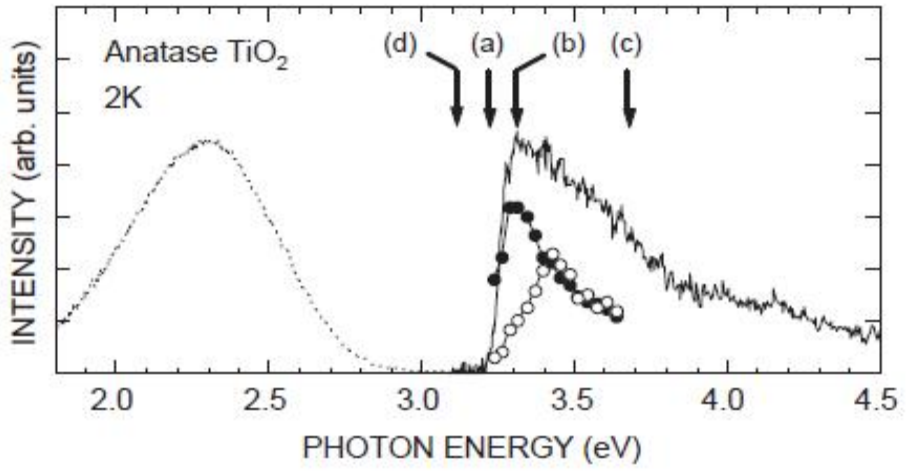


Fig. 1. Luminescence (dotted line) and excitation (solid line) spectra of anatase TiO_2.

LUMINESCENCE BAND ASSIGNED TO RADIATIVE RECOMBINATION OF SELF-TRAPPED EXCITONS (STES).

PHOTOEXCITED ANATASE TiO_2

GROUND STATE: SINGLET GROUND STATE

EXCITED STATE: TRIPLET GROUND STATE

THESE ARE CORRECTLY DESCRIBED BY DFT WHICH IS A GROUND STATE THEORY

SINGLE POINT CALCULATION

↓

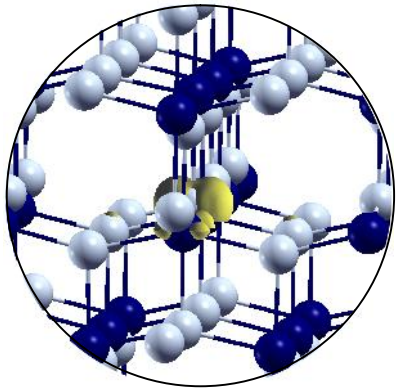
STRUCTURAL RELAXATION: SELF TRAPPING { **POLARONIC DISTORTION**, **SELF TRAPPING ENERGY**

