Photochemistry on TiO_2 Semiconductor Surfaces – How Kinetic Measurements Can Provide Insight Into The Behavior of Charge Carriers

John T. Yates, Jr.

Surface Science Center

Department of Chemistry

University of Pittsburgh

PIRE-ECCI/ICMR Summer Program on

Techniques of Surface Science and Catalysis

University of California – Santa Barbara

August 2006

1972: Water Splitting at n-TiO_2 Electrodes

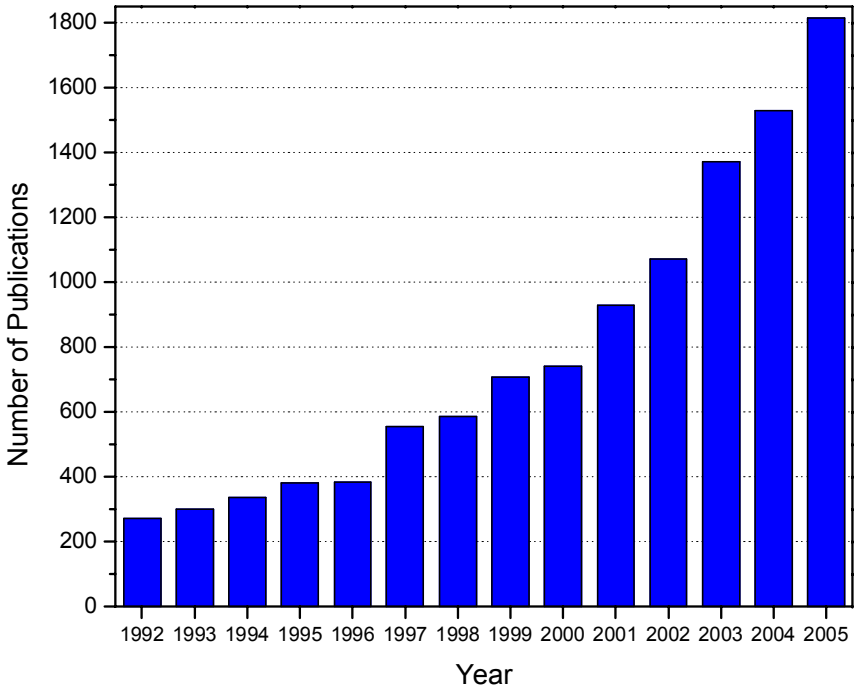
Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

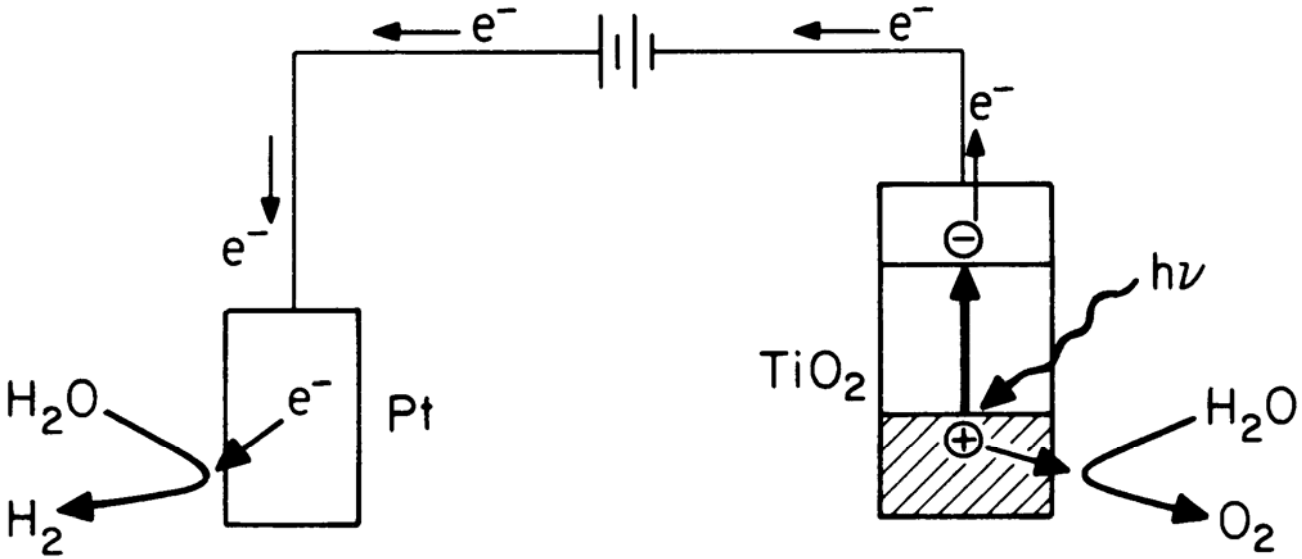
Current–voltage curves of a semiconducting n-type TiO_2



A. Fujishima and K. Honda, Nature 238 (1972) 37.

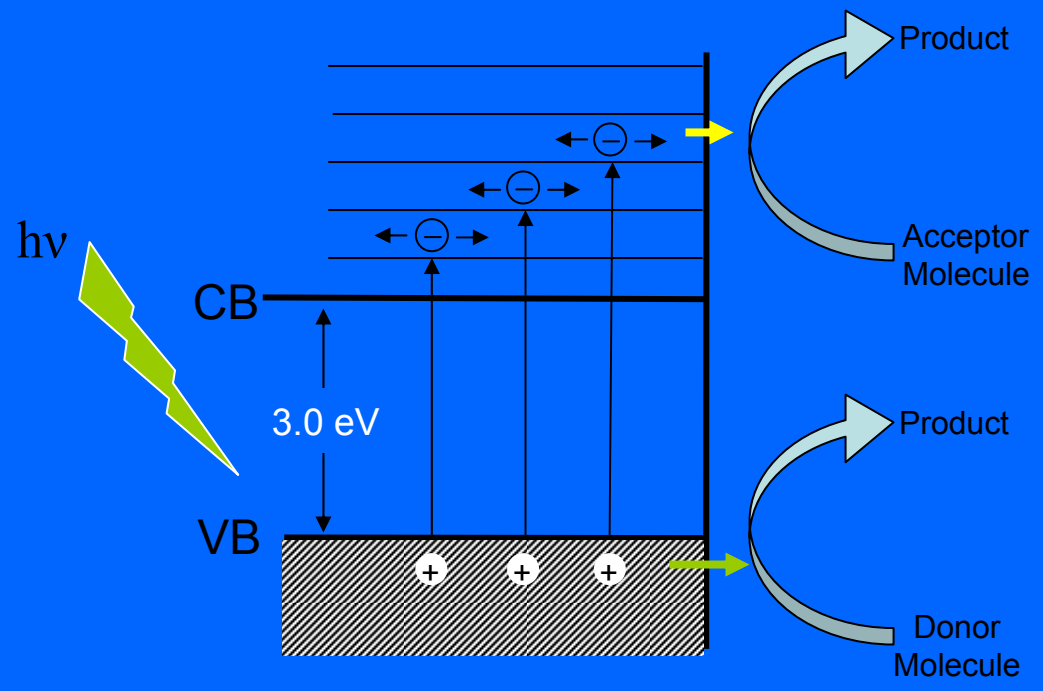
www.isiknowledge.com. Search terms = (TiO_2 OR titanium dioxide AND photo*)

PHOTOSPLITING OF WATER IN A PHOTOELECTROCHEMICAL CELL

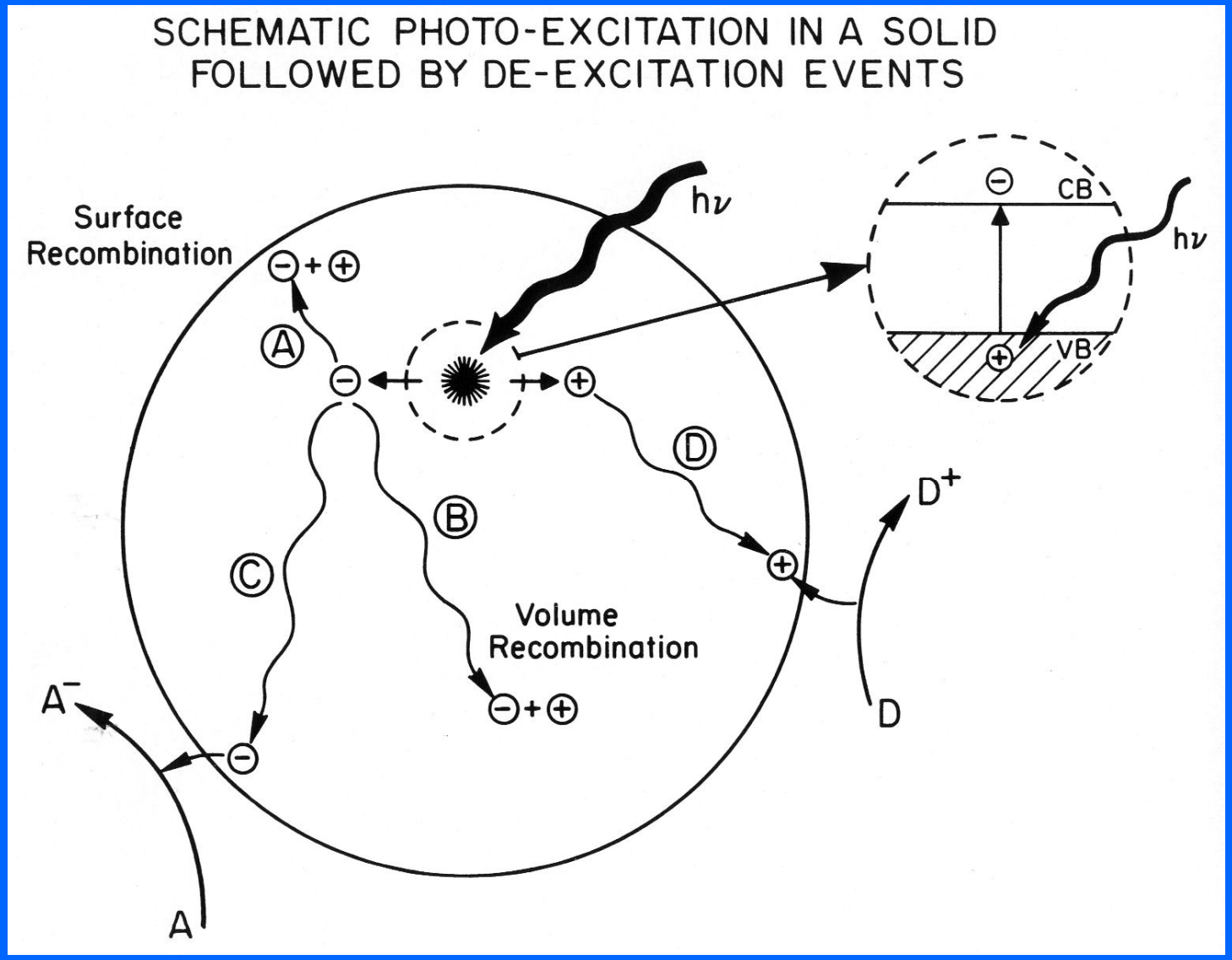


$$H_2O \xrightarrow[Pt-TiO_2]{h\nu} H_2 + \frac{1}{2} O_2$$

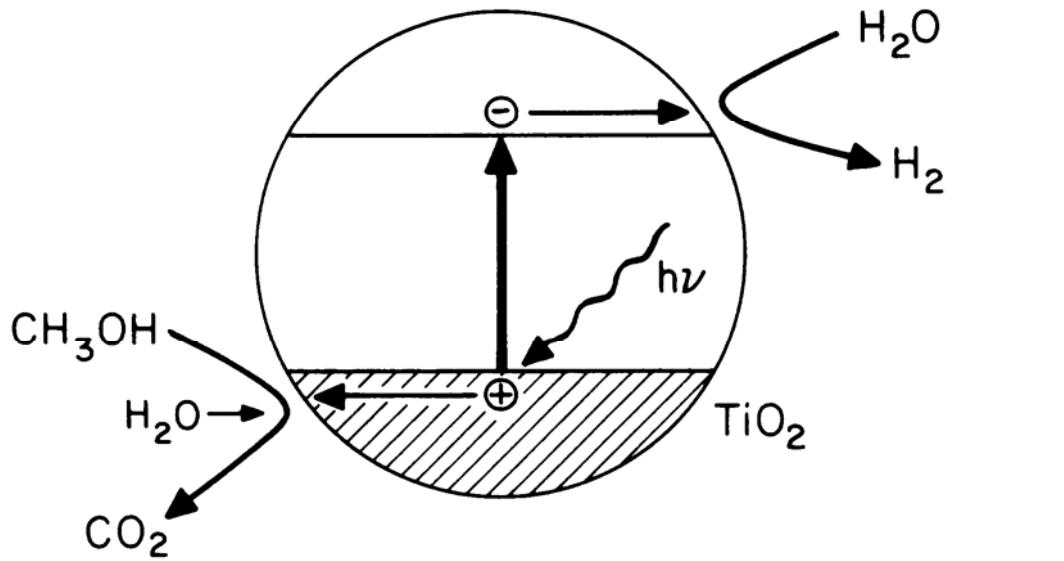
Semiconductor Photoexcitation : TiO_2



Upon UV excitation, both electrons and holes are photochemically active towards adsorbates on the TiO_2 surface.


SCHEMATIC PHOTO-EXCITATION IN A SOLID
FOLLOWED BY DE-EXCITATION EVENTS
Surface
Recombination
hν
CB
VB
hν
A
B
C
D
Volume
Recombination
D+
D
A−
A

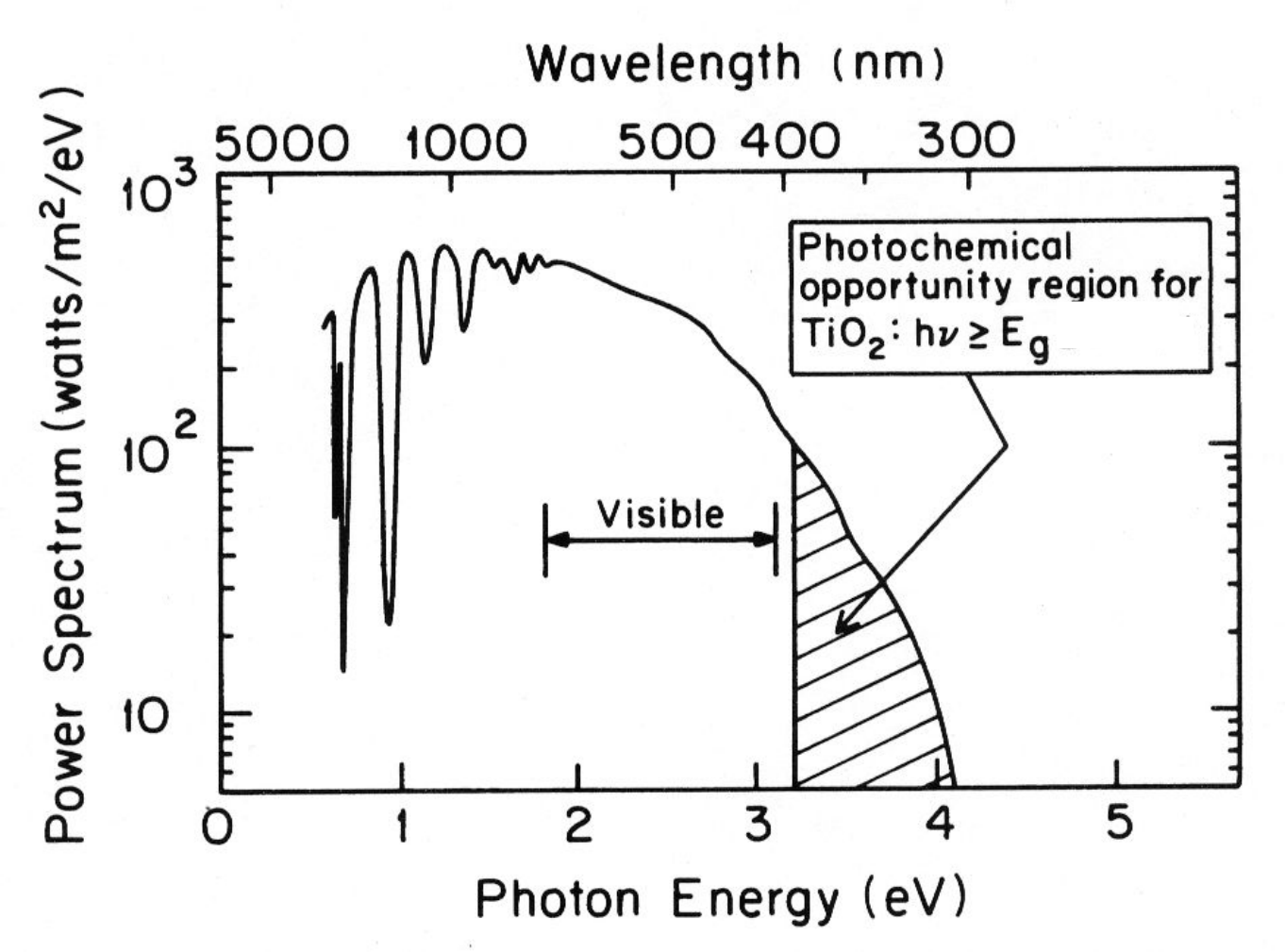
Sacrificial Hole Scavenger Action



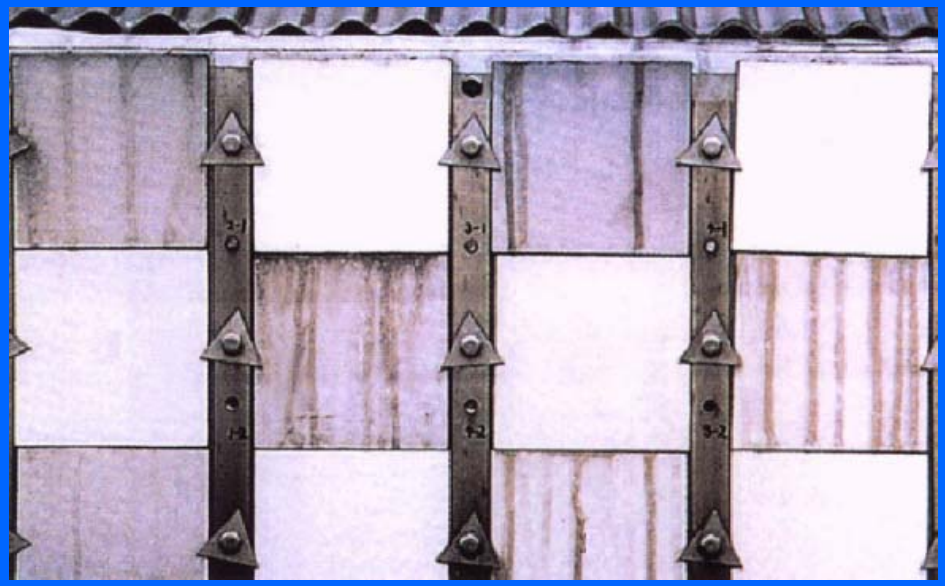
$$H_2O \xrightarrow[TiO_2]{h\nu} H_2 + \frac{1}{2} O_2$$

$$\xrightarrow{CH_3OH} CO_2$$

Solar Spectrum on Earth



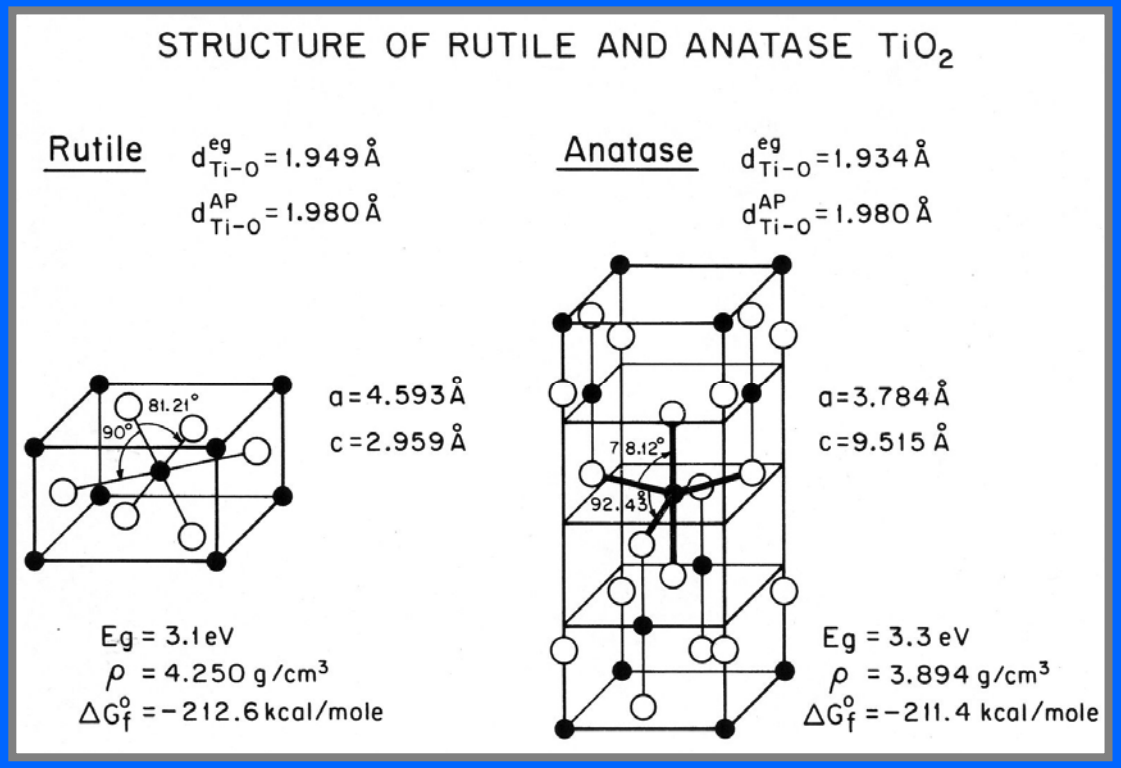
Motivation? TiO_2 Based Photocatalytic Technology Works!

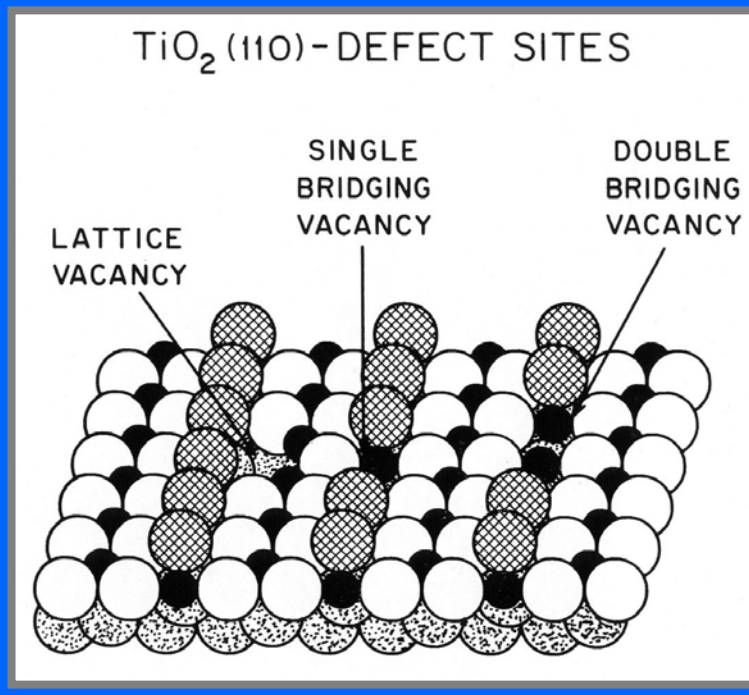


Taken from: Fujishima, Hashimoto, Watanabe, "TiO_2-Photocatalysis, Fundamentals and Applications", BKC Inc. Tokyo, 1999

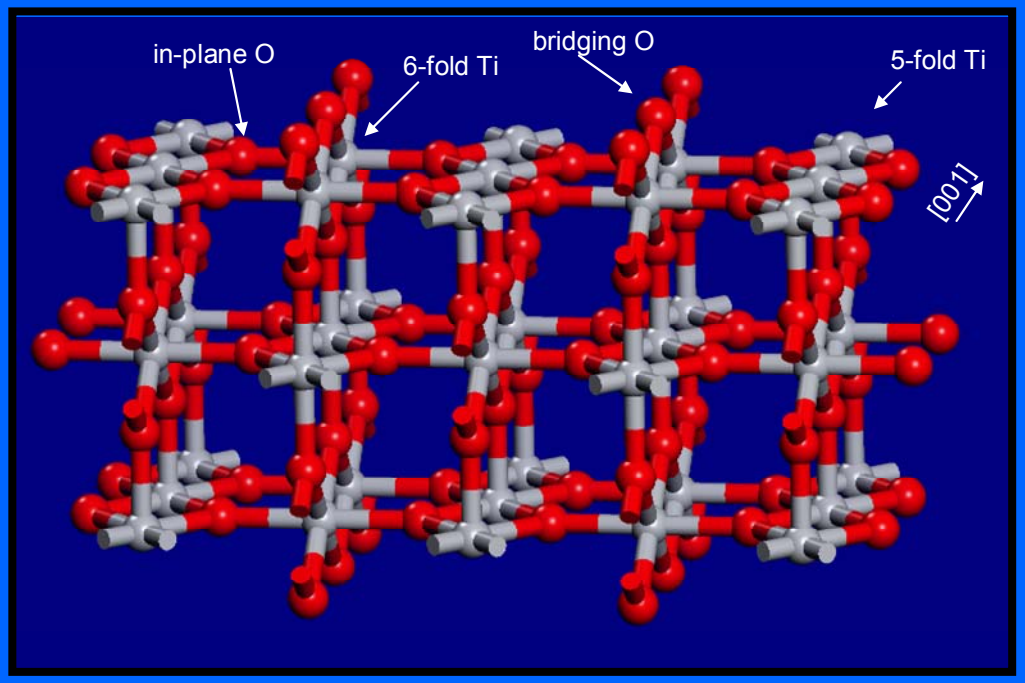
TiO_2 Based Systems are Efficient Photocatalysts

TiO_2 as a Photochemical Substrate



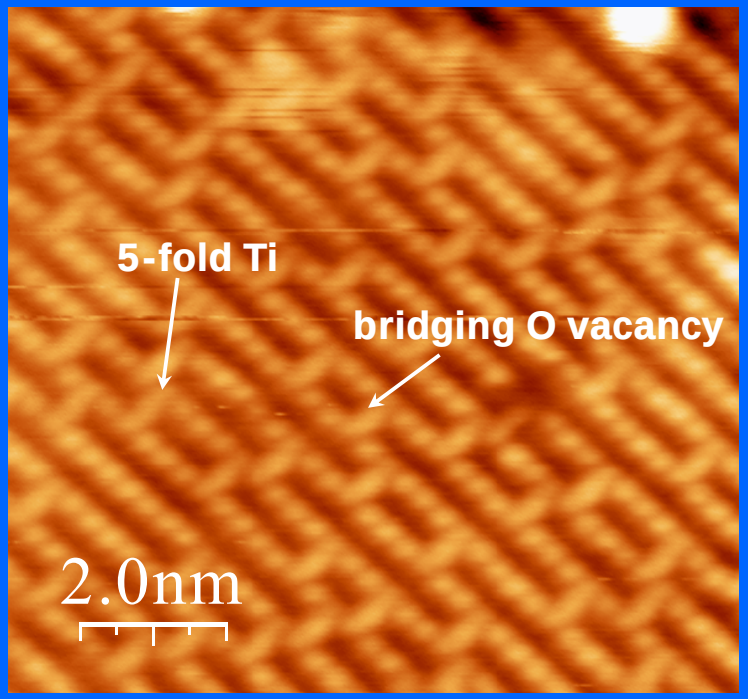


Atomic Structure of TiO_2(110) Surface



TiO_2(110)-(1x1) surface without oxygen vacancies is <u>stochiometric</u> (TiO_2)

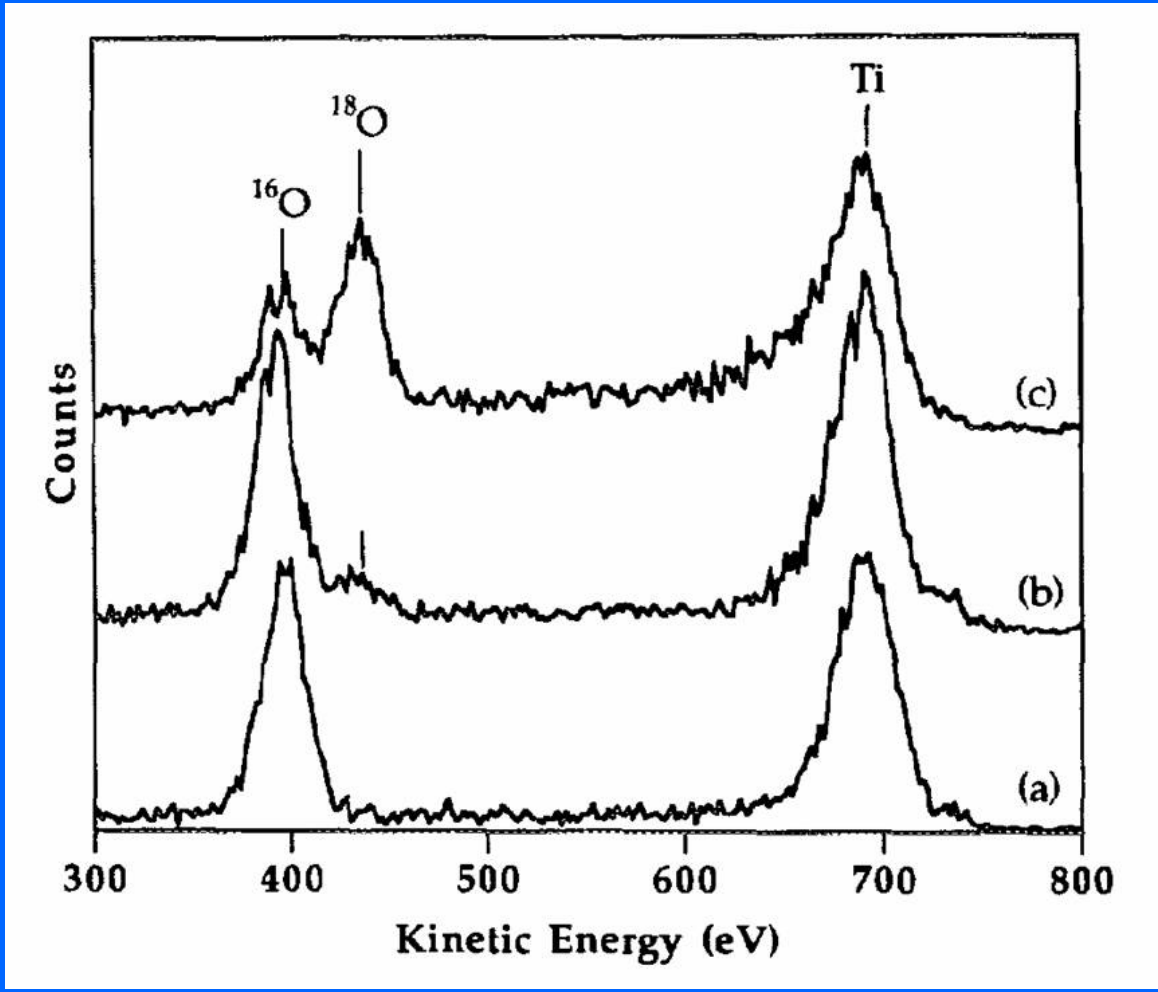
The surface density of oxygen vacancy sites is regulated by annealing conditions (time, presence of O_2)



Mezhenney et al. Chemical Physics Letters, 369 (2003) 152.