CDV, Selloni JPC Lett. 2 (2011) 2223

EXCITONS AND POLARONS IN BULK ANATASE TiO_2

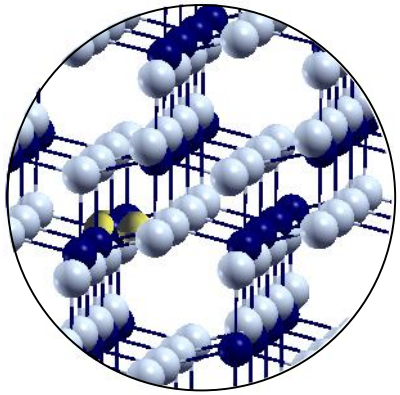
e^-----h^+ pair

Ti_{6c}^{3+}----O_{3c}^-



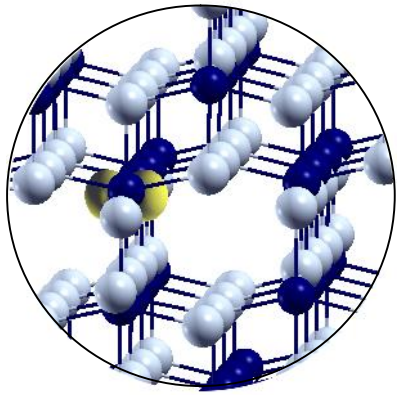
e^-

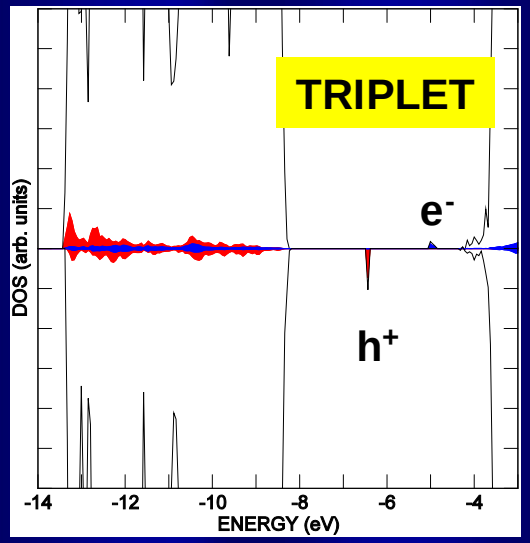
Ti_{6c}^{3+}

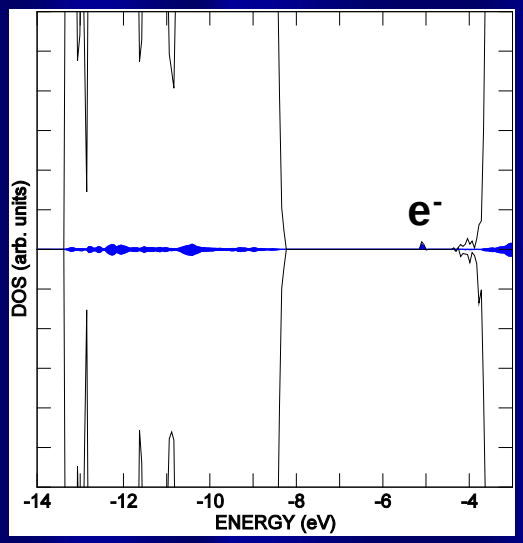


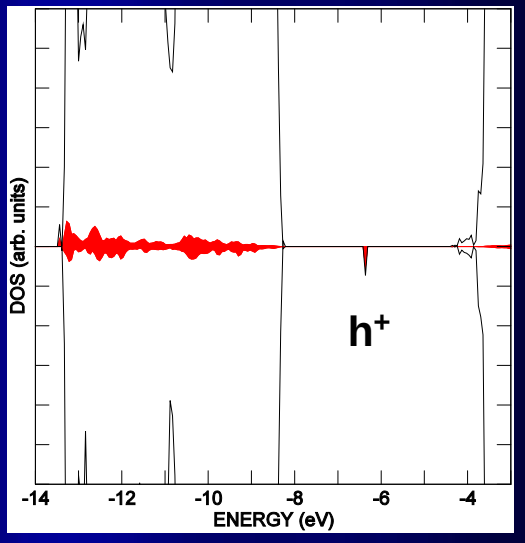
h^+

O_{3c}^-

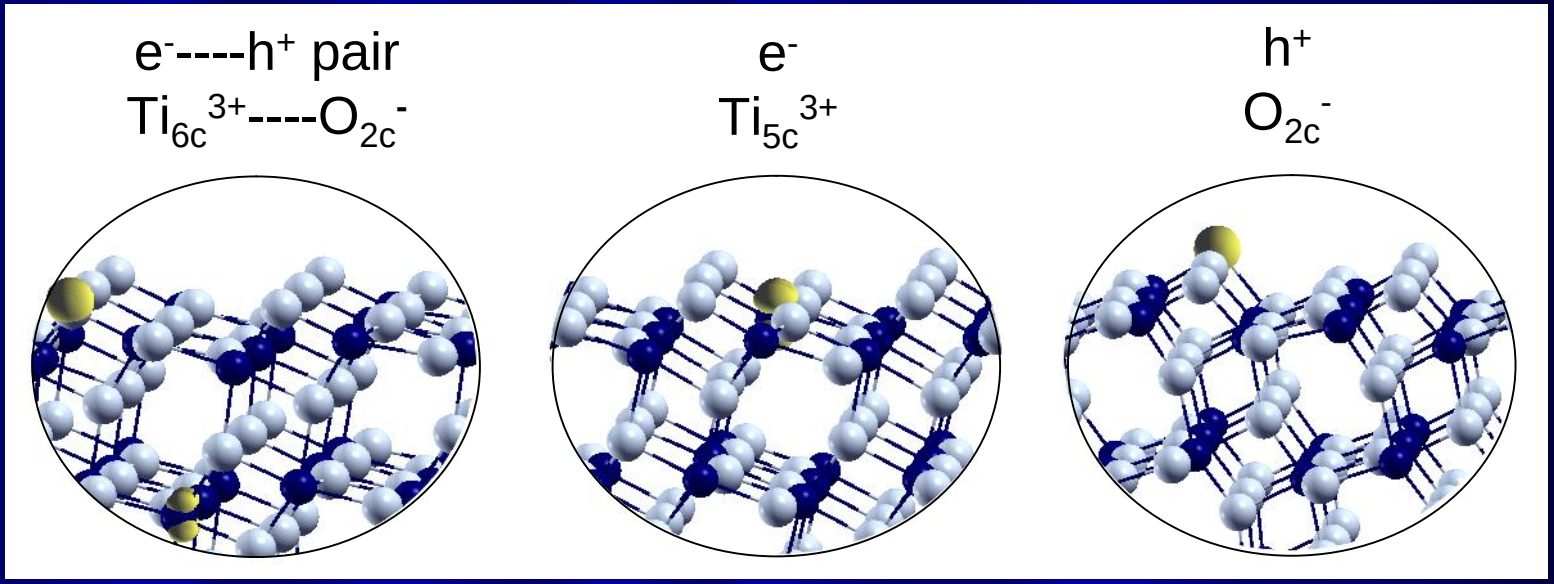


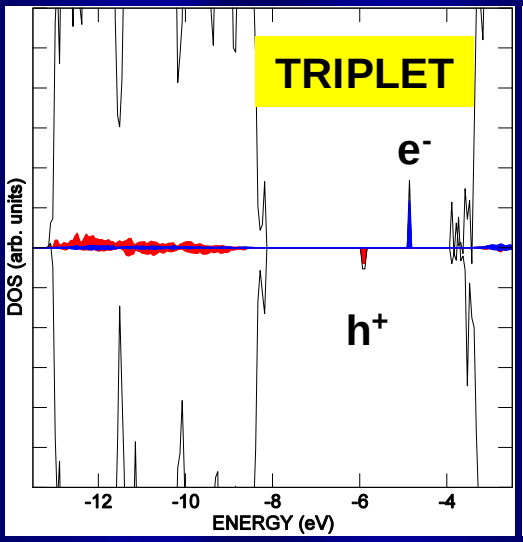


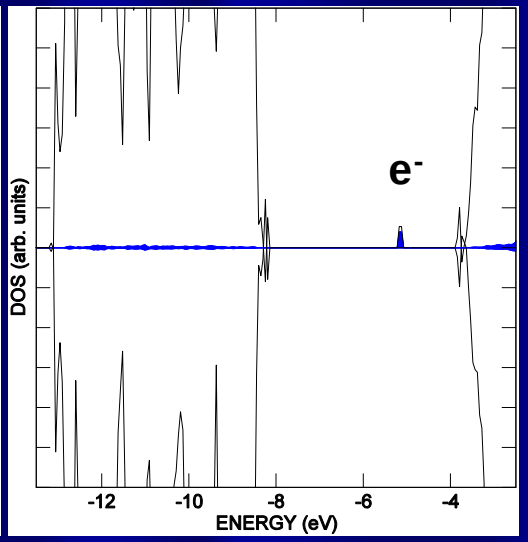


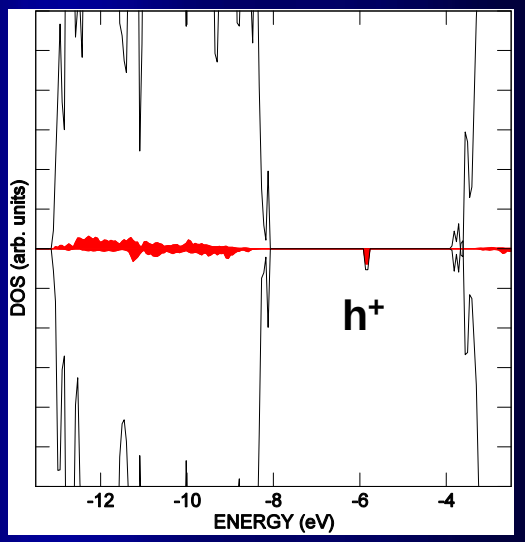


EXCITONS AND POLARONS ON ANATASE TiO_2 (101) SURFACE

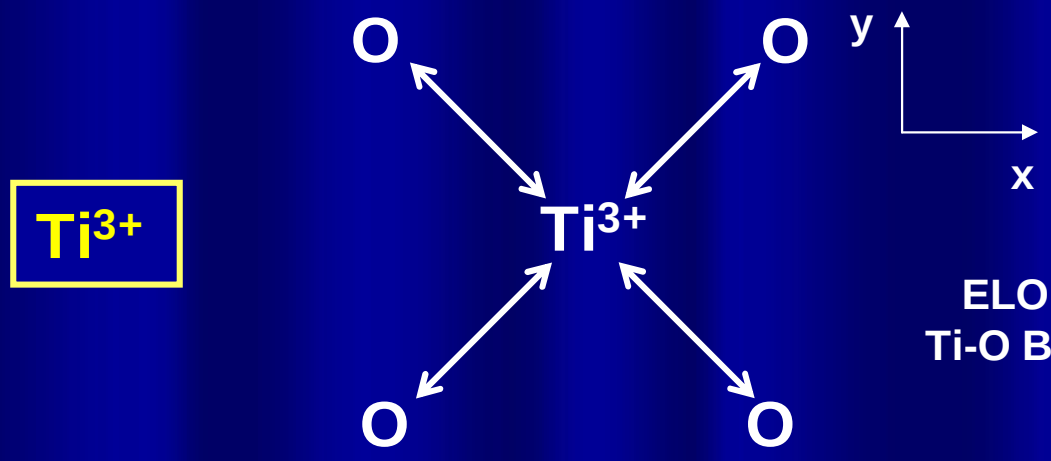








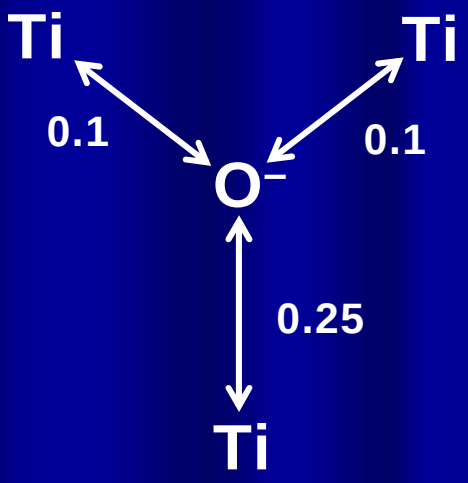
POLARONIC DISTORSION

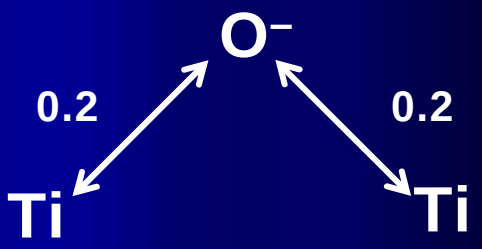


Ti^{3+}

ELONGATION OF EQUATORIAL Ti-O BONDS OF ABOUT 0.1 - 0.15 Å

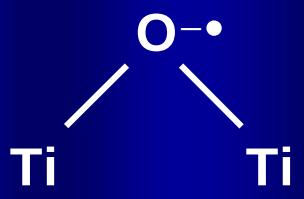
O^{-}



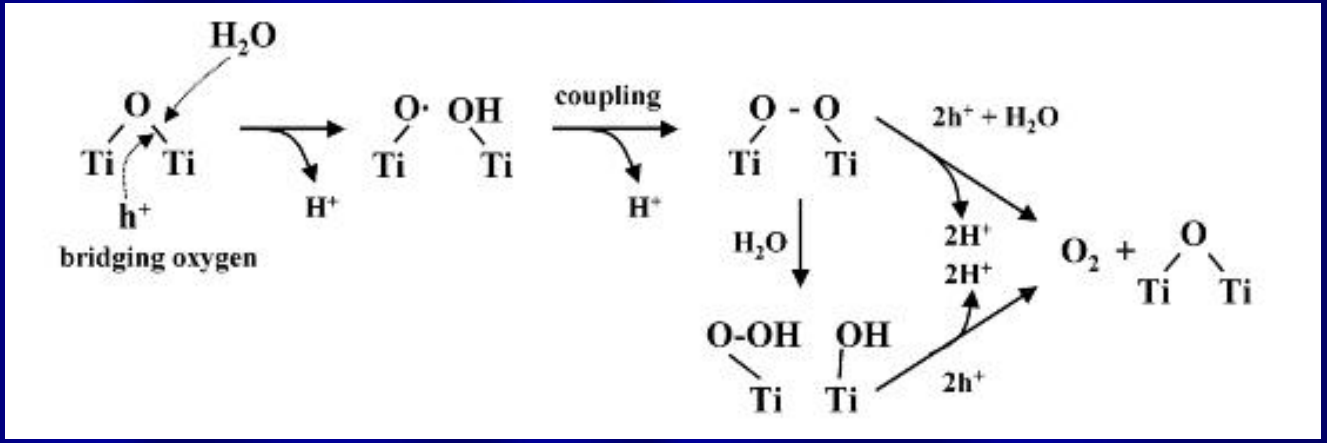


HOLE TRAPPING: DIRECT OR INDIRECT MECHANISM?

DIRECT



INDIRECT

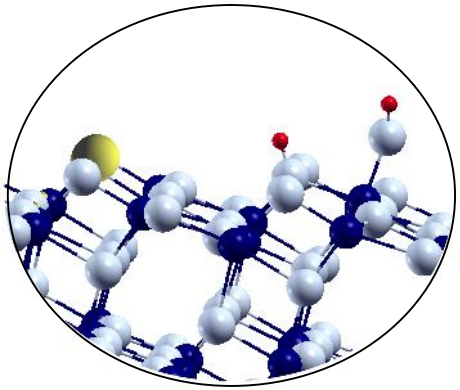


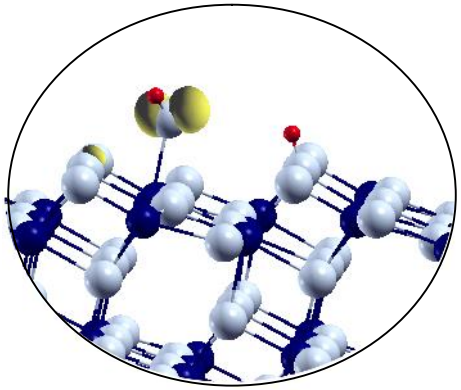
R. Nakamura, Y. Nakato JACS 2004 126 1290

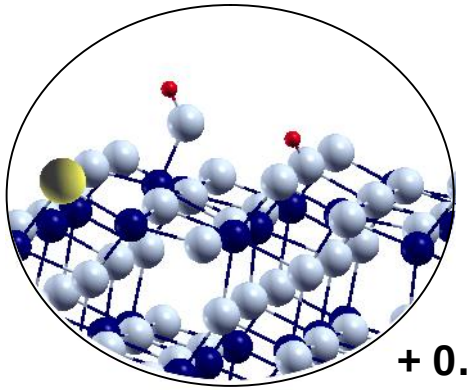
HOLE POLARONS ON ANATASE TiO_2 (101) OH SURFACE

h^+
INTRAPAIR OHs

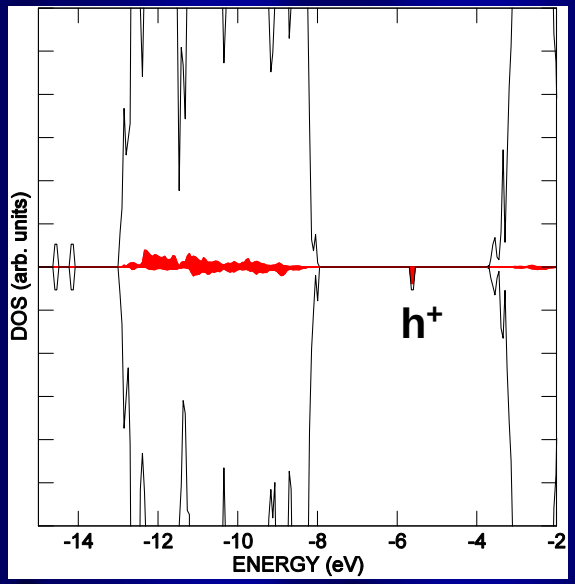
h^+
SPLITPAIR OHs

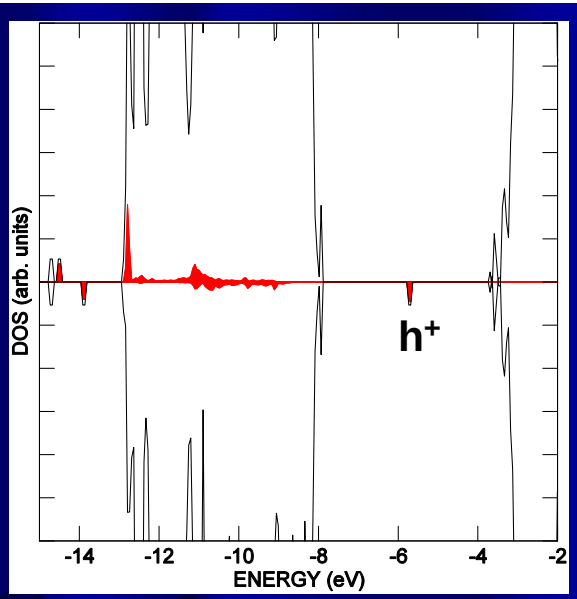


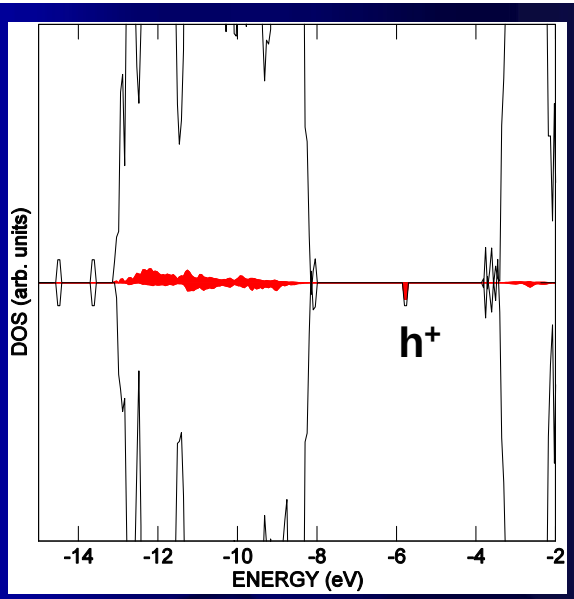




+ 0.2 eV

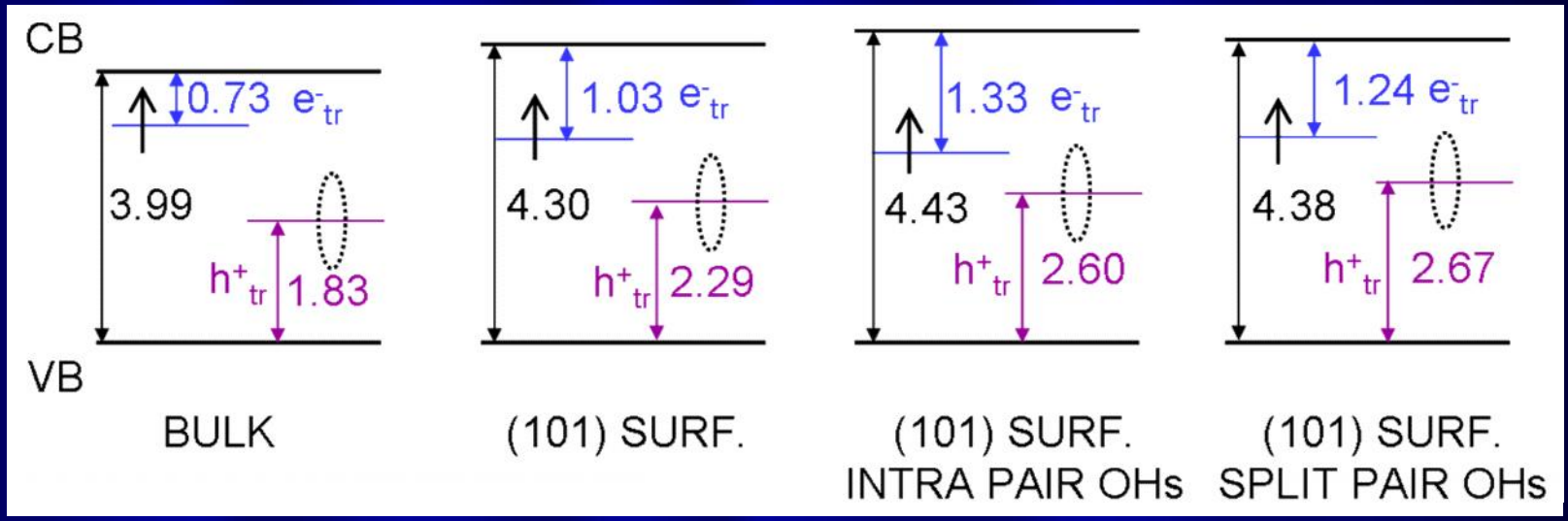






EXCITONS AND POLARONS IN ANATASE TiO_2

ONE-ELECTRON KOHN-SHAM EIGENSTATES



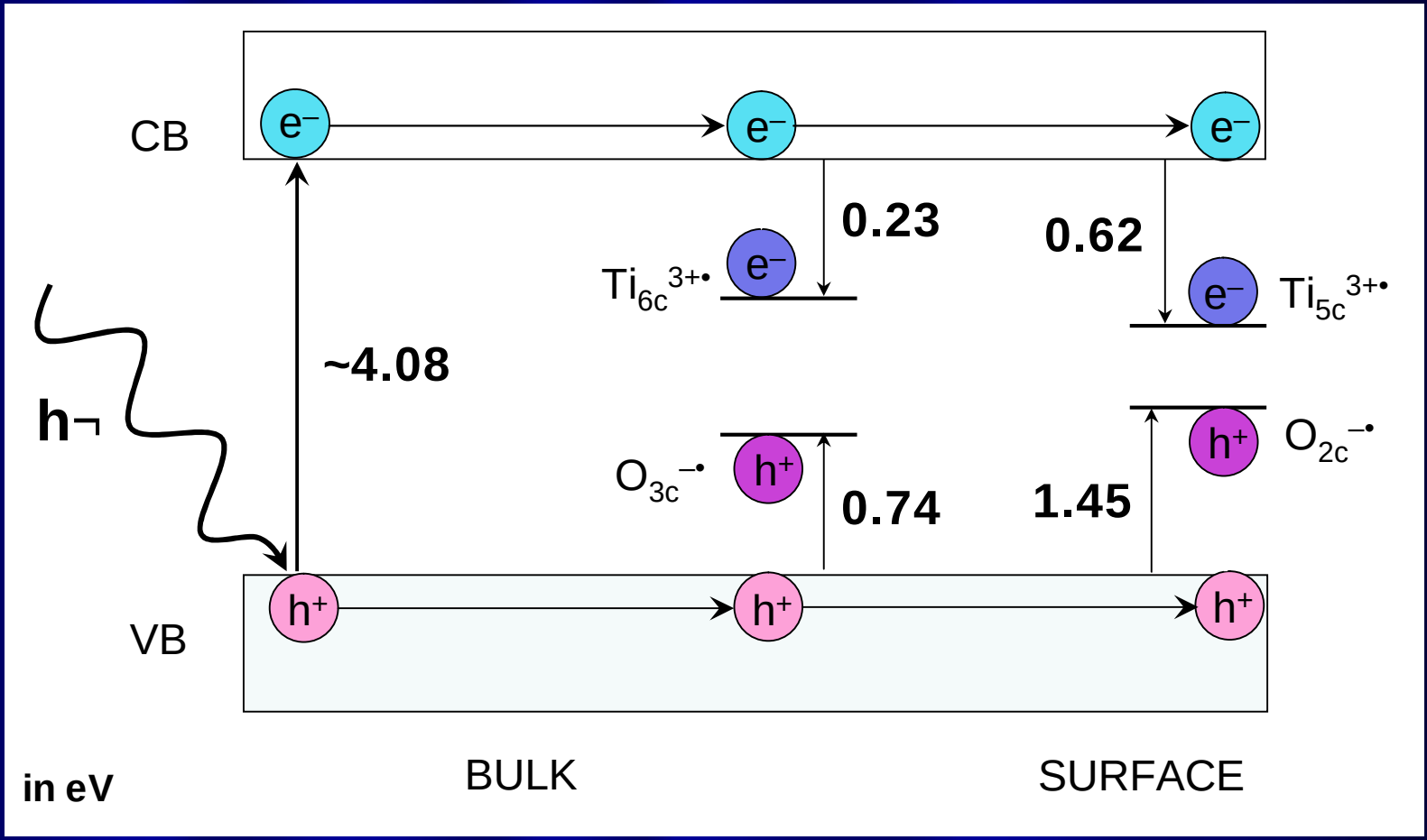
TRIPLET STATES

Electron associated (Ti^{3+}) state similar to ground state (n-type TiO_2) Ti^{3+} species
Hole associated (O^-) state much lower than for ground state (p-type TiO_2) N species: 2.7 eV!

in line with lower photooxidation properties of N-doped TiO_2

EXCITONS AND POLARONS IN ANATASE TiO_2

TOTAL ENERGY DIFFERENCES



DRIVING FORCE TO TRAVEL FROM BULK TO SURFACE

EXP. HOLE OXIDATION POTENTIALS ARE REDUCED OF 1.3-1.4 V UPON TRAPPING

CDV, Selloni JPC Lett. 2 (2011) 2223

TRAPPED ELECTRONS IN TiO_2

SCIENTIFIC REPORTS

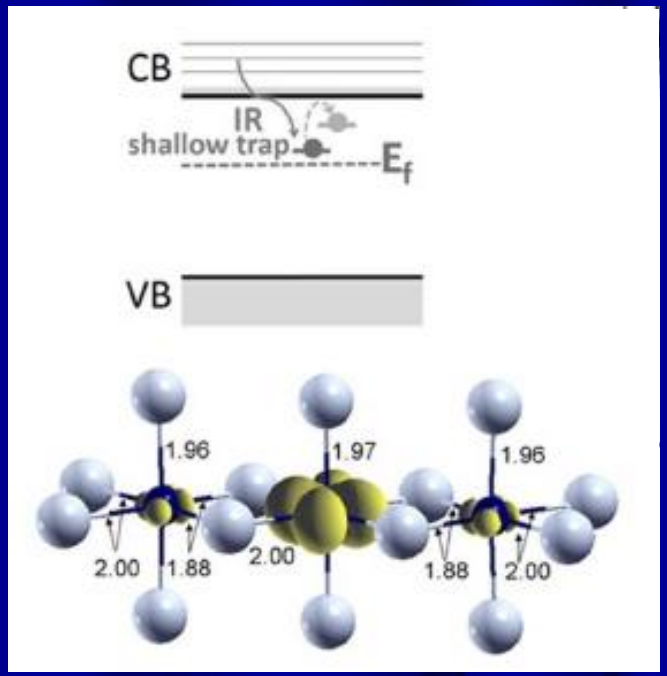
OPEN

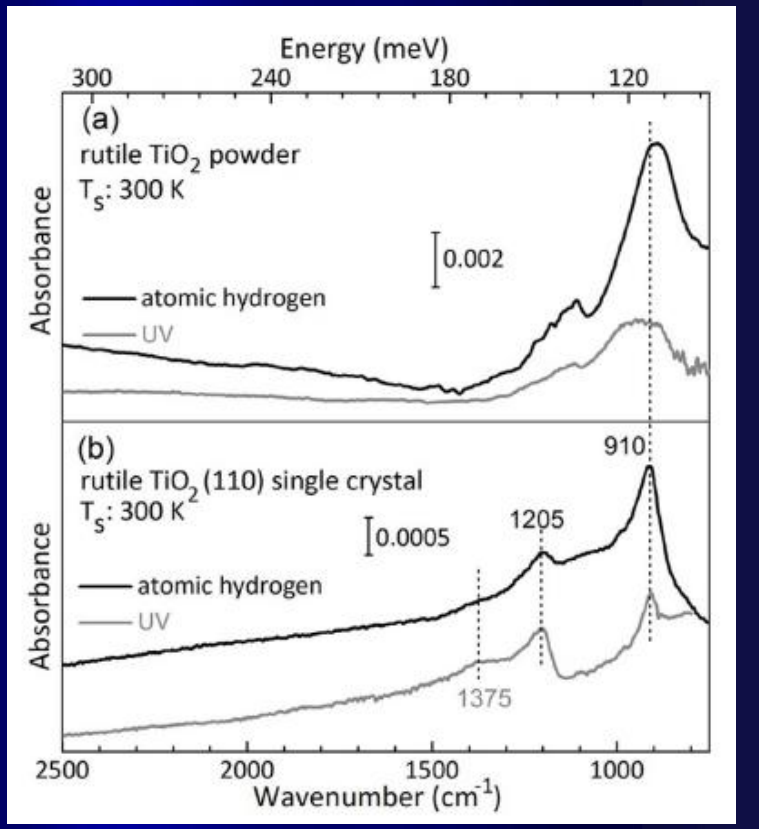
SUBJECT AREAS:
PHOTOCATALYSIS
ELECTRONIC STRUCTURE

Received
4 November 2013

Probing electrons in TiO_2 polaronic trap states by IR-absorption: Evidence for the existence of hydrogenic states

Hikmet Sezen[1], Maria Buchholz[1], Alexei Nefedov[1], Carsten Natzeck[1], Stefan Heissler[1], Cristiana Di Valentin[2] & Christof Wöll[1]