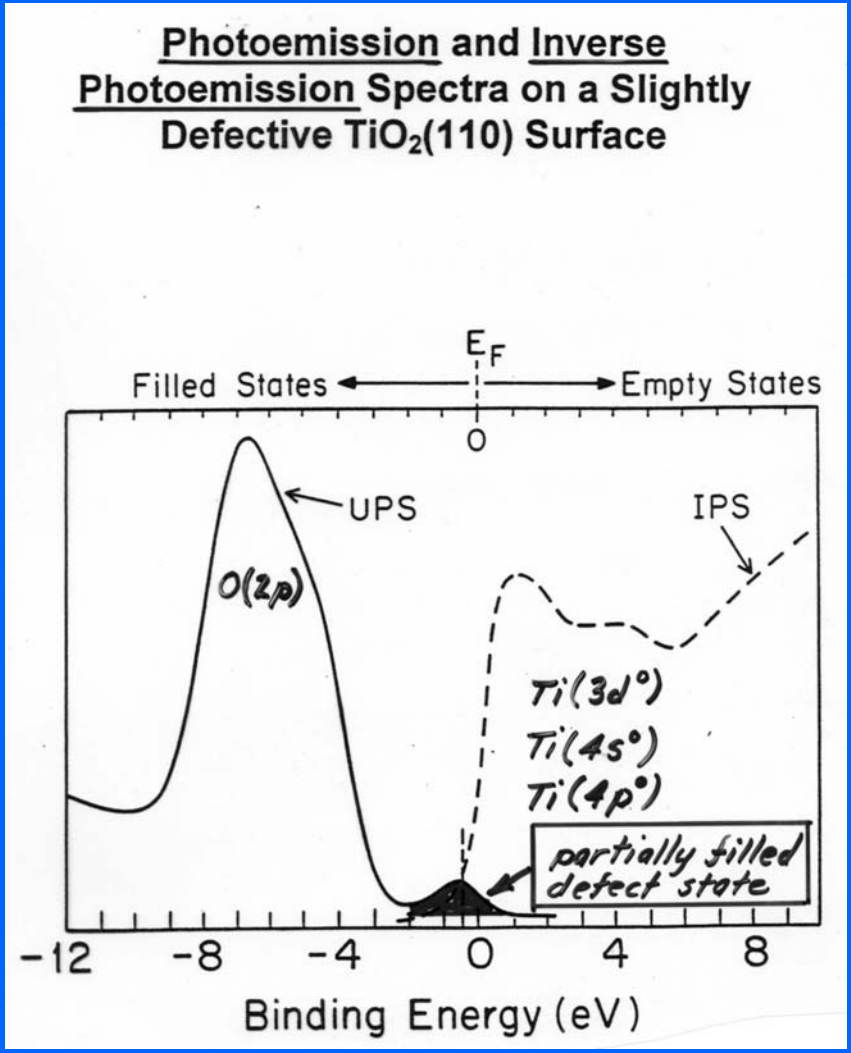
Heating TiO_2 above ~ 700 – 800 K $\rightarrow$ O-vacancy defects (reduced TiO_2)

He Ion Scattering Spectroscopy – Detects $^{18}O_2$ on Vacancy Defect Sites



~8% defects in surface adsorb $^{18}O_2$

Pan, J. M.; Maschhoff, B. L.; Diebold, U.; Madey, T. E. *J. Vac. Sci. Technol. A* 1992, *10*, 2470.



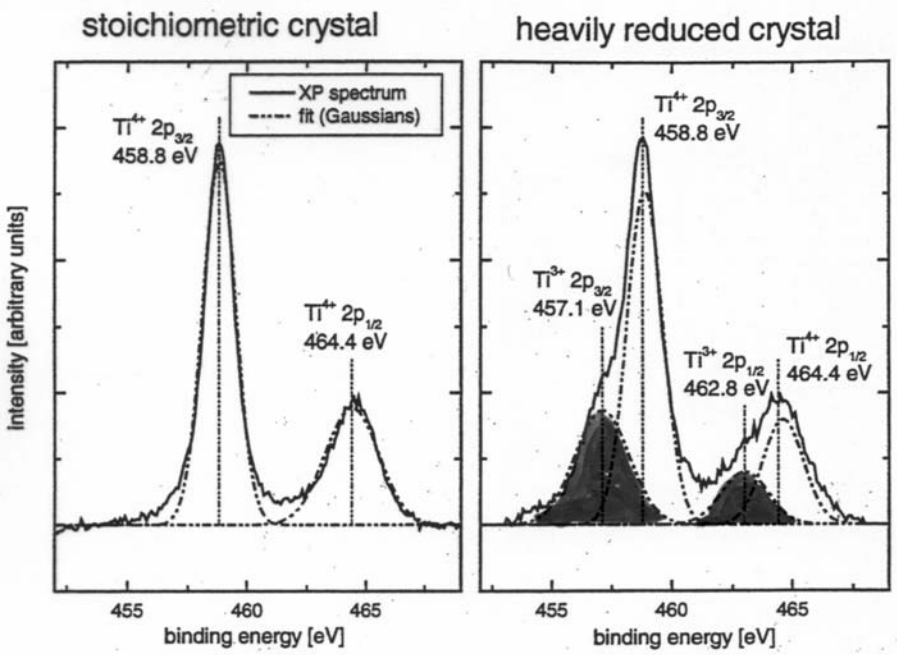
R.A. Bartynski, et al.

JVST A10, 2591 (1992)

Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2 4p^0$

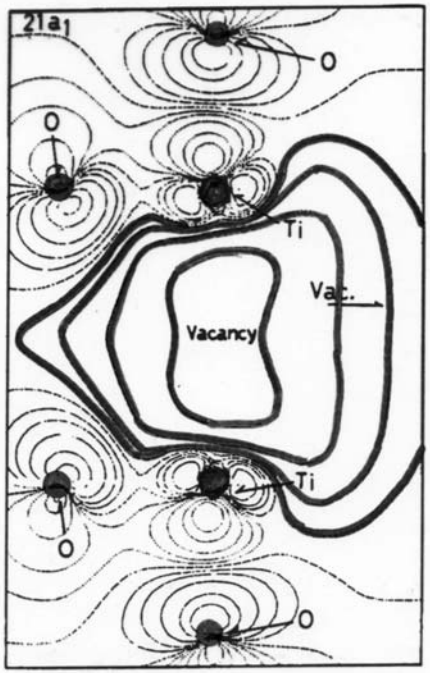
Ti^{+4}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^0 4s^0 4p^0$

XPS Evidence for TiO_2 Reduction by Heating



S. Reiβ, H. Krumm, A. Niklewski, V. Staemmier, Ch. Wöll, *Journal of Chemical Physics* 116, 7704 (2002)

HOMO: O-Vacancy Defect Site - $SrTiO_3(100)$



- 16% Ti (3d)
- 41% Ti (4p)
- 43% Ti (4s)

M. Tsukada, H. Adachi and C. Satoko,
Prog. Surf. Sci. 14, 113 (1983).

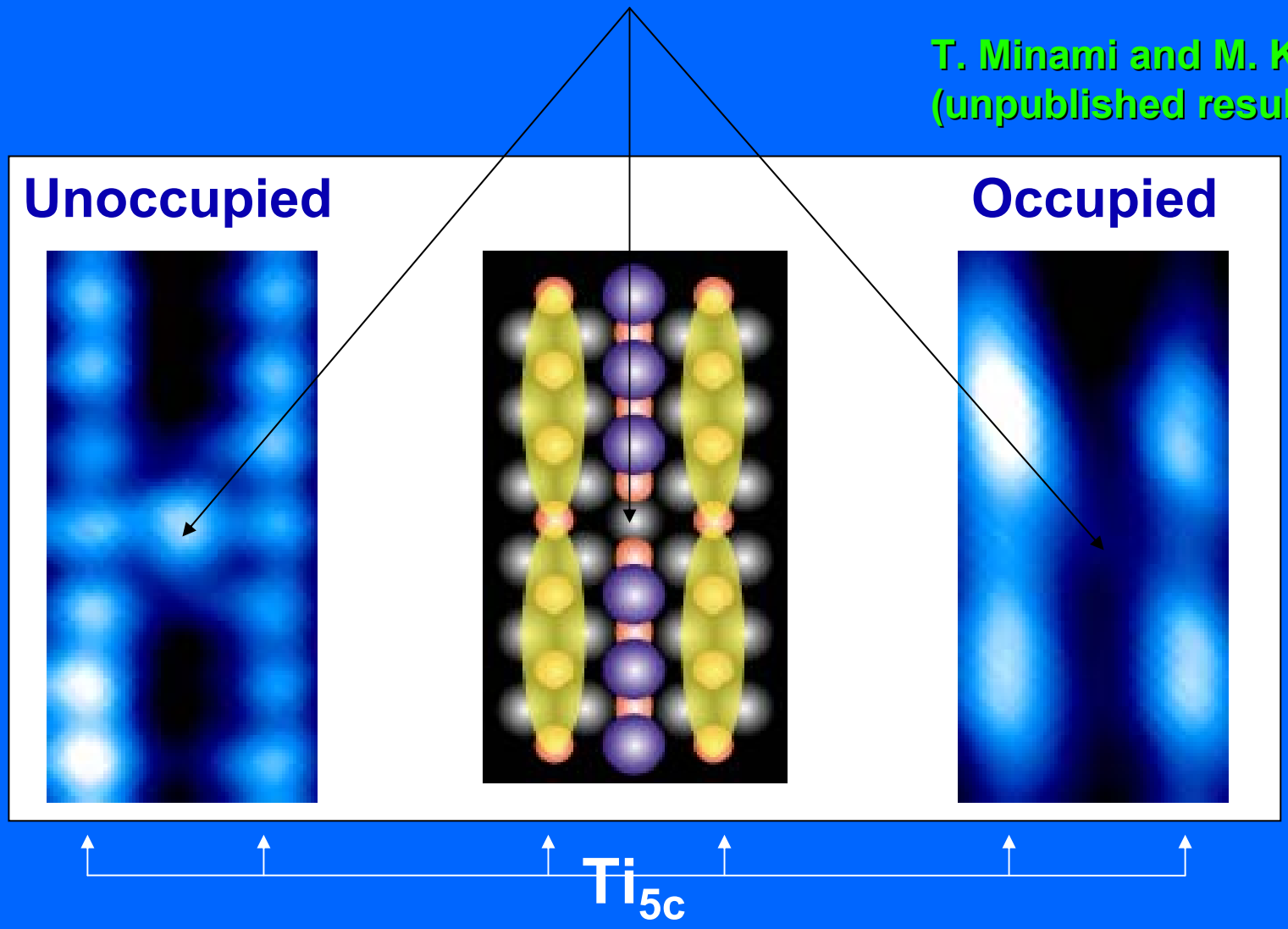
A More Recent Look at Electronic Structure of Oxygen Defects/TiO_2(110)