E_{STe} = 380 meV

Total energy difference between free CB e^- and self-trapped e^-

In collaboration with C. Wöll KIT
Scientific Reports 4 (2014) 3808

TRAPPED HOLES IN ANATASE TiO_2

EPR MEASUREMENTS: ^{17}O HYPERFINE COUPLING CONSTANTS

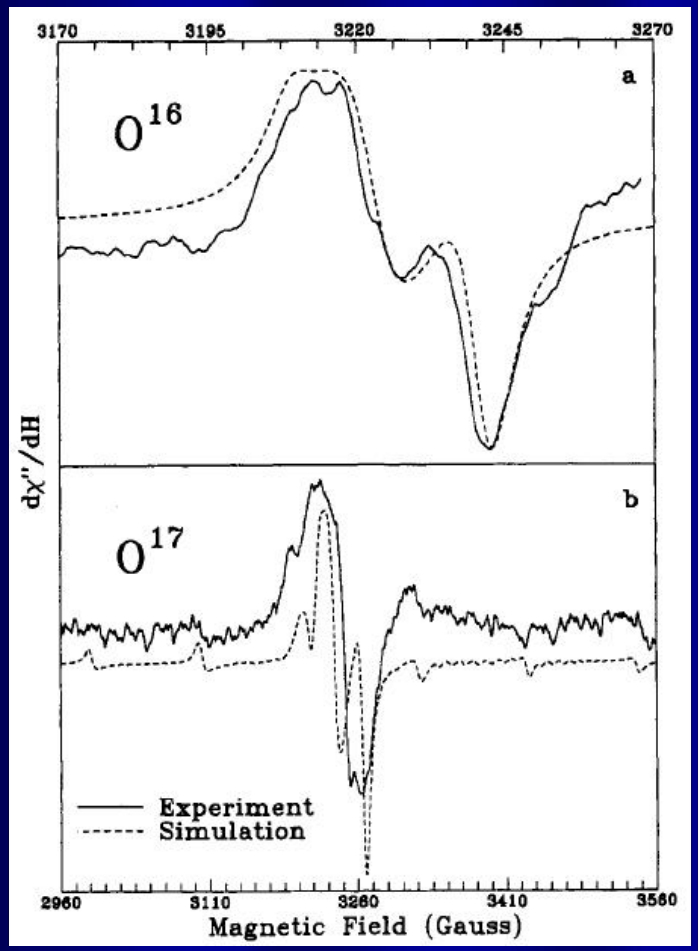


TABLE II: EPR Parameters of Trapped $O^{\bullet-}$ in Various Systems

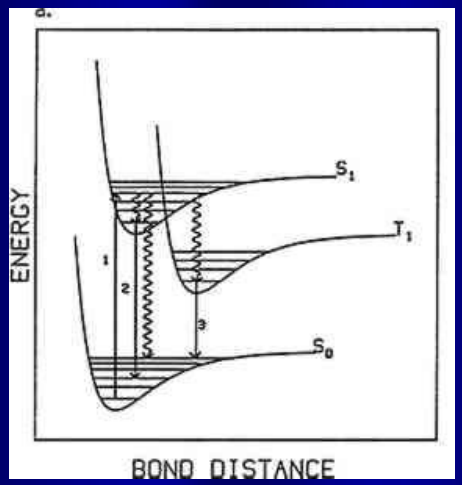
system (T, K)	g-tensor[a] g_z	g_y	g_x	^{17}O hyperfine coupling[b] A_z	A_y	A_x
TiO_2/H_2O colloids (8)[c]	2.0073	2.0188	2.0273			
TiO_2/H_2O with ^{17}O[c]	2.0073	2.0188	2.0273	104	19	19
$NaOH/H_2O$ (77)[d]	2.002	2.07	2.07	99		
MgO (77)[e]	2.002	2.042	2.042	103.5	19.5	19.5
BeO (1.5)[f]	2.0026	2.0149	2.0149			
ZnO (77)[g]	2.0026	2.021	2.021			

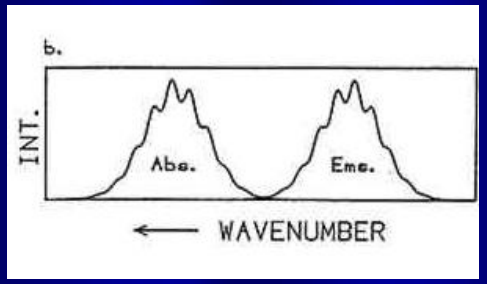
Micic et al. JPC 97 (1993) 7277

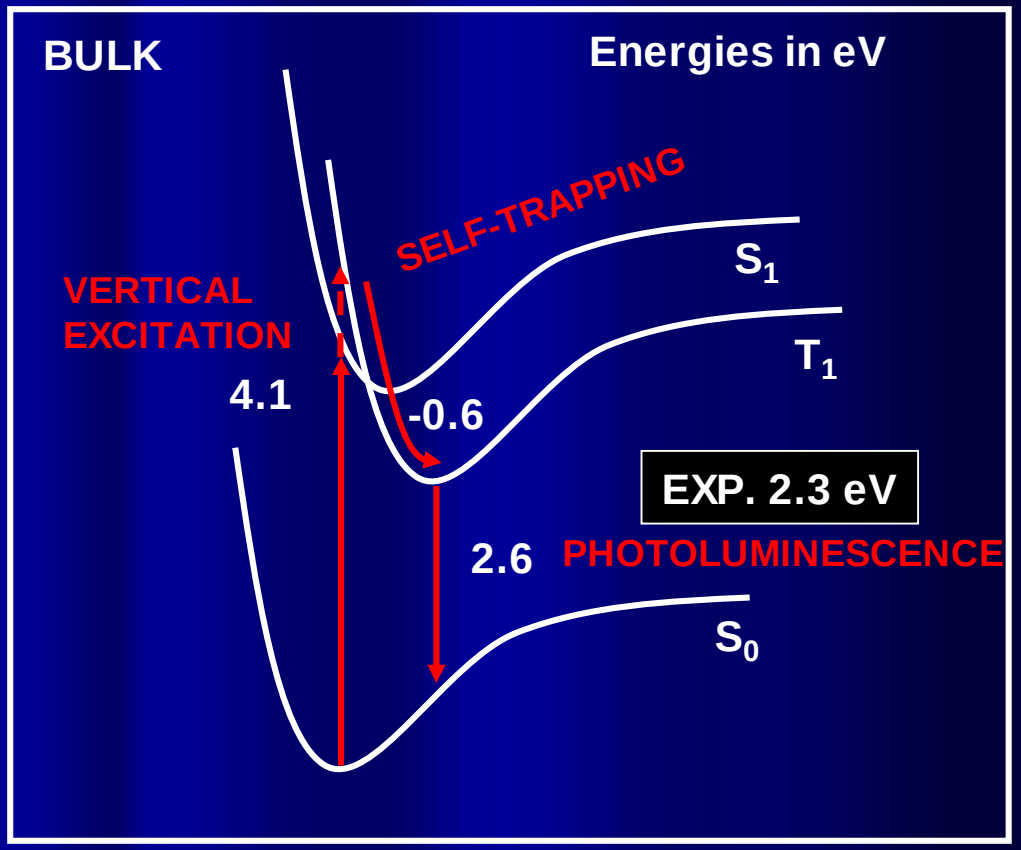
O_{2c}^-	a_{iso}	B_x	B_y	B_z
EXP.	-22	41	41	-82
B3LYP	-37	45	45	-90

DEGREE OF LOCALIZATION BY B3LYP IN EXCELLENT AGREEMENT WITH EPR DATA

SCHEMATIC REPRESENTATION OF BULK ANATASE TiO_2 SPECTROSCOPY

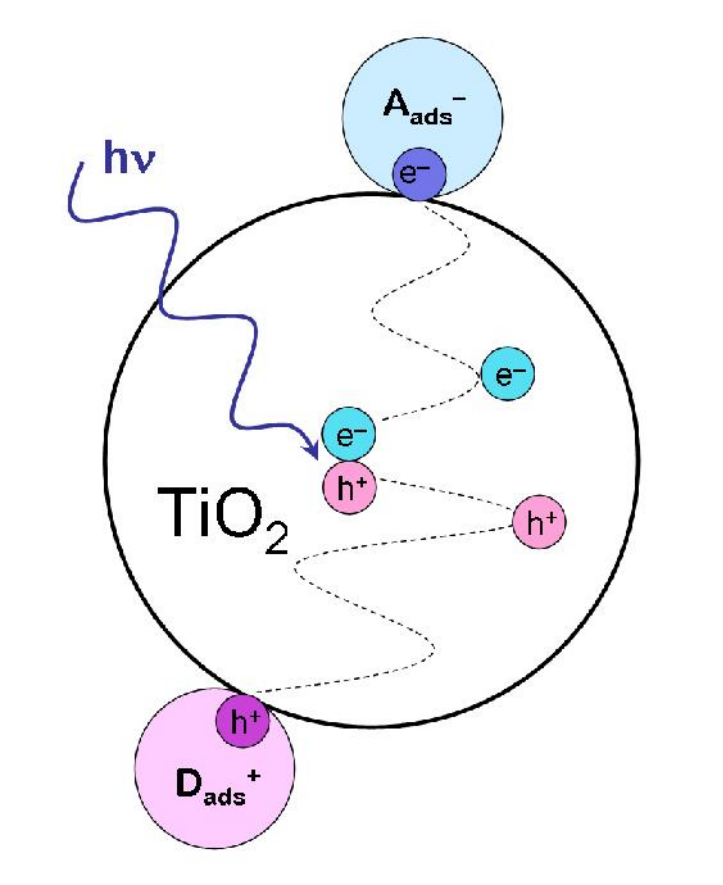






Ongoing collaboration with Claudia Draxl (Berlin) for comparison with BSE calculations including excitonic effects but no ionic relaxation

PHOTOREDUCTION AND PHOTOOXIDATION AT TiO_2 SURFACE



ELECTRON SCAVENGER

O_2

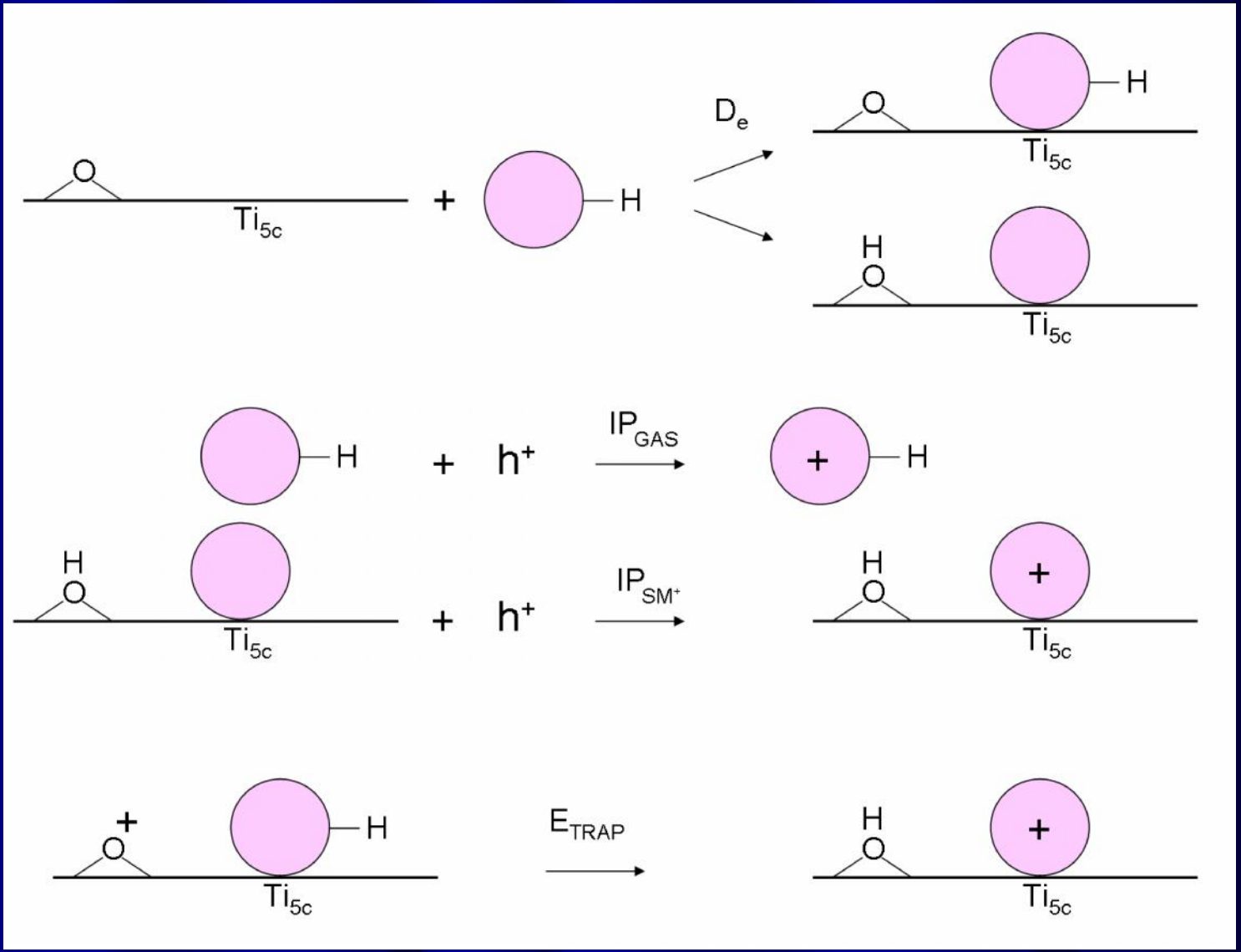
HOLE SCAVENGERS

ORGANIC ACIDS AND ALCOHOLS

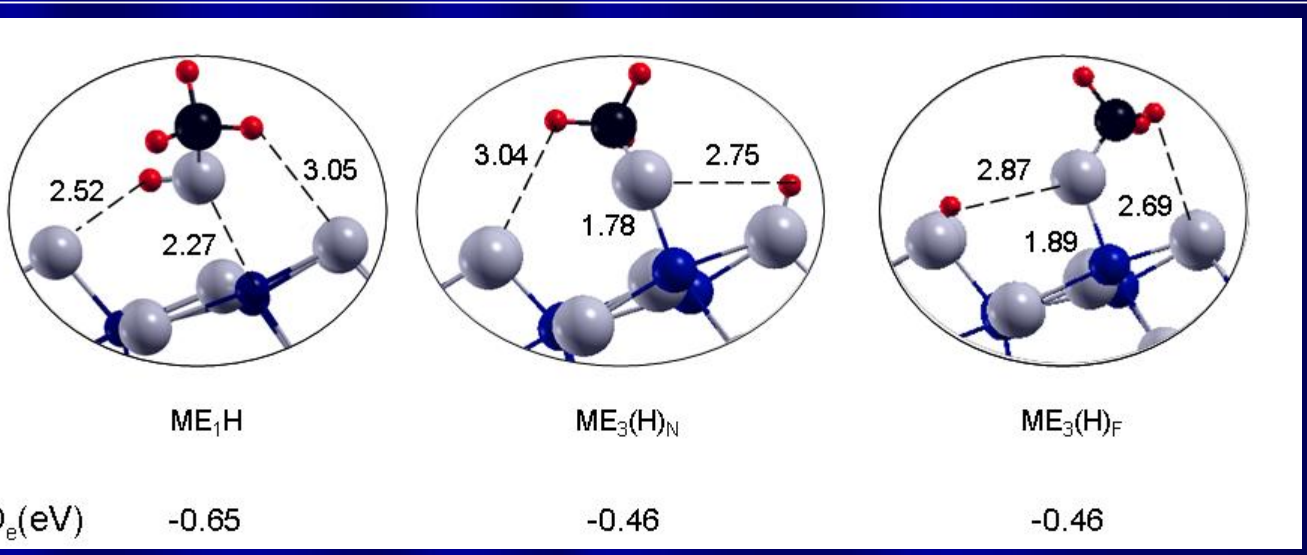
FORMIC ACID – METHANOL – ISOPROPANOL
TERT-BUTANOL – GLYCEROL – CATECHOL

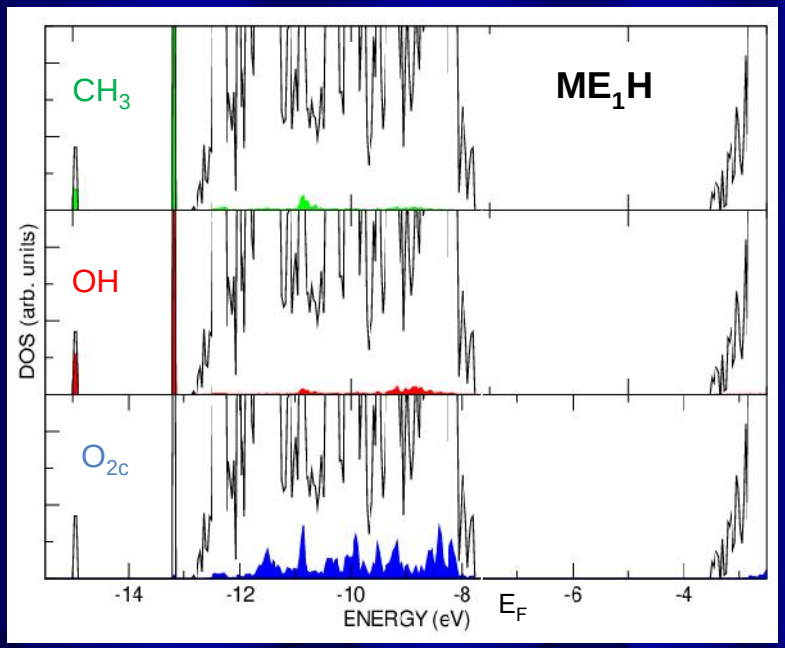
CDV and D. Fittipaldi JPC Lett. 4 (2013) 1901

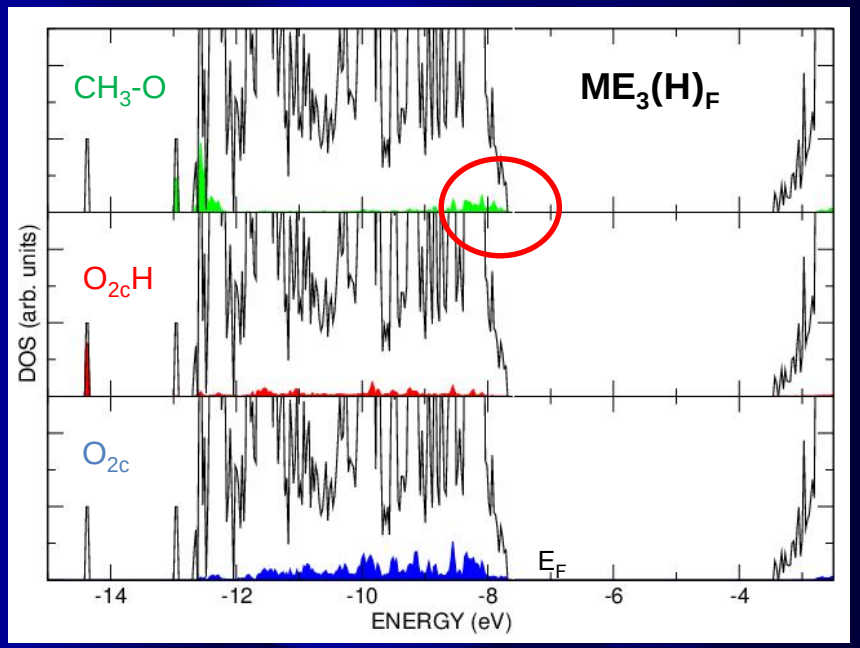
DEFINITIONS



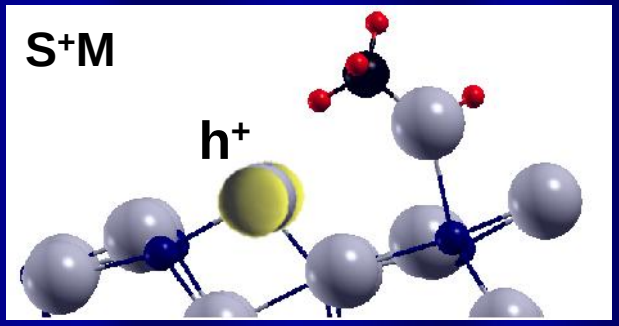
METHANOL: UNDISSOCIATED VS DISSOCIATED ADSORPTION MODES





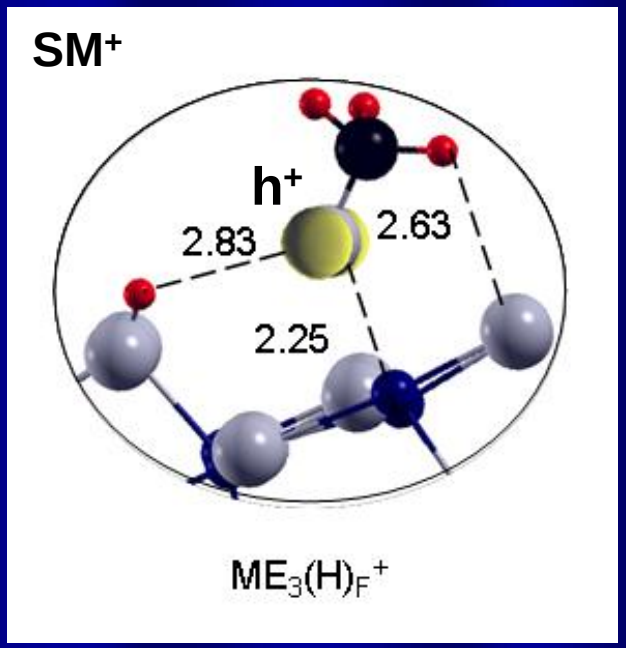


METHANOL: HOLE TRAPPING



$$S^+M \rightarrow SM^+$$

$$E_{TRAP} = E_{SM^+} - E_{S^+M}$$



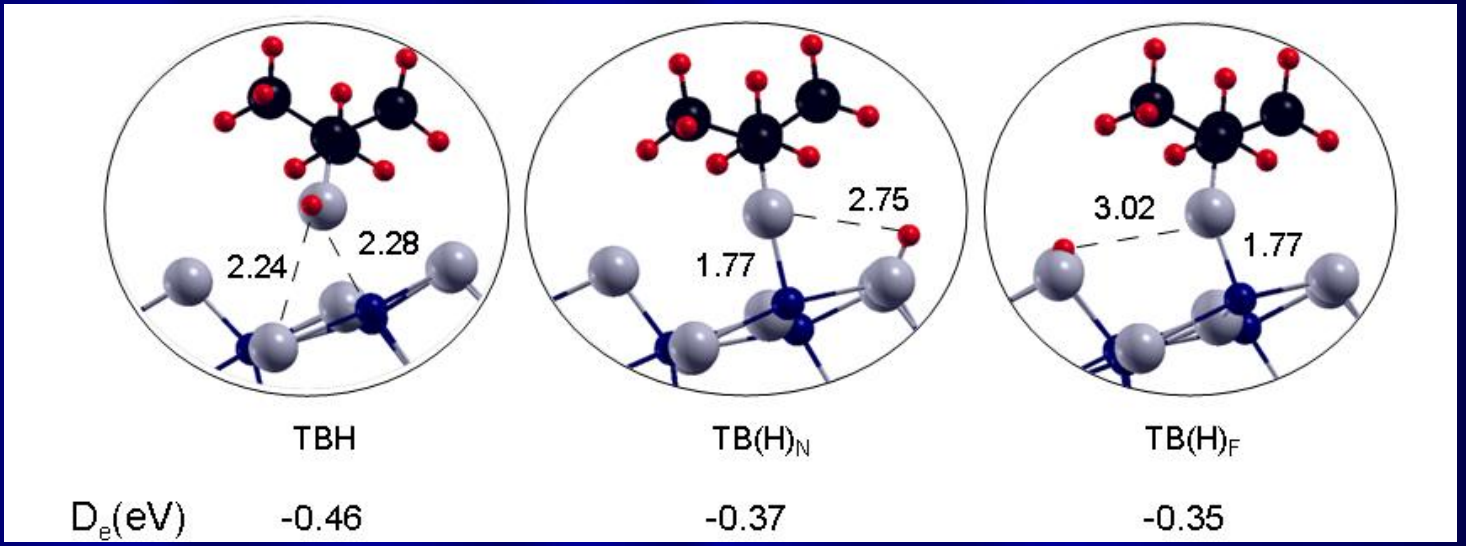
IP_{GAS}	10.6 eV
$IP_{ME_3(H)_F^+}$	6.2 eV
E_{TRAP}	-0.65 eV