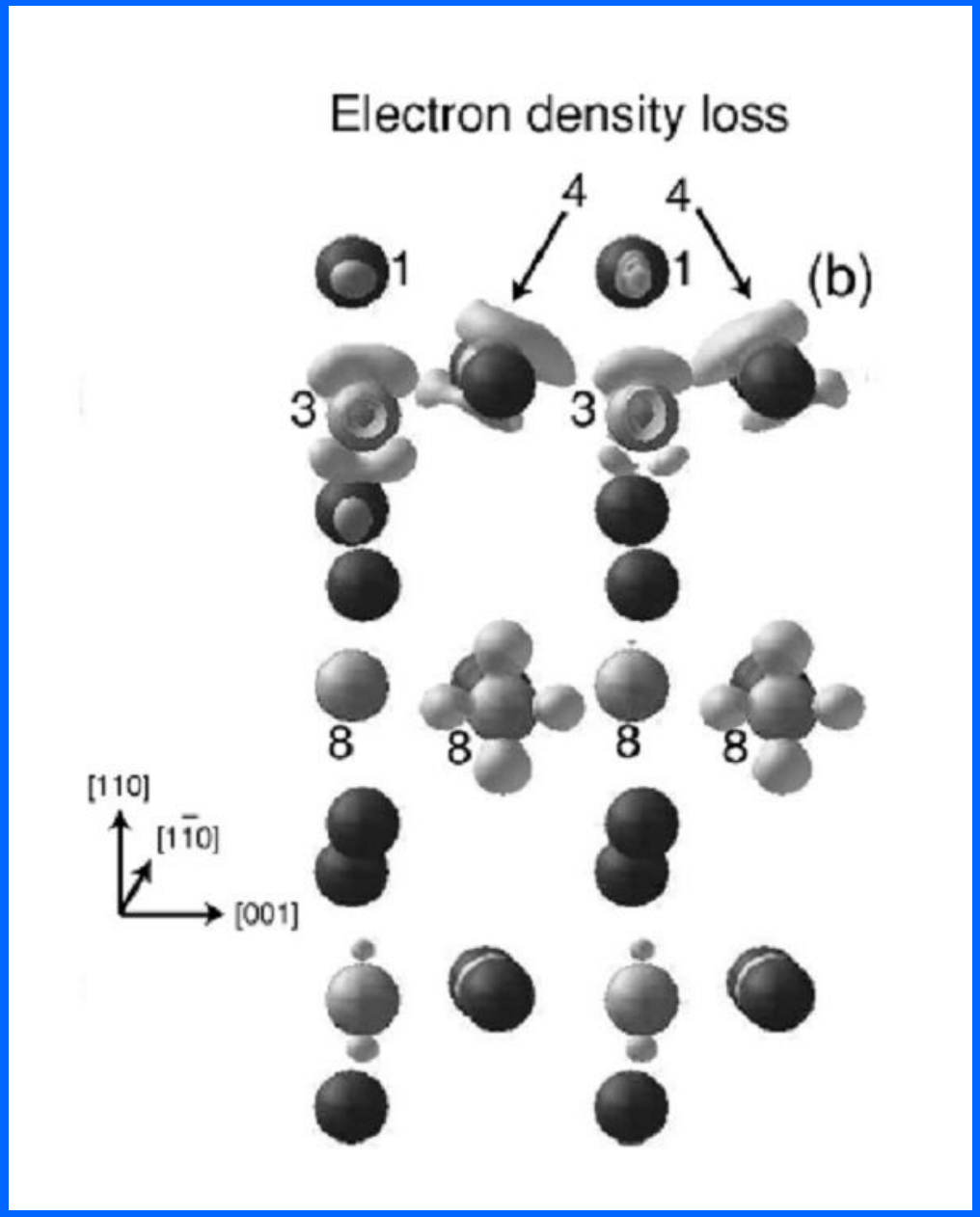
STM - STS

Spatial distribution of Ti 3d state

Oxygen Defect State

T. Minami and M. Kawai
(unpublished results)



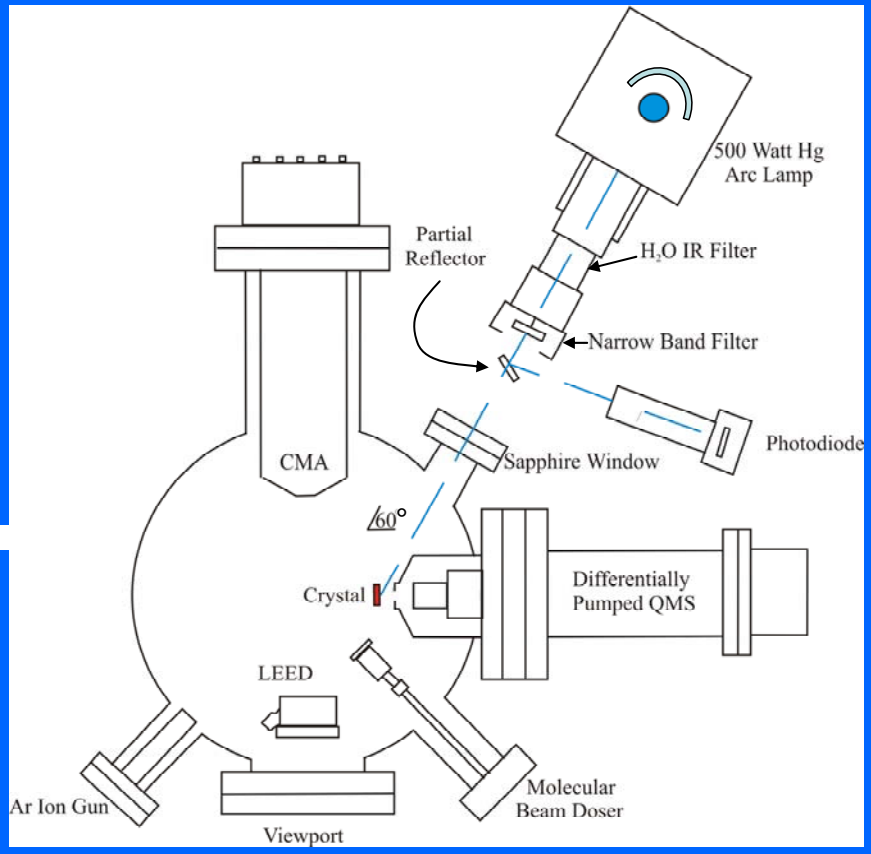


Vijay, A.; Mills, G.; Metiu, H. *J. Chem. Phys.* 2003, *118*, 6536.

Use of CO_2 Adsorption to Detect Surface Defect Sites Produced by Heating

UHV Studies of Photochemical Processes on $TiO_2(110)$

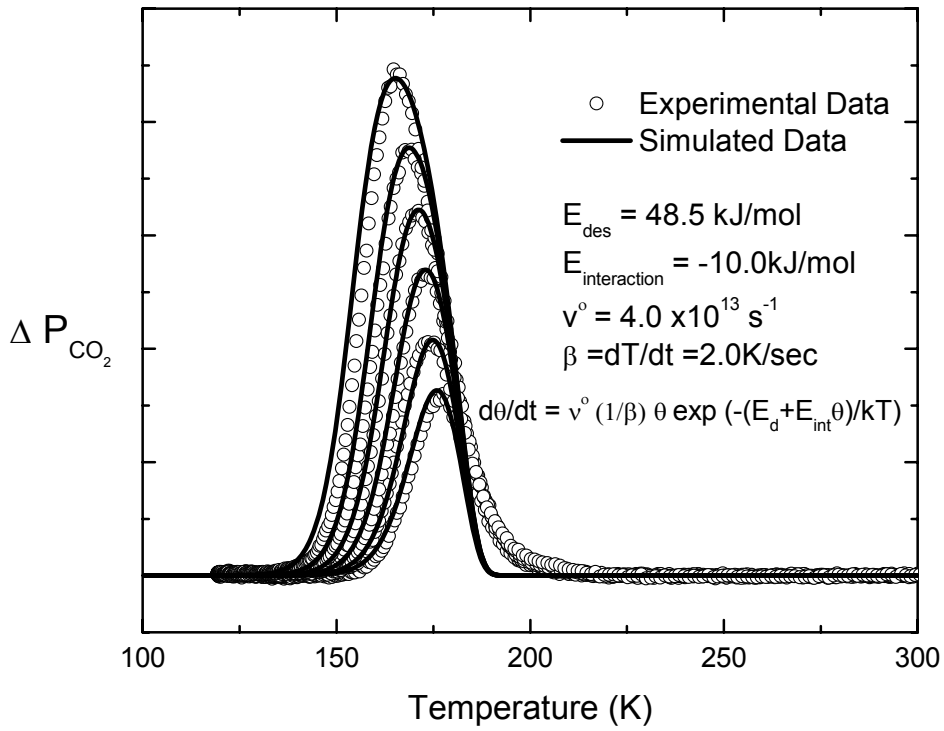
Apparatus for Photodesorption Studies from $TiO_2(110)$



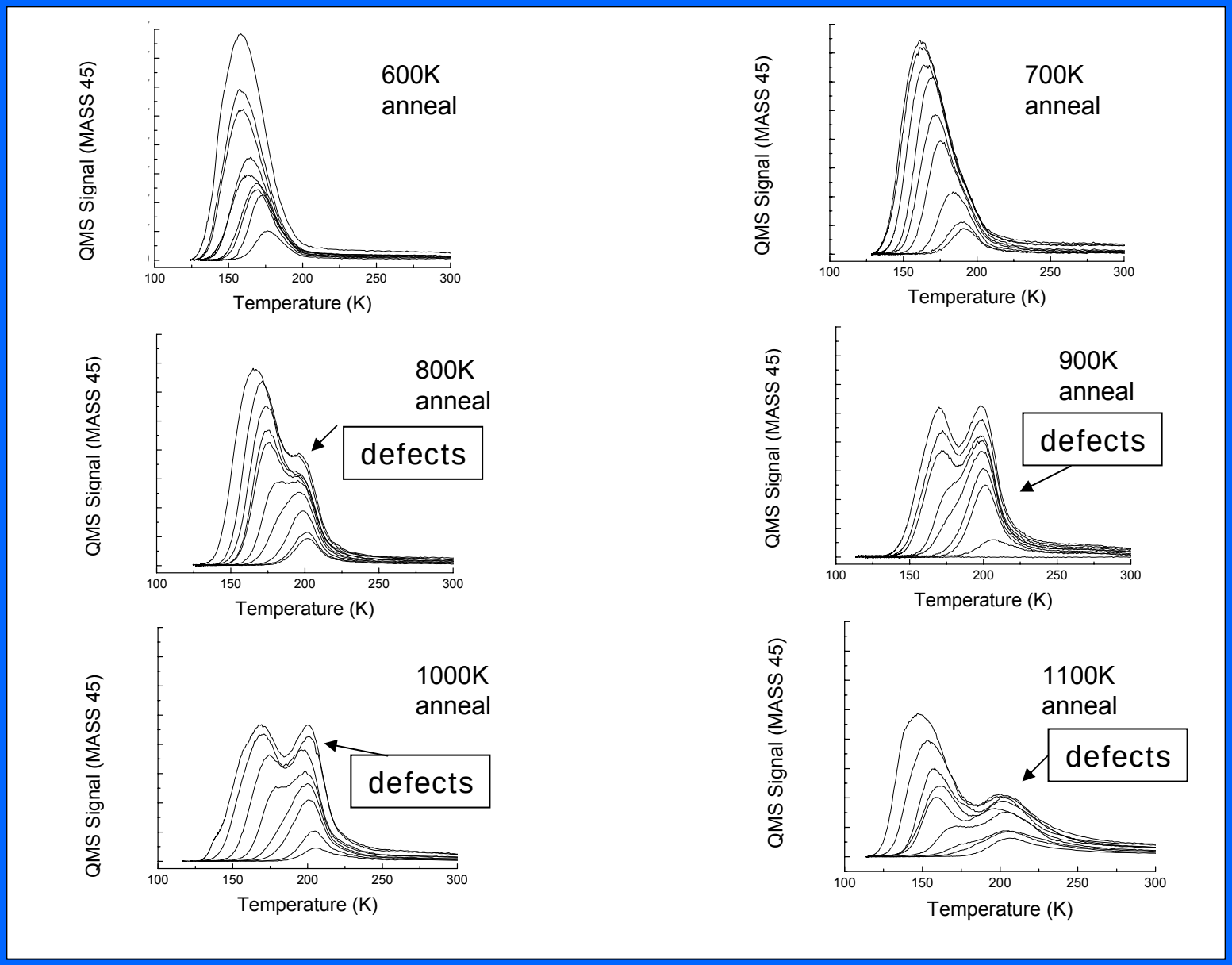
Measurement Capabilities:

- ***Auger Electron Spectroscopy***
- ***Temperature Programmed Desorption (TPD)***
- ***Photo-induced Desorption (PD)***

Comparison of Experimental and Simulated $^{13}CO_2$ Desorption Spectra on $TiO_2(110)$ – Fully Oxidized Surface



Successive Reduction of TiO_2(110) Using CO_2 to Detect Vacancy Defect Sites



T. L. Thompson, O. Diwald and J. T. Yates, Jr.
J. Phys. Chem. B 107 (2003) 11700.

A Recent Controversy About Vacancy Defect Sites on TiO_2(110)

Oxygen-Mediated Vacancy Diffusion on TiO_2

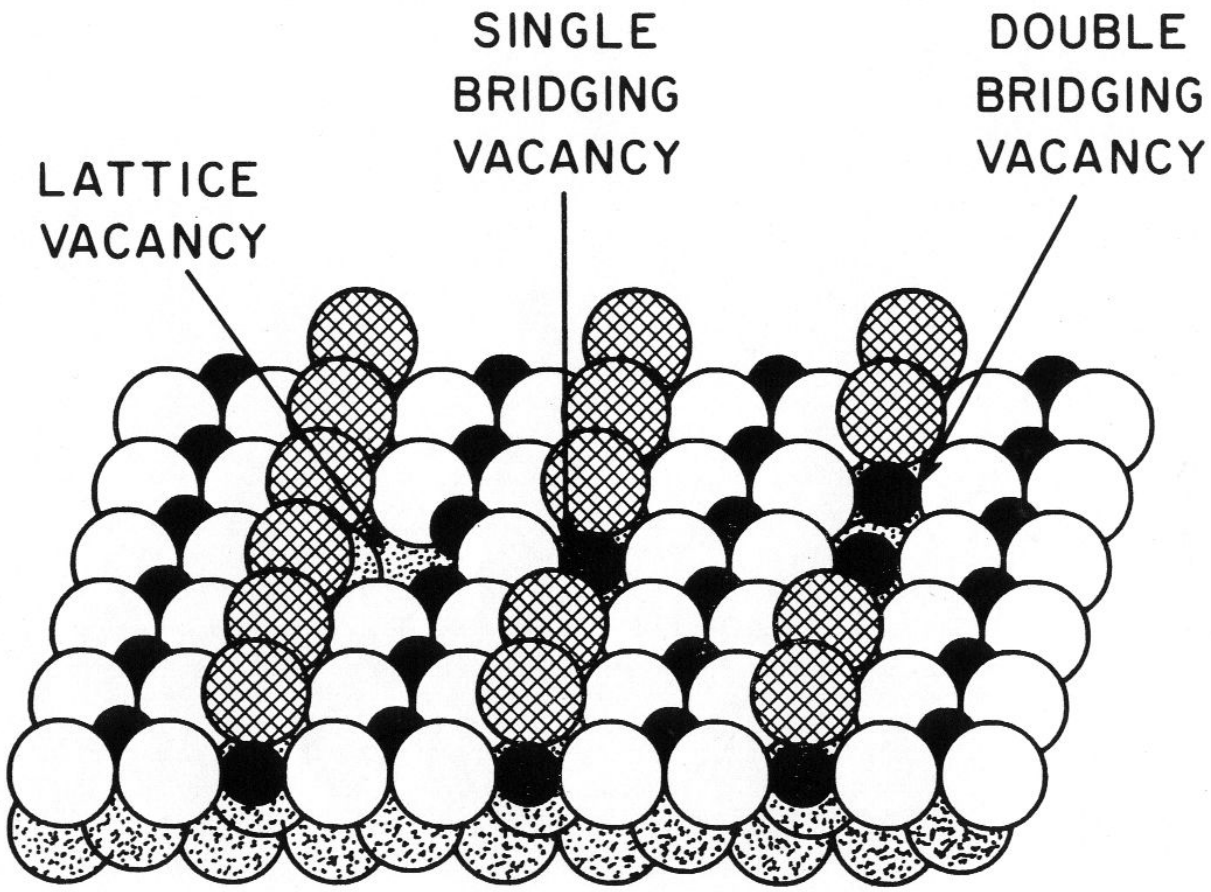
17 JANUARY 2003 VOL 299 SCIENCE www.sciencemag.org

Oxygen-Mediated Diffusion of Oxygen Vacancies on the TiO_2(110) Surface

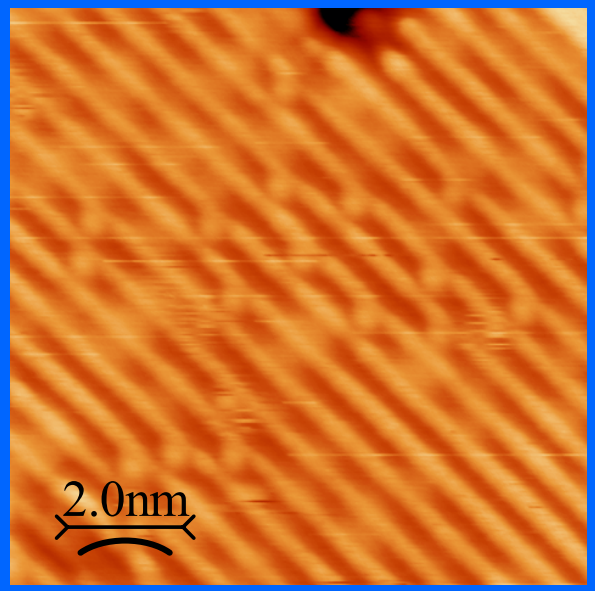
Renald Schaub, Erik Wahlström, Anders Rønnau, Erik Lægsgaard, Ivan Stensgaard, Flemming Besenbacher*

Defects such as oxygen vacancies play a crucial role in the surface properties of transition metal oxides. By means of time-resolved, high-resolution scanning tunneling microscopy, we unraveled an adsorbate-mediated diffusion mechanism of oxygen vacancies on rutile TiO_2(110). Adsorbed oxygen molecules mediate vacancy diffusion through the loss of an oxygen atom to a vacancy and the sequential capture of an oxygen atom from a neighboring bridging oxygen row, leading to an anisotropic oxygen vacancy diffusion pathway perpendicular to the bridging oxygen rows.