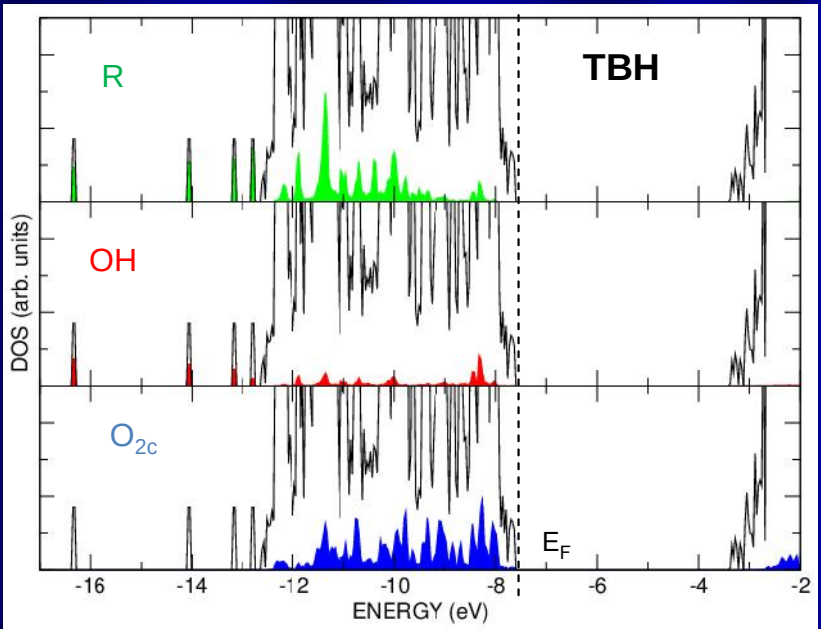
$$-0.52 \text{ eV} < E_{TRAP} < -0.65 \text{ eV}$$

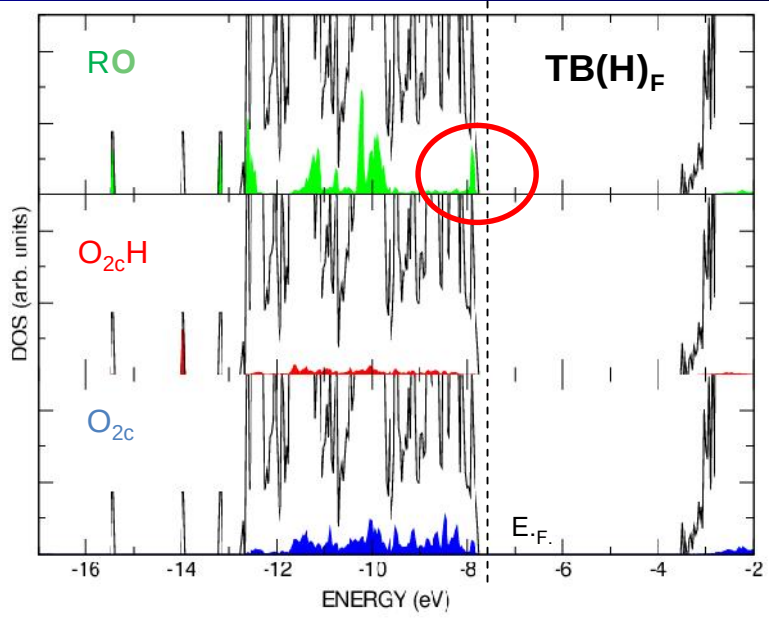
M. Shen, M. A. Henderson JPC Lett. 2011 2 2707:
adsorbed methoxy and not molecularly adsorbed methanol is
the reactive species for hole-mediated oxidation of methanol on TiO_2 (110)

PHOTOINDUCED PROTON DISSOCIATION
COUPLED PROTON AND HOLE TRANSFERS

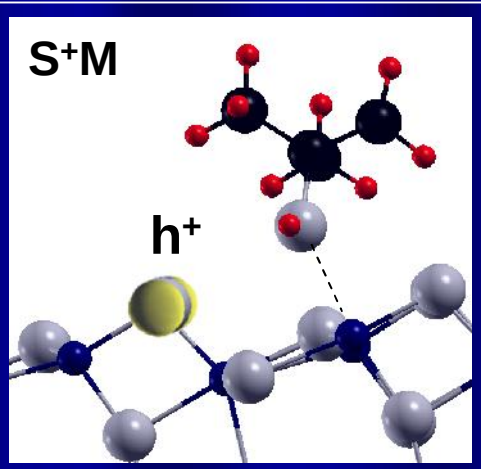
TERT-BUTANOL: UNDISSOCIATED VS DISSOCIATED ADSORPTION MODES





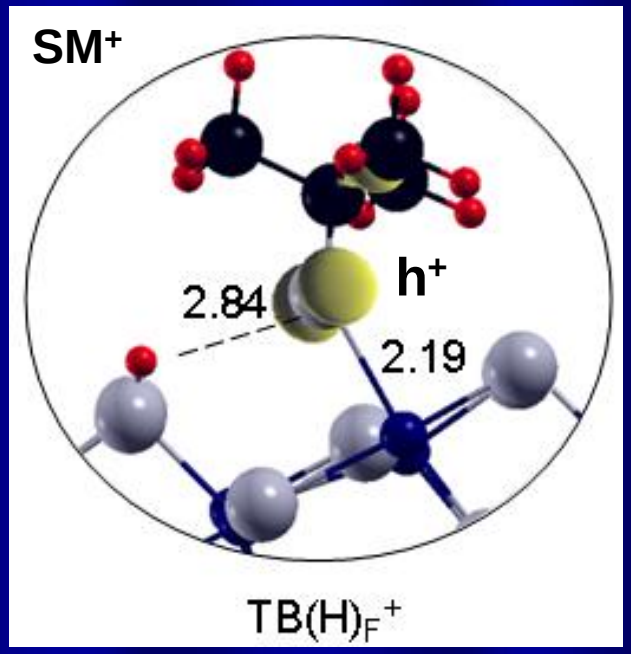


TERT-BUTANOL: HOLE TRAPPING



$$S^+M \rightarrow SM^+$$

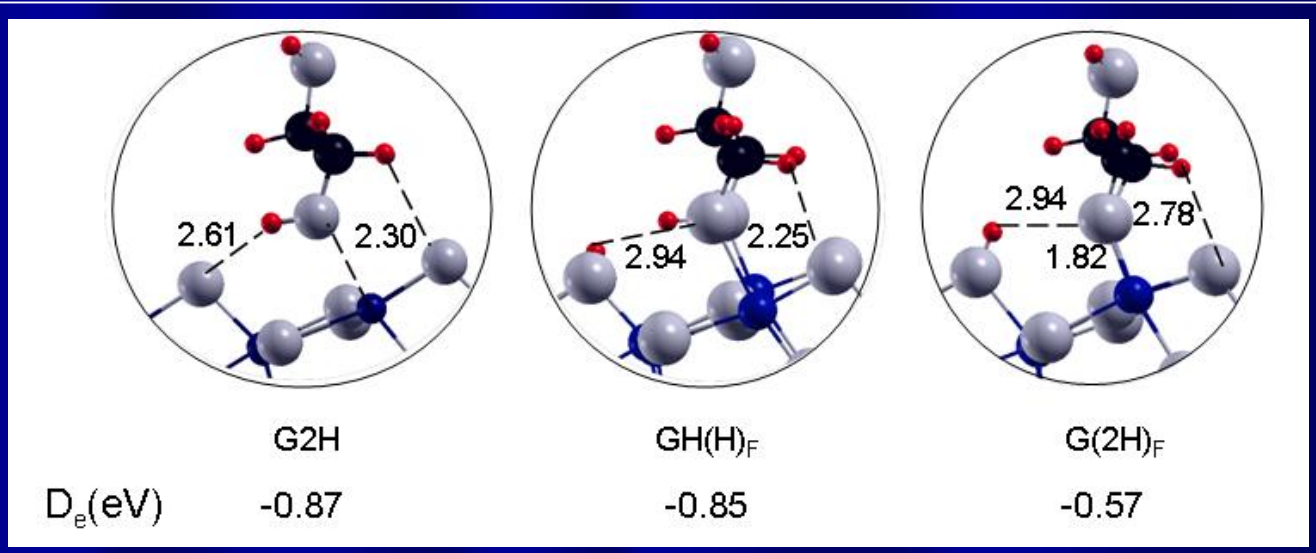
$$E_{TRAP} = E_{SM^+} - E_{S^+M}$$

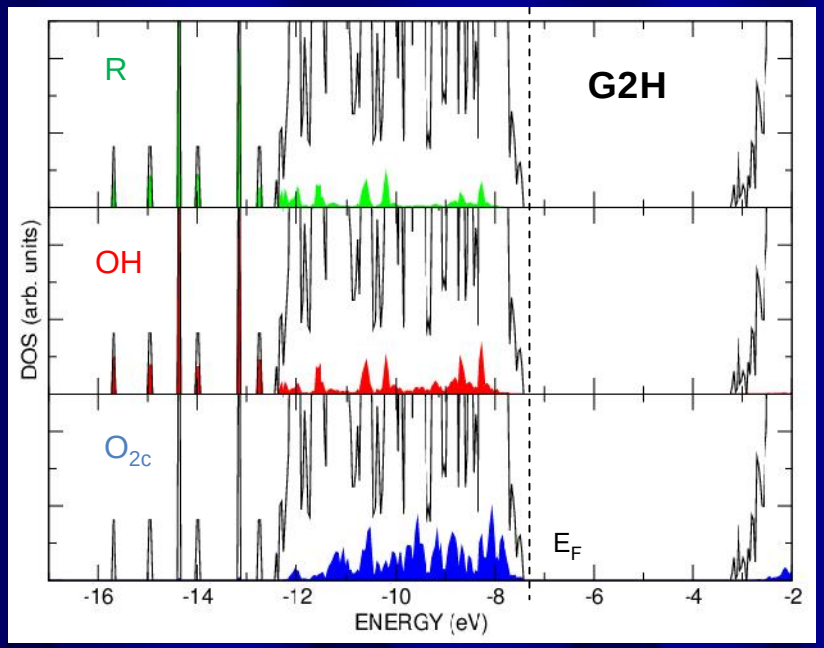


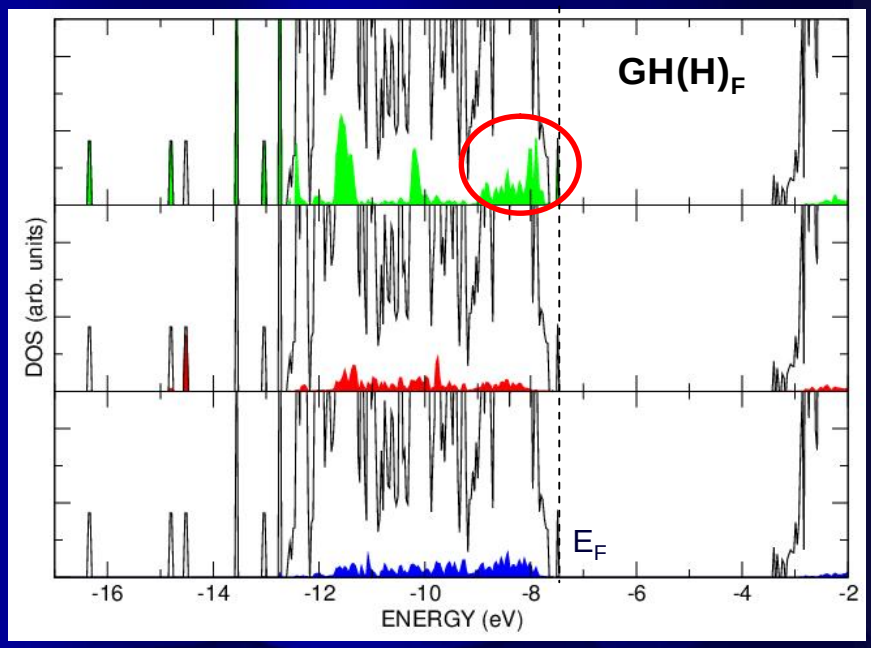
IP_{GAS}	9.4 eV
$IP_{TB(H)_F^+}$	6.0 eV
E_{TRAP}	-0.64 eV

$$-0.56\ eV < E_{TRAP} < -0.64\ eV$$

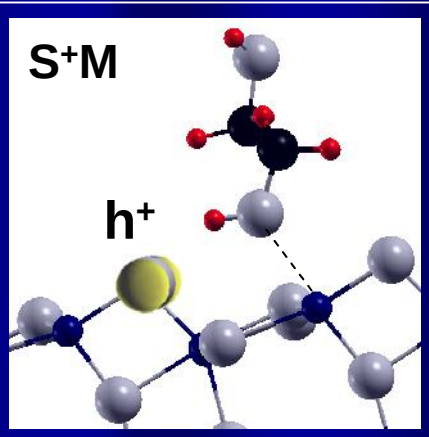
GLYCEROL: UNDISSOCIATED VS DISSOCIATED ADSORPTION MODES





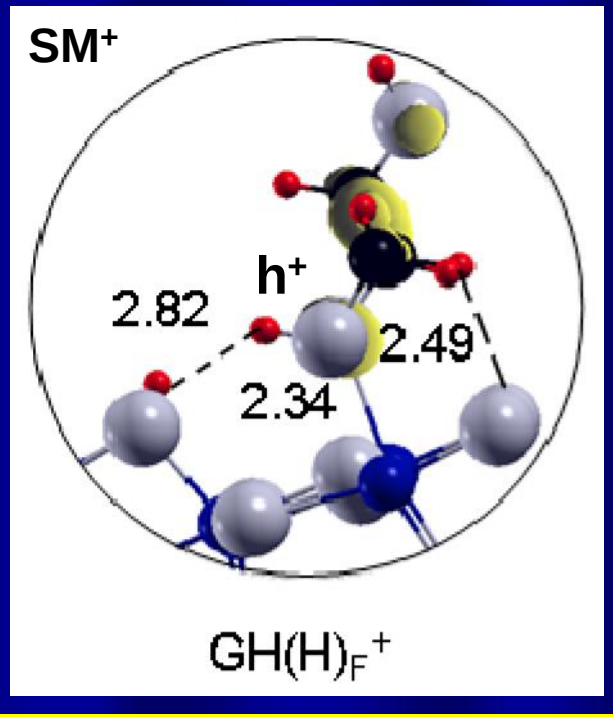


GLYCEROL: HOLE TRAPPING



$S^+M \rightarrow SM^+$

$E_{TRAP} = E_{SM^+} - E_{S^+M}$

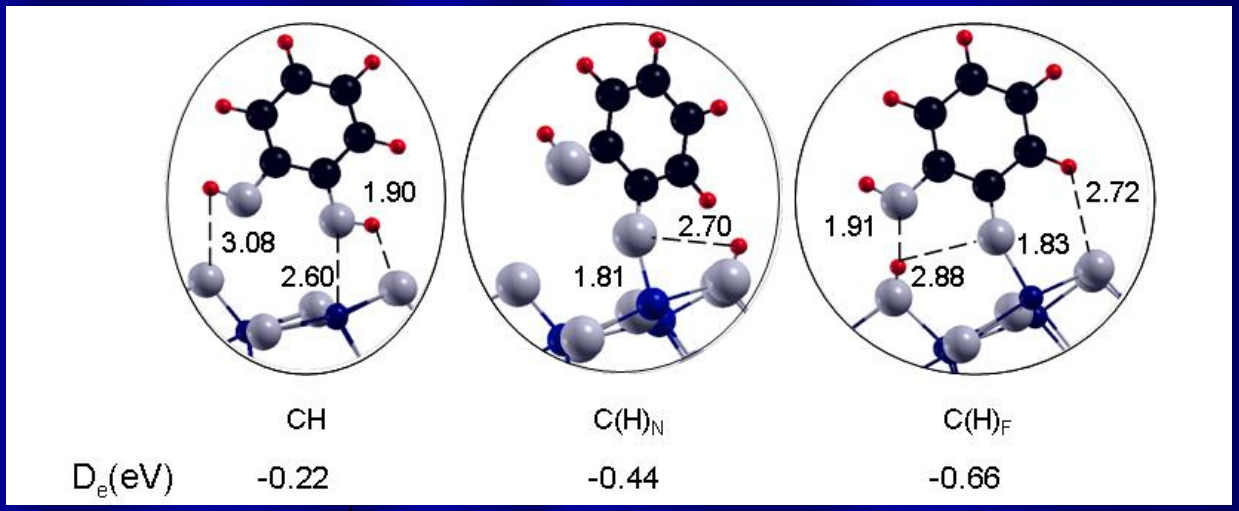


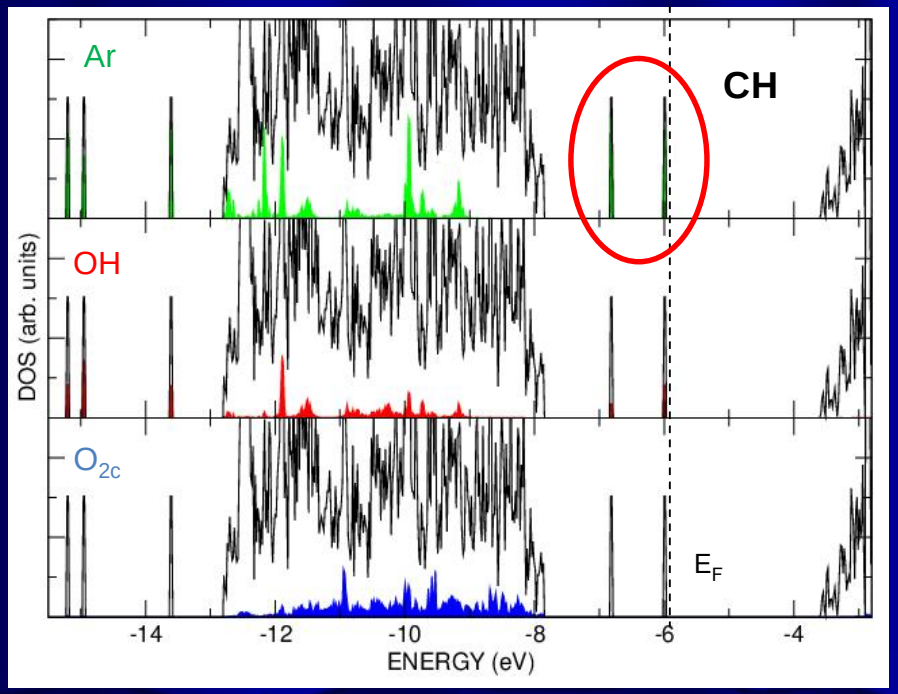
IP_{GAS}	8.8 eV
$IP_{ME_3(H)_F^+}$	5.9 eV
E_{TRAP}	-0.78 eV