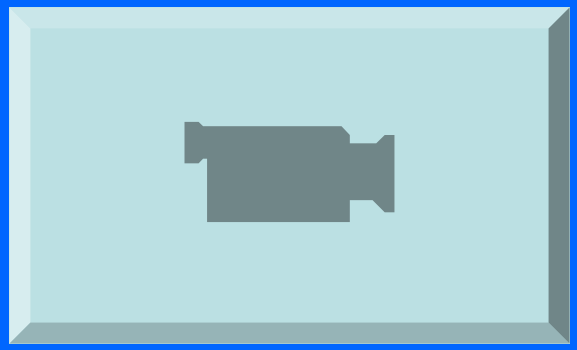
TiO_2 (110) - DEFECT SITES



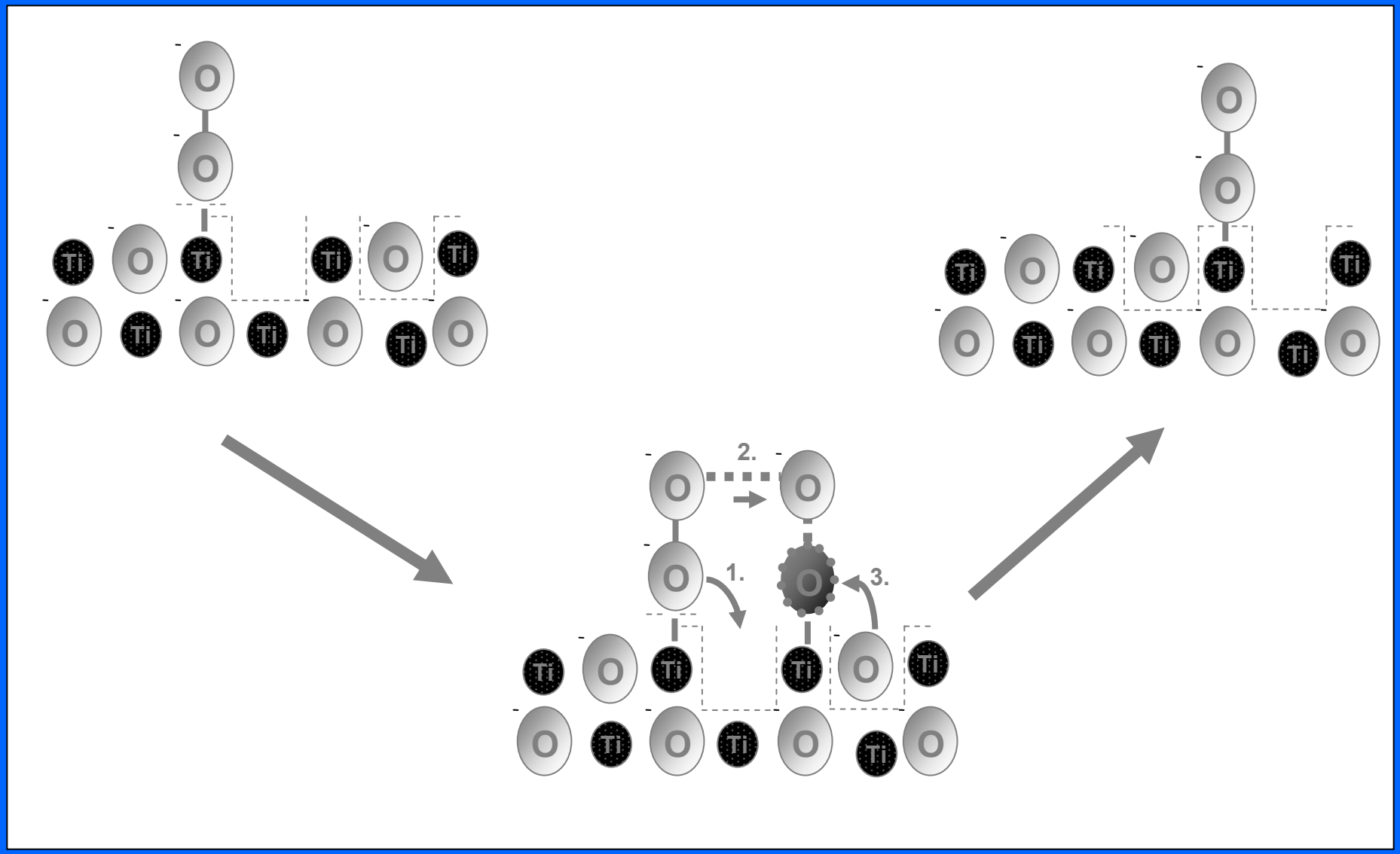
STM Image of TiO_2(110) Showing Oxygen Vacancy Defect Sites

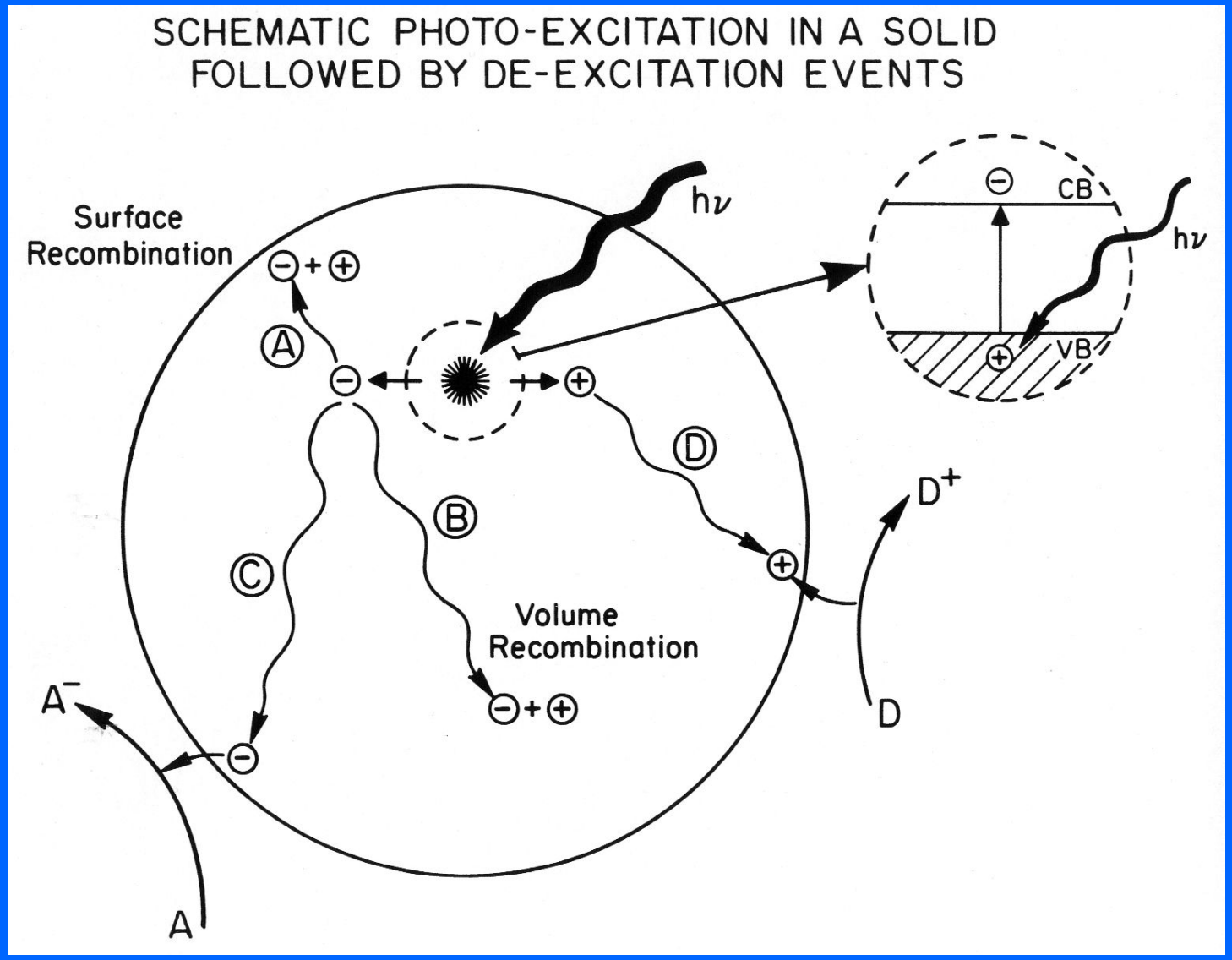


Mezhenny, Maksymovych, Thompson, Diwald, Stahl, Walck and Yates. Chem. Phys. Lett. 369 (2003) 152.

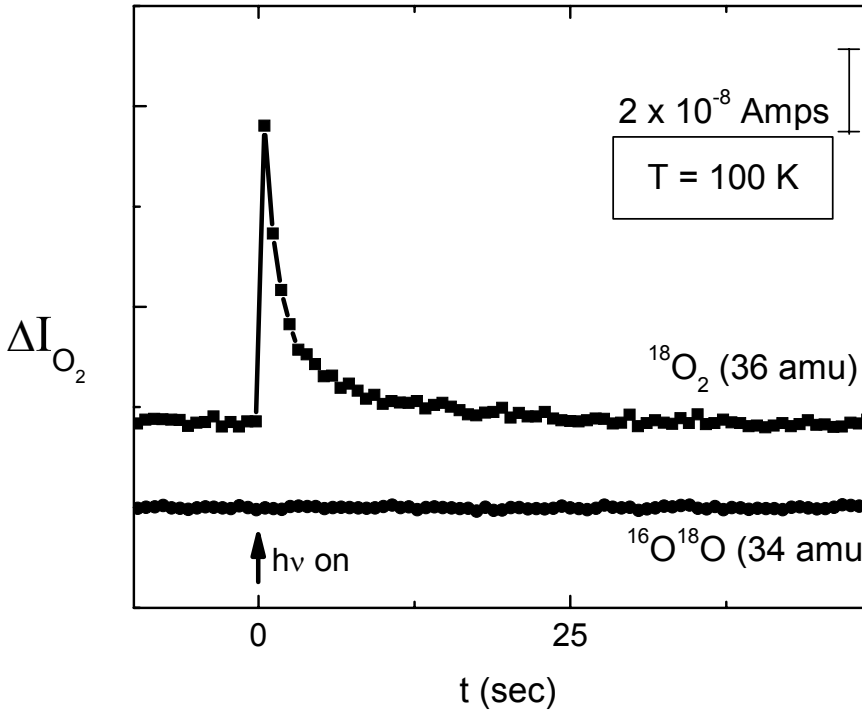


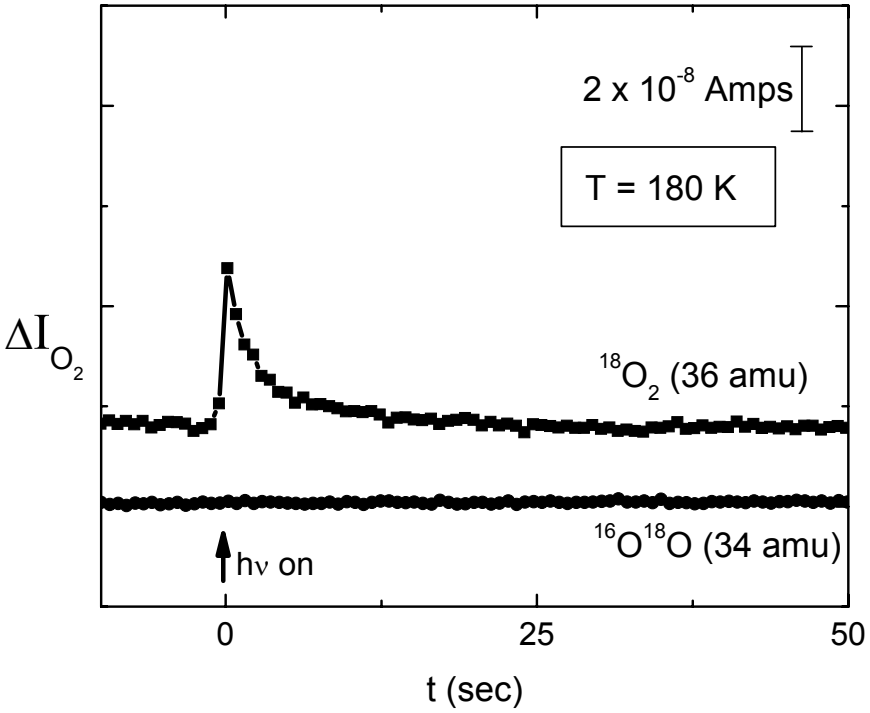
Schematic of O_2 - Mediated Vacancy Diffusion - $TiO_2(110)$




SCHEMATIC PHOTO-EXCITATION IN A SOLID
FOLLOWED BY DE-EXCITATION EVENTS
Surface
Recombination
hν
CB
VB
hν
A
B
C
D
Volume
Recombination
D+
D
A−
A