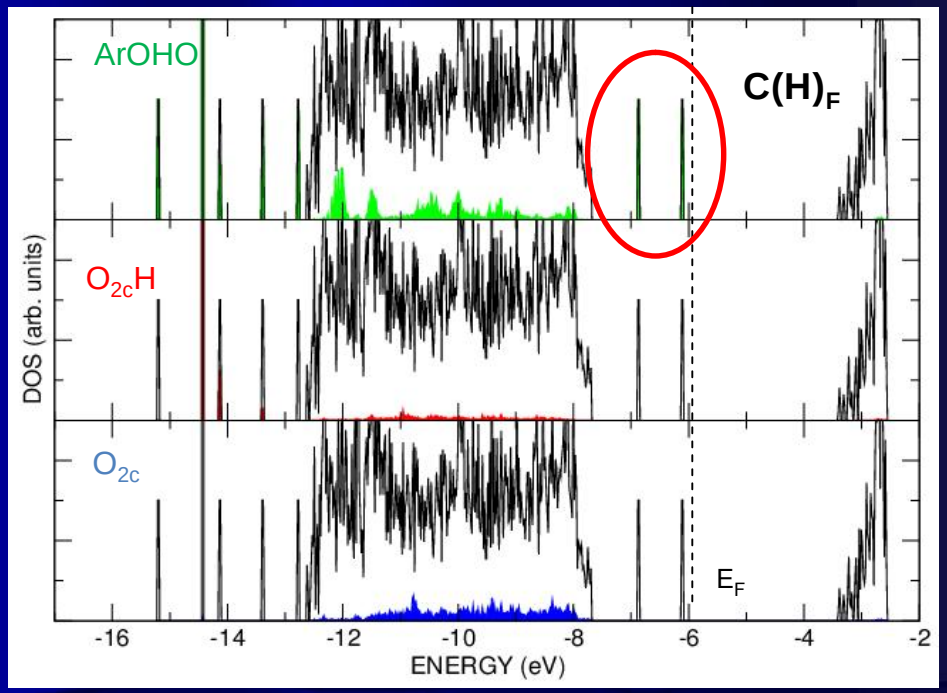
$-0.38\ eV < E_{TRAP} < -0.78\ eV$

C-C BOND ELONGATION:
IN THE PROCESS OF FORMING FORMALDEHYDE AND ETHYLENE GLYCOL

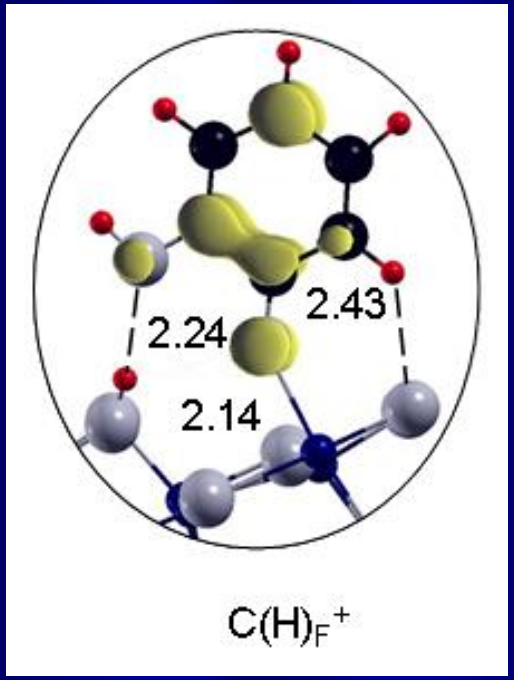
CATECHOL: UNDISSOCIATED VS DISSOCIATED ADSORPTION MODES

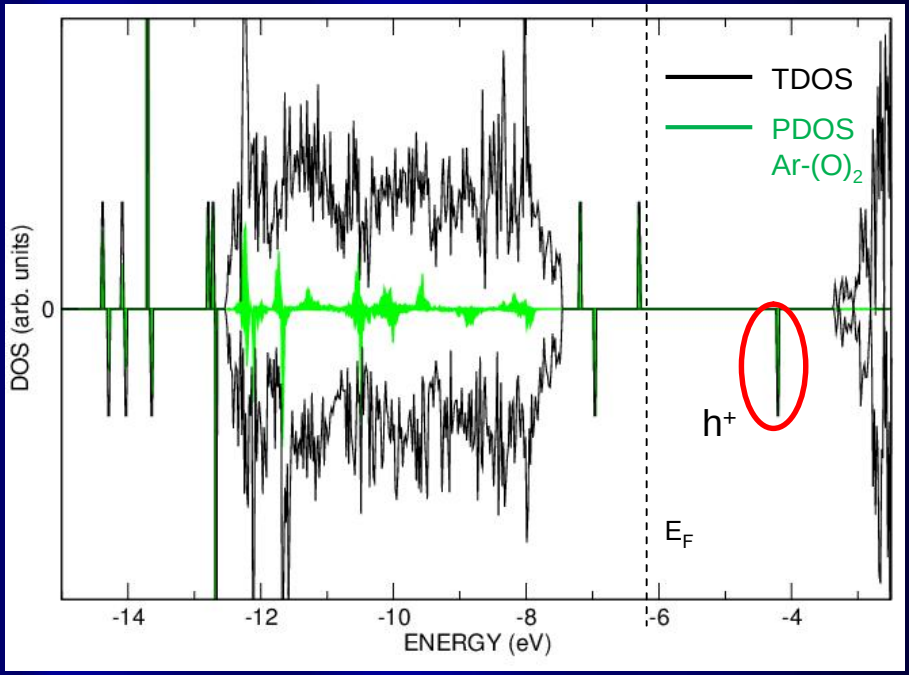






CATECHOL: HOLE TRAPPING

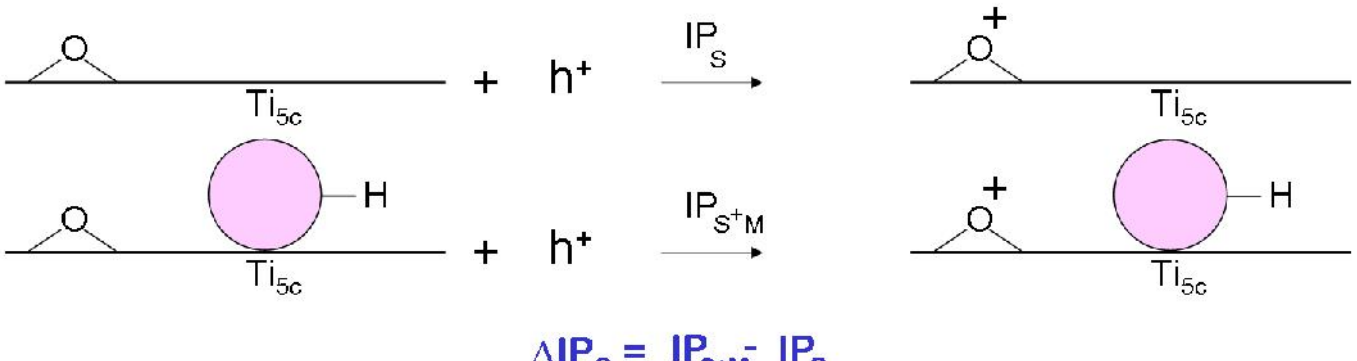




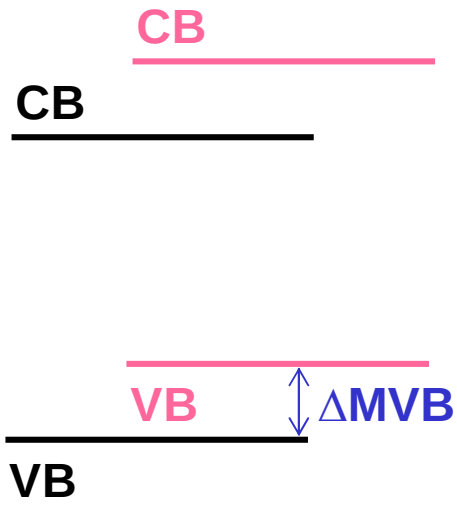
HIGH HOLE STABILIZATION THROUGH DELOCALIZATION ON THE AROMATIC RING

COMPARATIVE ANALYSIS OF SCAVENGING POWER

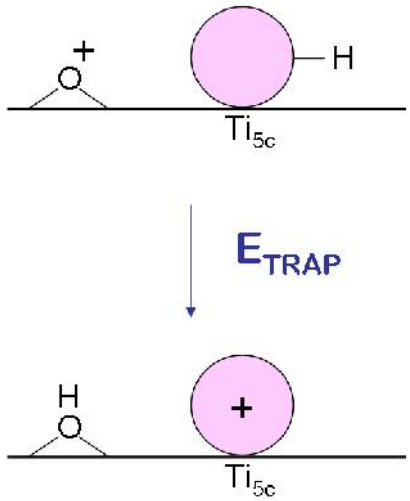
SURFACE IP CHANGE



CHANGE IN WORKFUNCTION



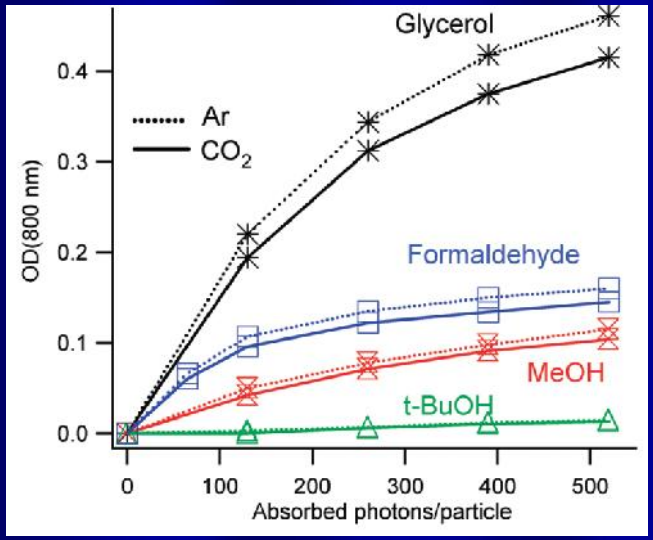
TRAPPING ENERGY



COMPARATIVE ANALYSIS OF SCAVENGING POWER

M	ΔIP_s	ΔMVB	E_{TRAP}	$\Delta MVB+E_{TRAP}$
Formic Acid	-0.59	-0.31	-0.22	-0.53
Methanol	-0.69	-0.44	-0.65	-1.09
Tert-butanol	-1.07	-0.57	-0.64	-1.21
Isopropanol	-0.91	-0.48	-0.90	-1.38
Glycerol	-1.32	-0.76	-0.77	-1.53

GLYCEROL > ISOPROPANOL > TERT-BUTANOL > METHANOL > FORMIC ACID



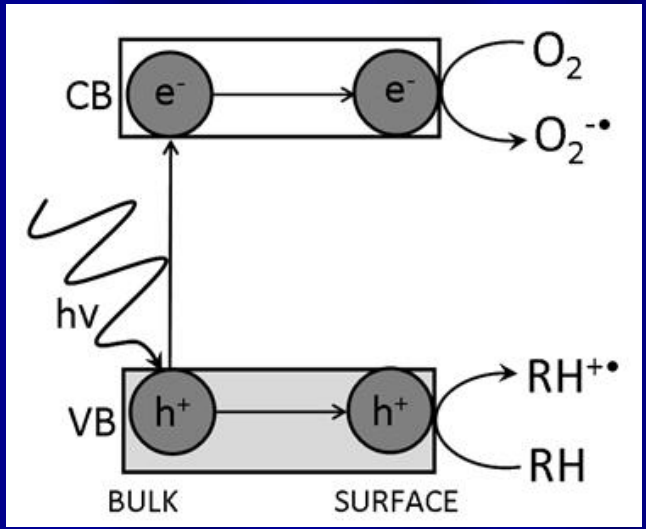
T. RAJH AND CO. JPC C 2012, 116, 878

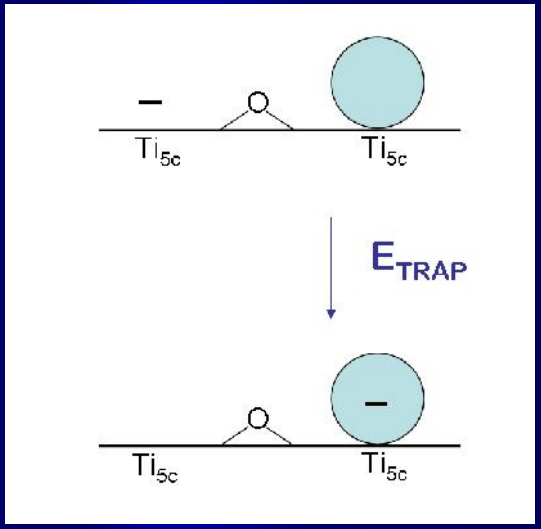
REDUCED SURFACE WORKFUNCTION
DUE TO SURFACE DIPOLE CHANGE
EASIER FORMATION OF HOLE AT SURFACE

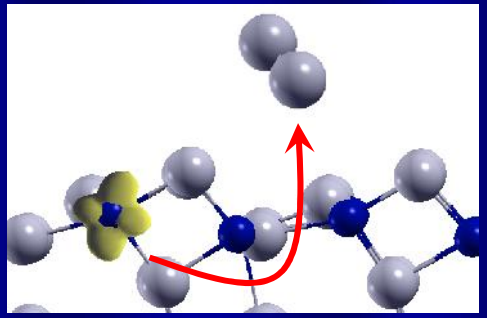
CDV and D. Fittipaldi JPC Lett. 4 (2013) 1901

OPTICAL ABSORPTION MEASUREMENTS OF PHOTOEXCITED ELECTRONS IN THE PRESENCE OF HOLE SCAVENGERS

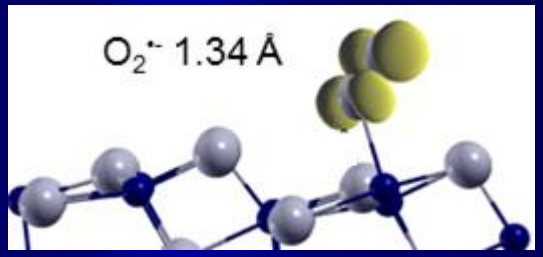
O_2 ELECTRON SCAVENGER







Ti_{5c}^{3+}



E_{trap} = -1.4 eV

CONCLUSIONS

- bulk/surface excitons and polarons in photoexcited anatase TiO_2 can be described with a simplified approach which takes into account self-trapping energy and local relaxation
- we find that a driving force exists for photoexcited electrons and holes to travel from the bulk to the surface
- comparison with exp. data from IR, EPR and luminescence spectroscopies is very good for the photoexcited model system
- photoexcited holes trapping by adsorbed organic alcohols and acids induces proton dissociation (except for catecol which is an excellent hole scavenger - because of the states in the gap)
- the change in the surface workfunction as a consequence of adsorption together with the trapping ability of the molecular species enhance the driving force for photoexcited electrons and holes to travel from the bulk to the surface
- on these basis we could define a scale of scavenging power
- interesting comparison between trapping energies on anatase and rutile!