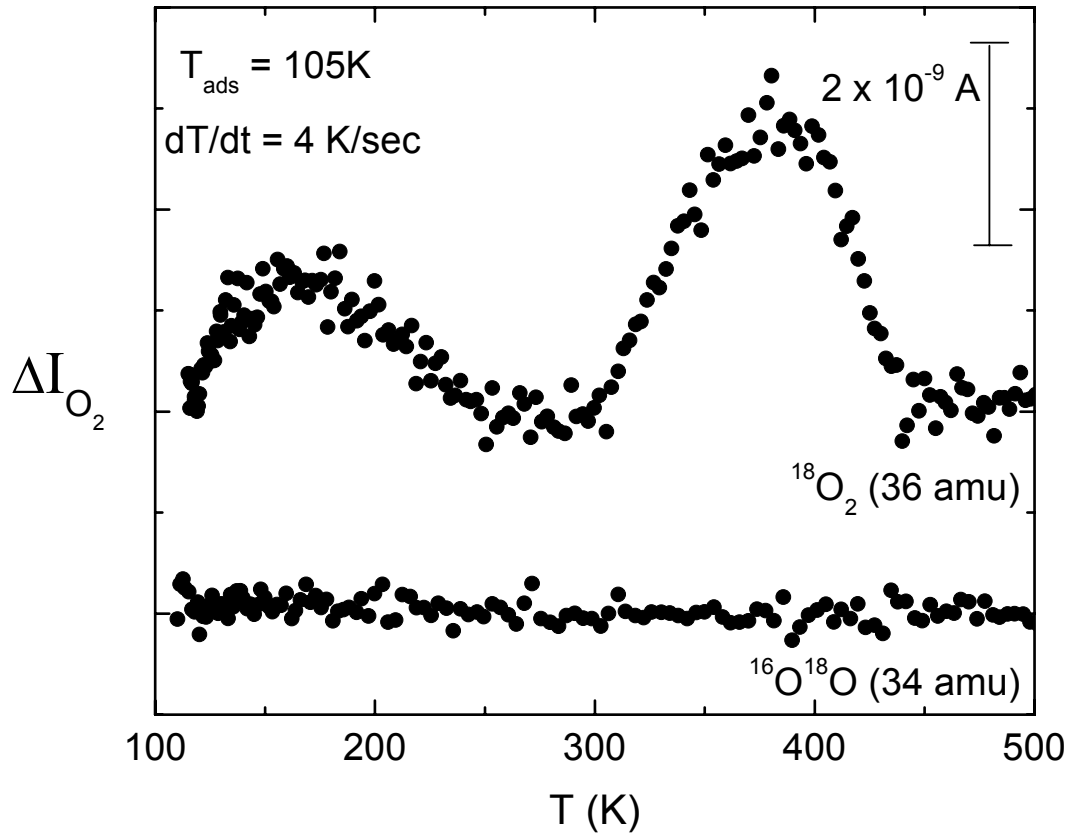
Isotopomer O_2 Photodesorption from $TiO_2(110)$ Containing Vacancy Sites





T. Thompson, O. Diwald, J. T. Yates, Jr. Chem. Phys. Lett. 393, 28, 2004.

Isotopomer O_2 Thermal Desorption from $TiO_2(110)$ Containing Vacancy Sites



T. Thompson, O. Diwald, J. T. Yates, Jr. Chem. Phys. Lett. 393, 28 (2004).

Summary

1. O_2-Mediated vacancy diffusion on $TiO_2(110)$ is observed by STM.

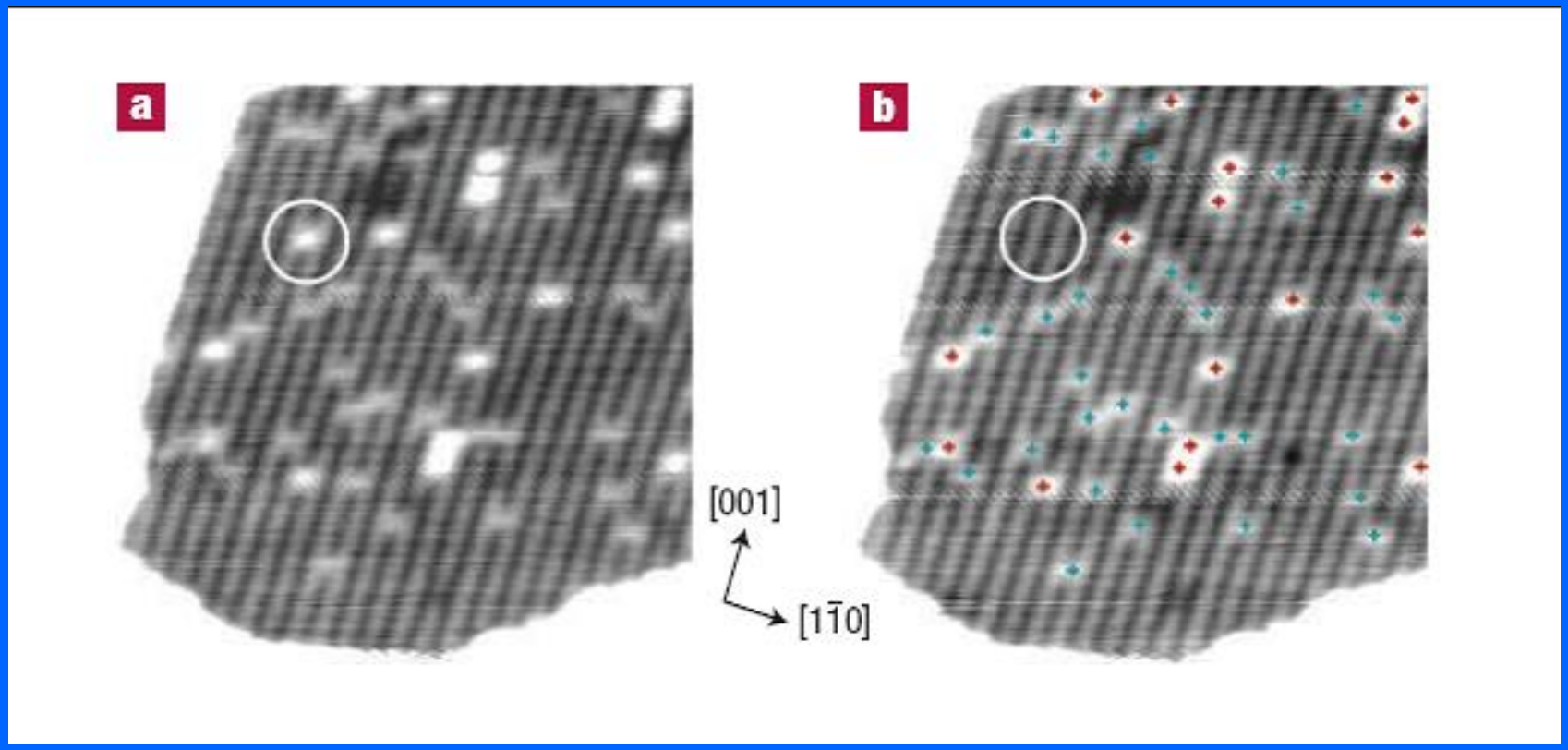
2. The mechanism proposed is incorrect since isotopic exchange does not occur from lattice oxygen to molecular oxygen.

3. Single Question: What other O_2-mediated models can be imagined?

The Controversy Has Been Settled

- Bright images were not O_2/defect site.
- They were Ti-OH groups due to H_2O impurity.

$$\text{vac} - \text{OH} + \text{e} \longrightarrow \text{TiO} + \text{H}$$

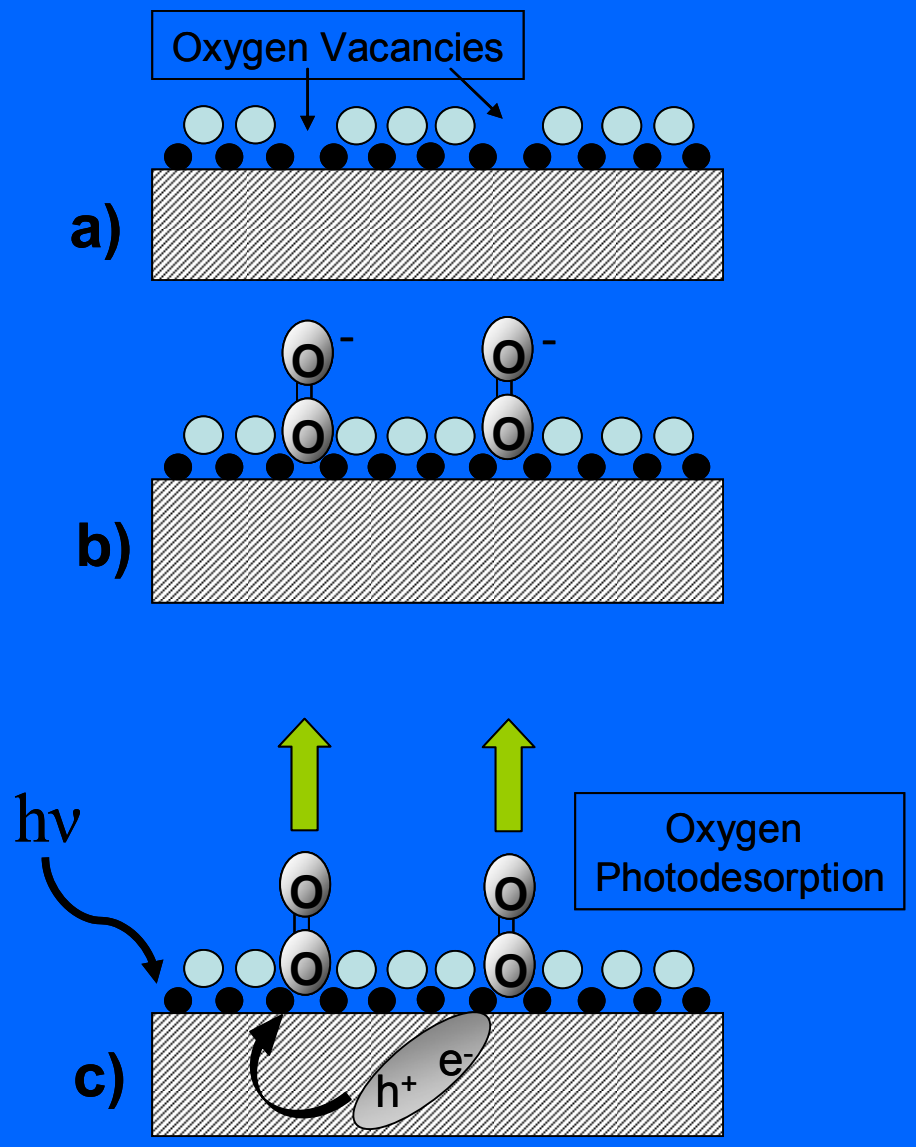


Bikondoa, O.; Pang, C. L.; Ithnin, R.; Muryn, C. A.; Onishi, H.; Thornton, G. *Nature Materials* 2006, *5*, 189.

Detailed Studies of O_2 Photodesorption from $TiO_2(110)$

- Providing insight into the mechanisms of photon-induced electron-hole pair production and the activation of adsorbed molecules by these charge carriers.

Mechanism for Oxygen Photodesorption from $TiO_2(110)$

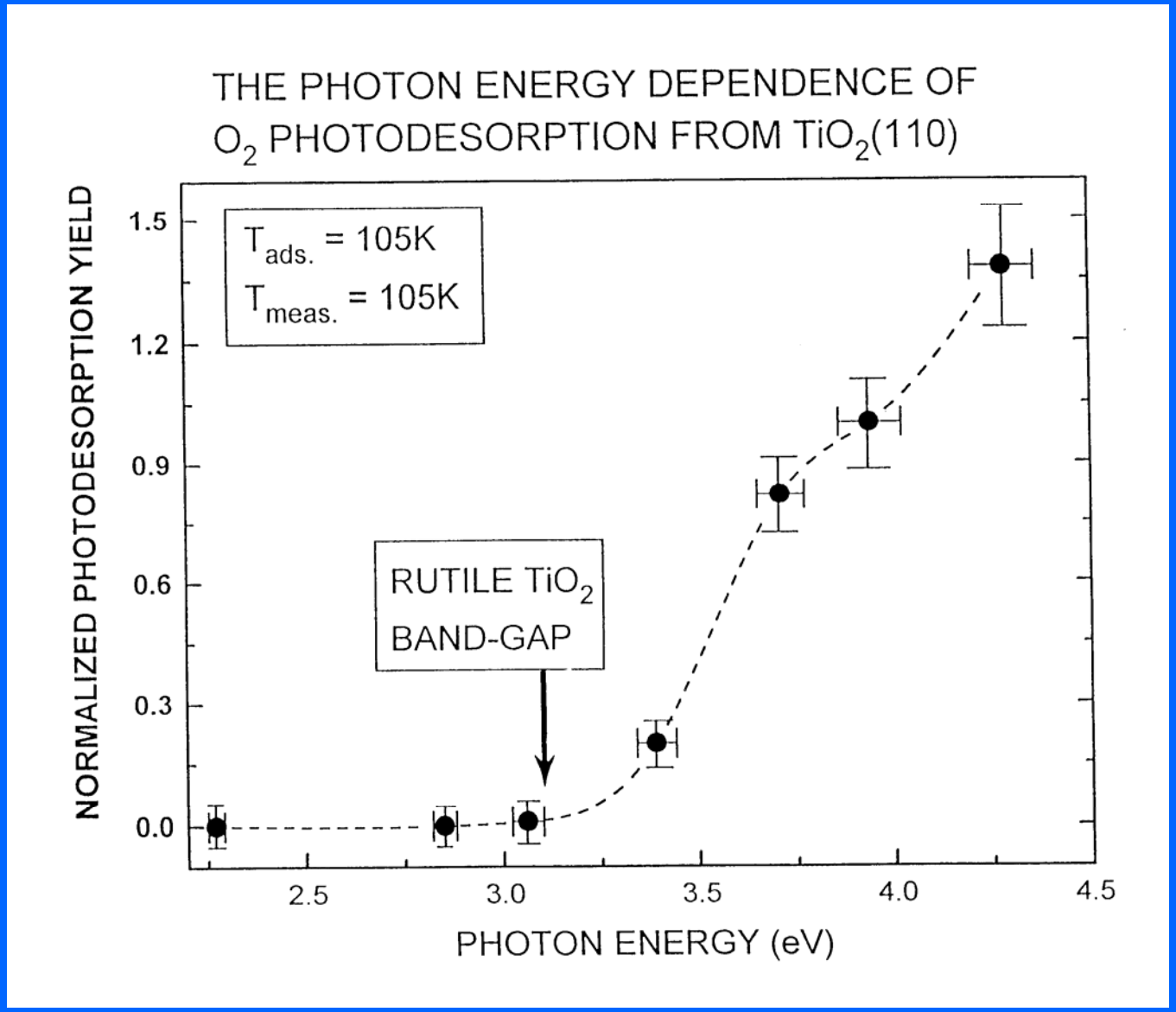


$$O_{VAC} + O_2 \rightarrow O_2^-$$

- de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* 2001, *115*, 4798-4810
- de Lara-Castells, M. P.; Krause, J. L. *Chem. Phys. Lett.* 2002, *354*, 483-490.
- Anpo, M.; Che, M.; Fubini, B.; Garrone, E.; Giamello, E.; Paganini, M. C. *Top. Catal.* **1999**, *8*, 189-198.

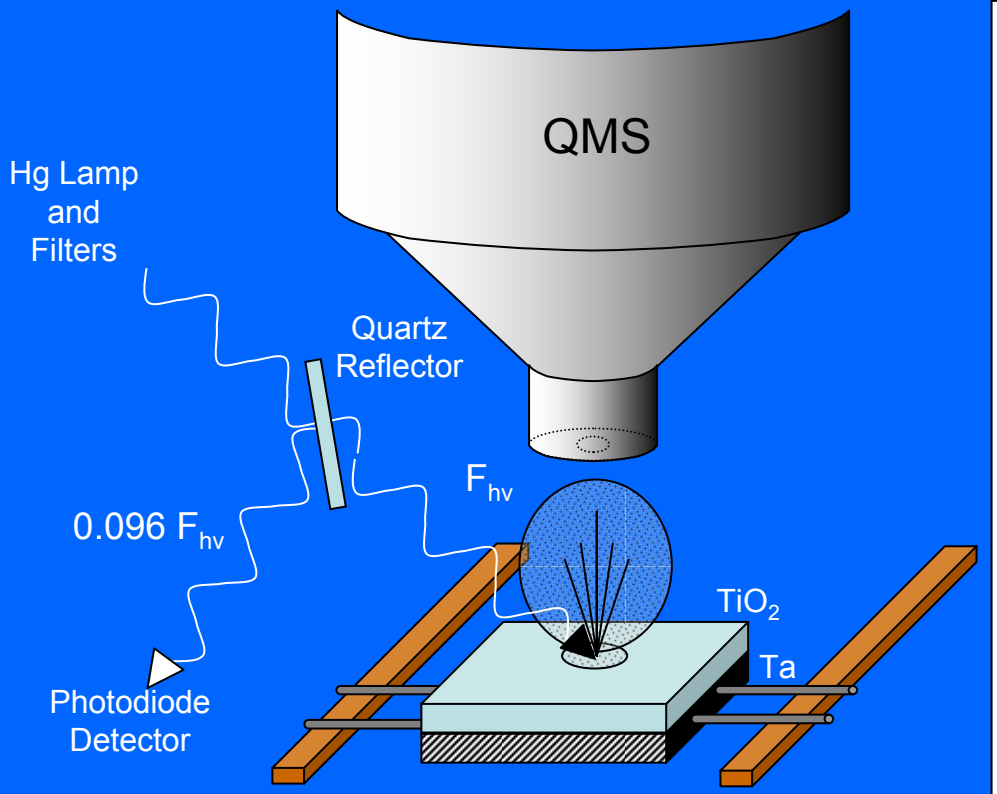
$$h^+ + O_2^- \rightarrow O_2\uparrow$$

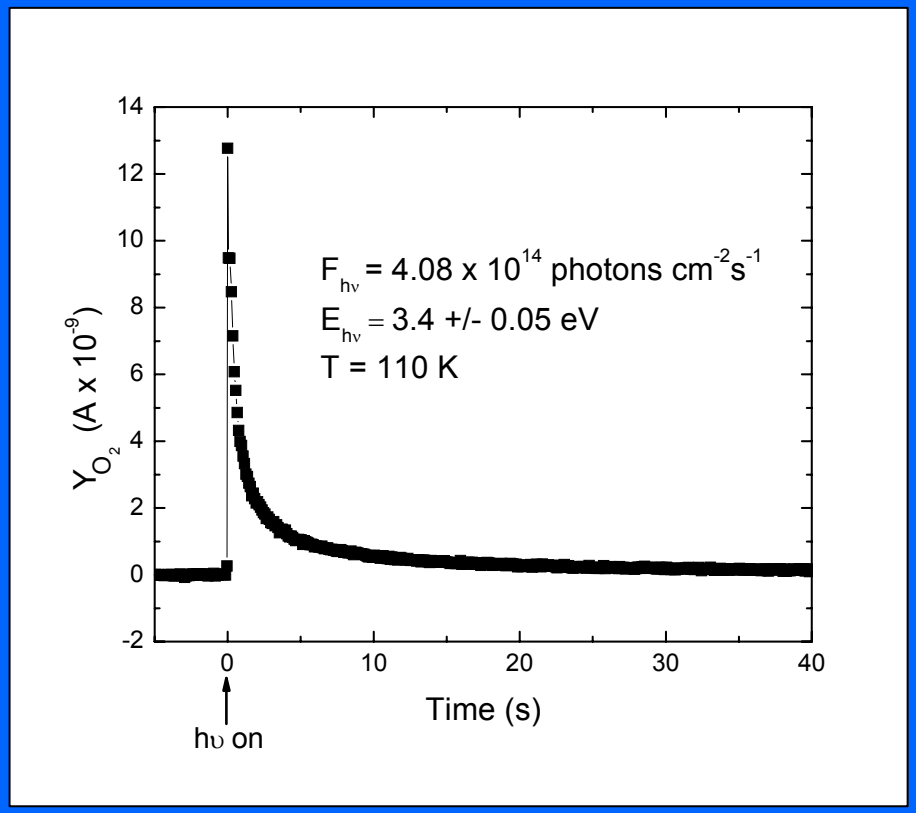
- de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* **2003**, *118*, 5098-5105.



G. Lu, A. Linsebigler and J. T. Yates, Jr., "The Adsorption and Photodesorption of Oxygen on the TiO2(110) Surface," J. Chem. Phys. 102, 4657 (1995).

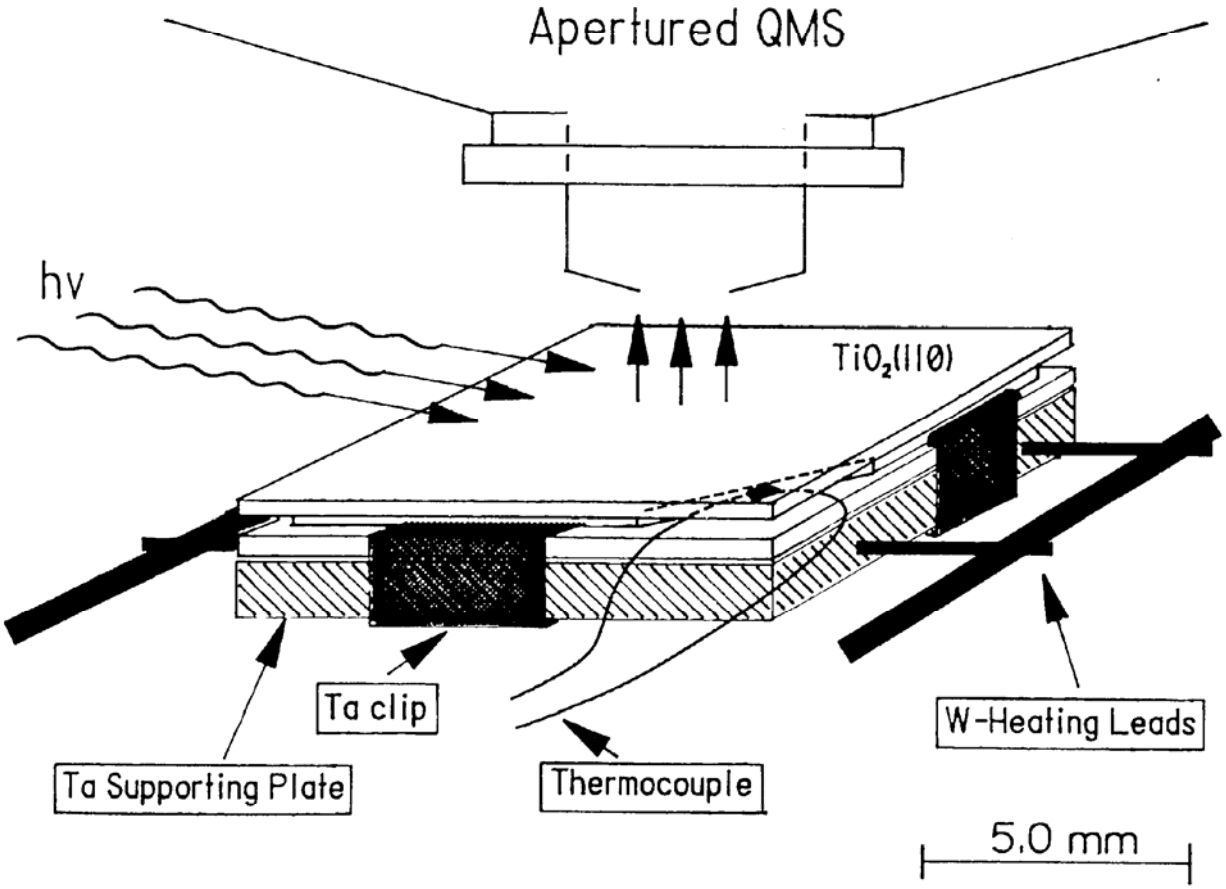
O_2 Photodesorption from $TiO_2(110)$





Tracy L. Thompson and John T. Yates, Jr. J. Phys. Chem. B, 109 (2005) 18230.

DESIGN OF CRYSTAL HOLDER FOR PHOTOCHEMISTRY ON $TiO_2(110)$ SINGLE CRYSTAL



O_2 Photodesorption from $TiO_2(110)$:

$$h\nu + TiO_2 \xrightarrow{k_1 F_{h\nu}} e + h$$

$$h + T \xrightarrow{k_2} T+ \quad \text{(hole capture by a hole trap)}$$

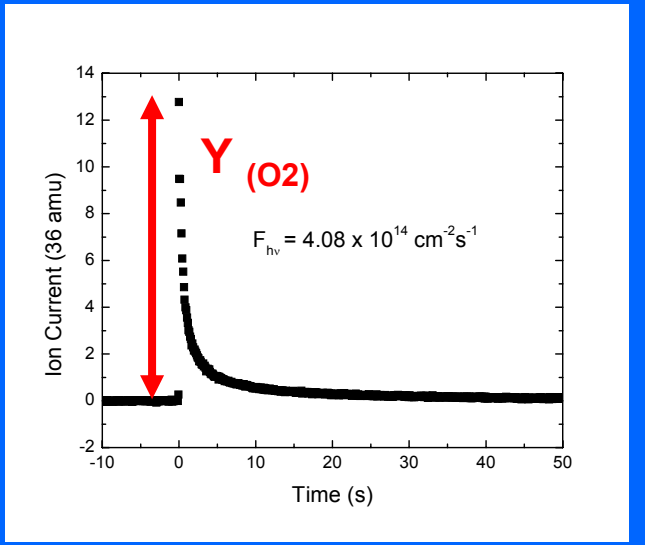
$$e + h \xrightarrow{k_3} heat \quad \text{(on recombination sites)}$$

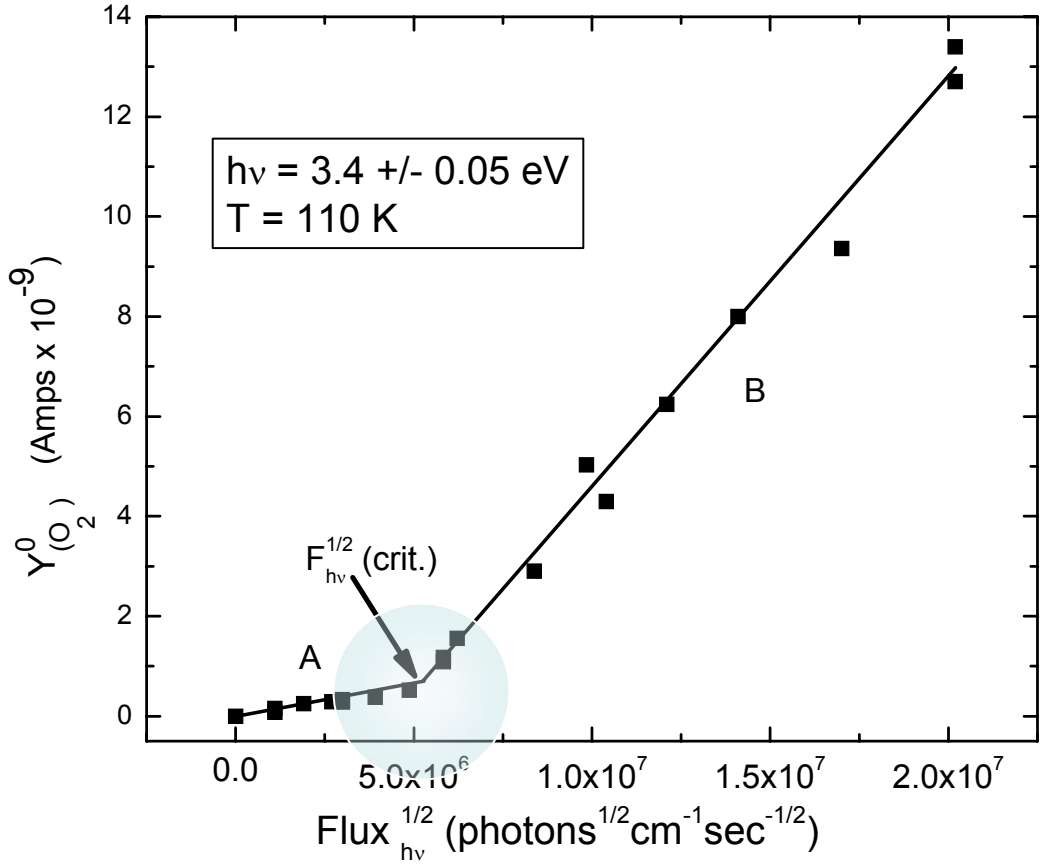
$$h + O_2^-(a) \xrightarrow{k_4} O_2(g) \uparrow$$

Rate of photodesorbing oxygen scales proportionally with the square root of the incident light intensity:

$$\frac{d[\theta_{O_2}]}{dt} = -k_4 \left(\frac{k_1}{k_2 + k_3} \right)^{1/2} F_{h\upsilon}^{1/2} [\theta_{O_2}]$$

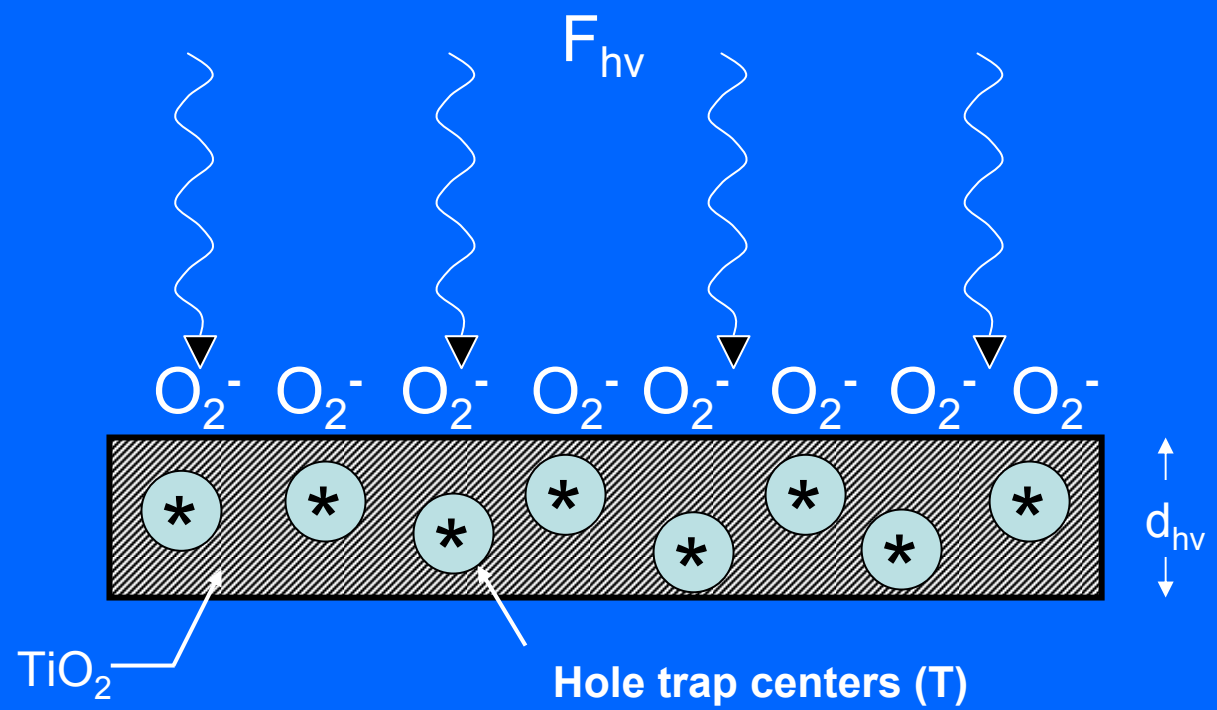
$^{18}O_2$ Initial Photodesorption Yield – $TiO_2(110)$





Bulk Hole Trapping Sites Within TiO_2

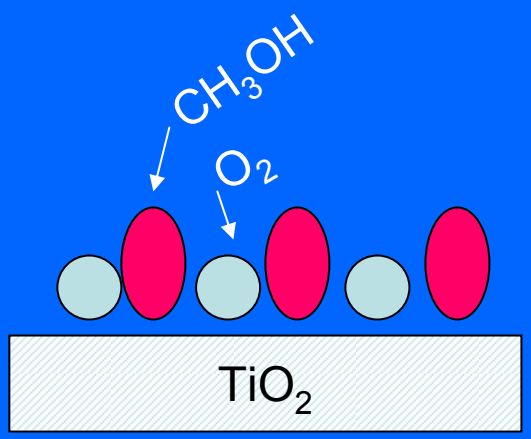
After hole trap filling, k_2 ceases to contribute to the charge exchange process.

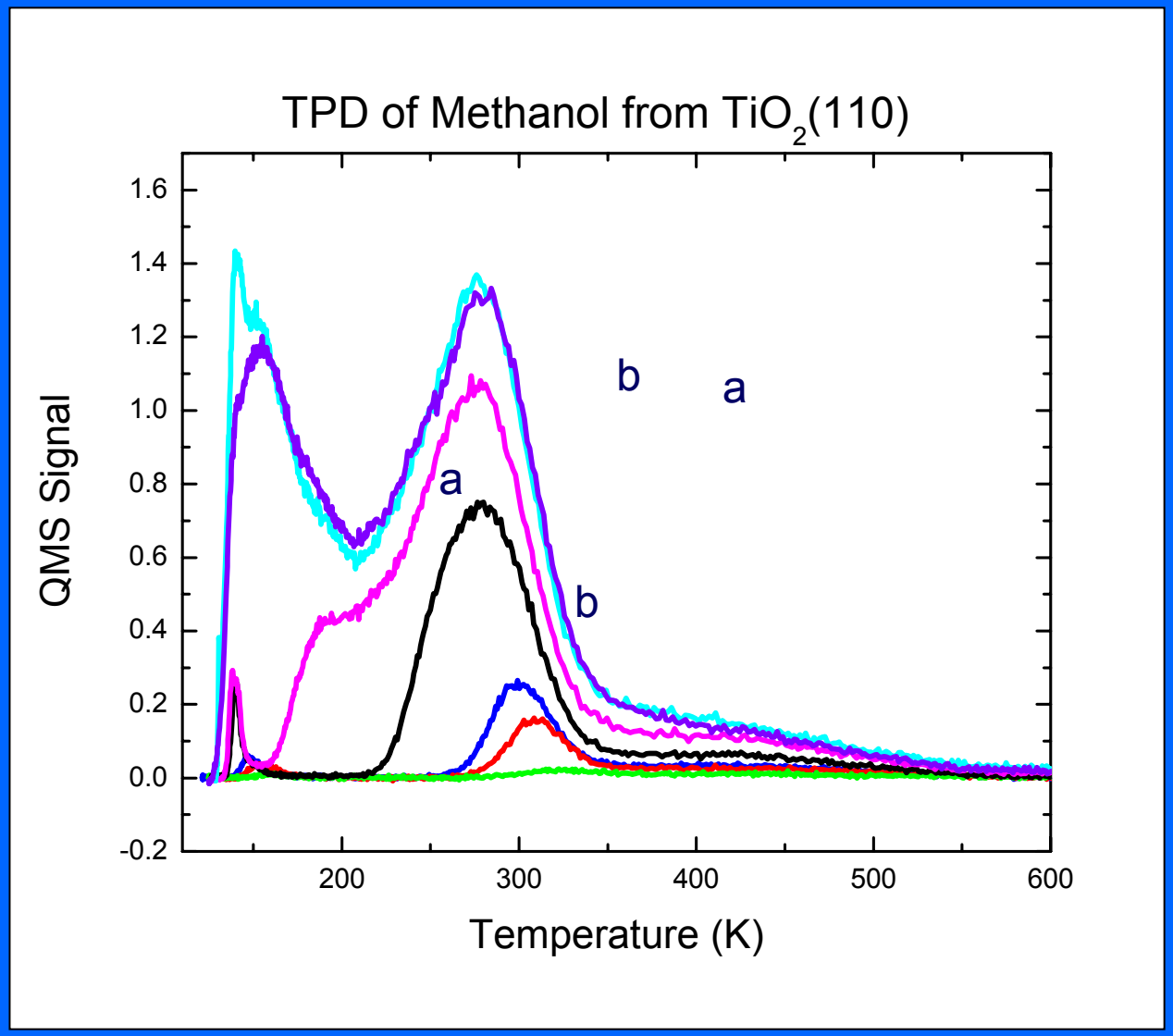


Hole trap centers (T) and average range of photogenerated holes which will be trapped.

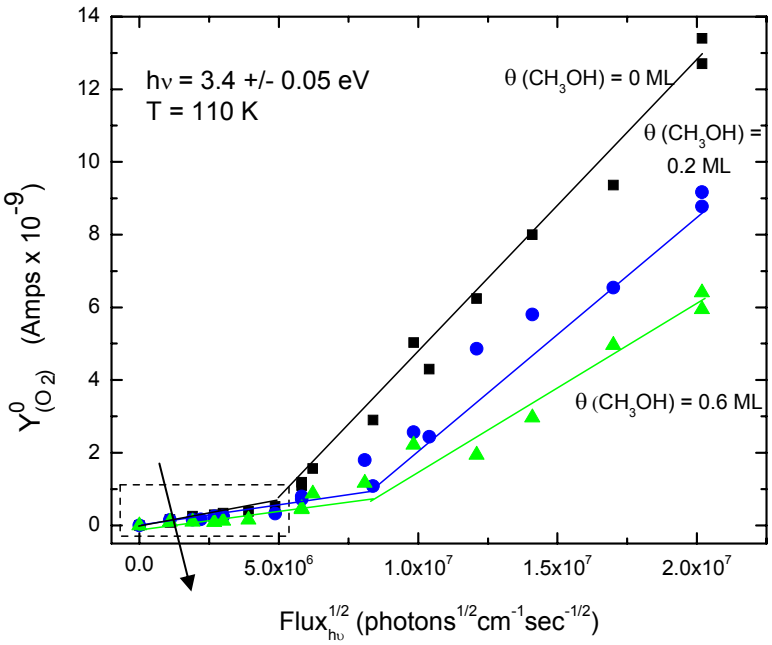
Use of Adsorbed Hole Trap Molecules to Increase Trap Density Above Bulk Density

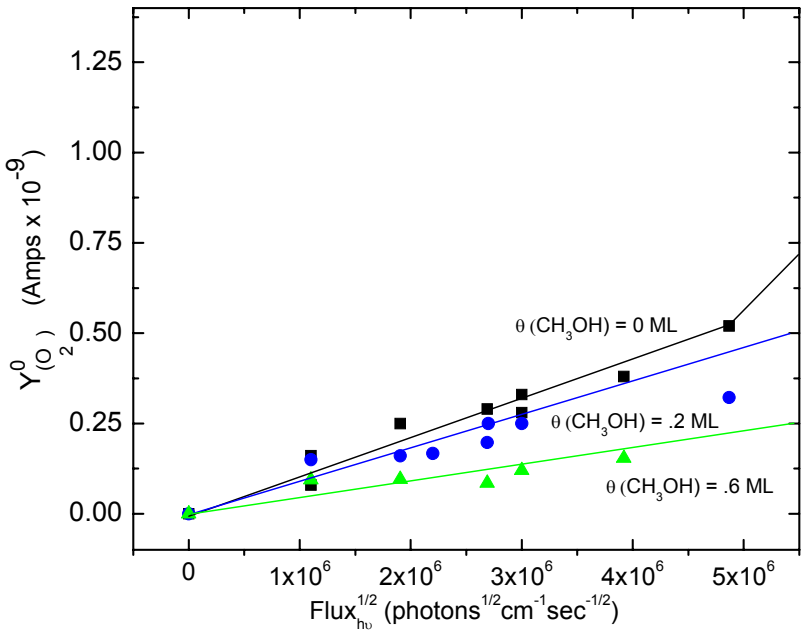
Role of CH_3OH Surface Hole Traps on O_2 Photodesorption Yield





Effect of CH_3OH (a) Hole Traps on Initial O_2 Photodesorption Yield



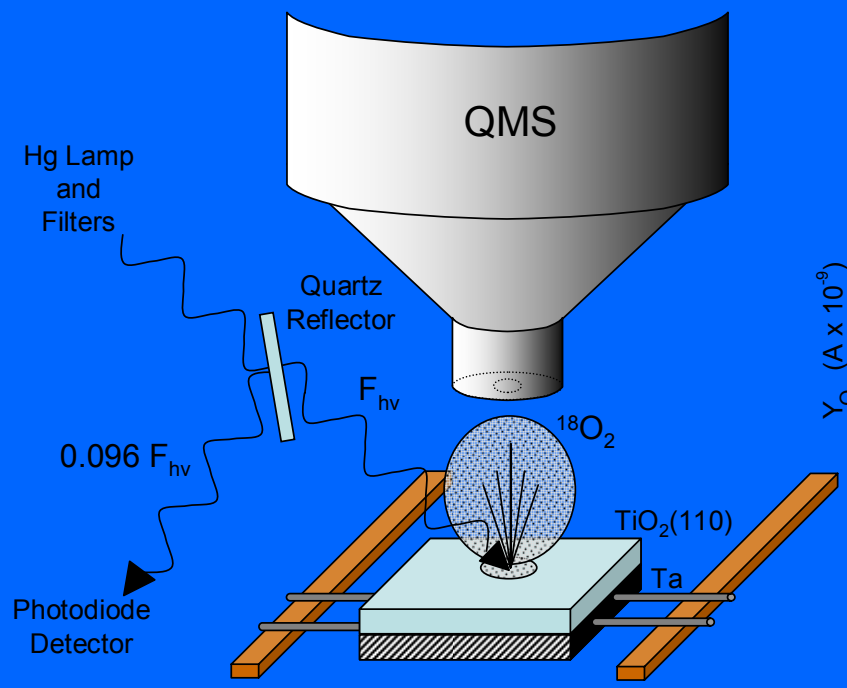


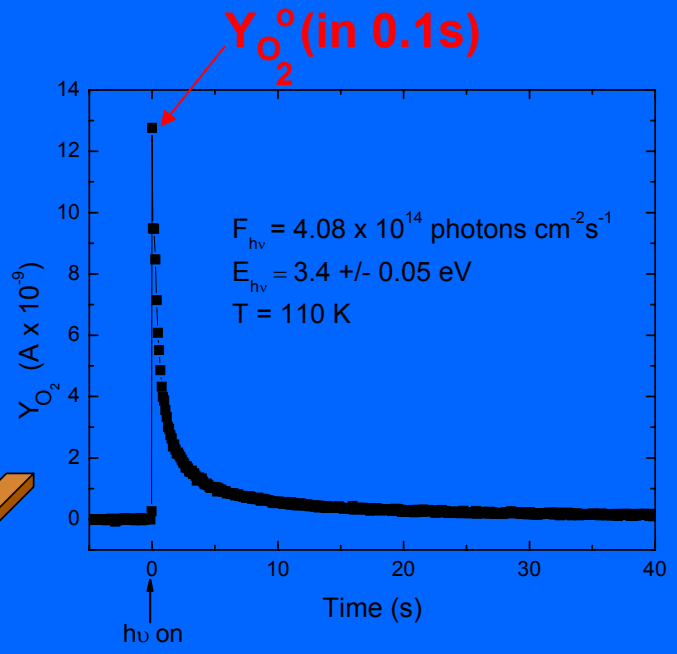
The critical point (where slope changes) is reflective of the filling of the active trap sites.
CH_3OH causes break point to move to higher $F_{h\upsilon}$.

Summary

- Charge carrier dynamics monitored by quantitatively studying a simple model photoreaction – O_2 photodesorption.
- $F_{h\upsilon}^{1/2}$ rate law found – caused by second-order e-h recombination kinetics.
- Artificial enhancement of hole trapping by adding CH_3OH – a hole trap molecule.

$^{18}O_2$ Photodesorption from $TiO_2(110)$





Kinetics of Hole Trapping-As Studied by O_2 Photodesorption

- Holes are either partially filled or completely filled by the time the first point is measured [in Δt (sampling)].
- Δt (sampling) = 0.10 seconds
- Therefore, at F_{hv}(crit.):
- 0.10 s x F_{hv}(critical) = # photons needed to saturate holes in photon penetration depth.
- Photon penetration depth = ~100Å x 10^{-8}cm $Å^{-1}$ = 10^{-6} cm
- Therefore, density of traps = ~ F_{hv}(crit) x Δt / 10^{-6} cm = ~ 3 x 10^{18} cm^{-3}

Conclusion- O_2 Photodesorption Detector of Hole Trapping Phenomenon

- First highly-controlled study of charge carrier trapping effect on TiO_2 single crystal.
- Hole trapping strongly inhibits surface photoreaction.
- Hole trap density estimated to be ~$3x10^{18}cm^{-3}$.
- This hole trap density corresponds to ~$3x10^{-5}$ fraction of atomic sites in the crystal bulk.

- So far you have seen only kinetic measurements of the initial rate of $O_2(a)$ photodesorption – $Y^{O}_{O_2}$ at constant θ_{O_2}

- Studies of the rate of photodesorption as a function of time and the depletion of $O_2(a)$ have yielded exciting new results.

O_2 Photodesorption from $TiO_2(110)$:

$$hv + TiO_2 \xrightarrow{k_1 F_{hv}} e + h$$

$$h + T \xrightarrow{k_2} T+ \quad \text{(hole capture by a hole trap)}$$

$$e + h \xrightarrow{k_3} heat \quad \text{(on recombination sites)}$$

$$h + O_2^-(a) \xrightarrow{k_4} O_2(g) \uparrow$$

Yield of photodesorbing oxygen scales proportionally with the square root of the incident light intensity:

$$\frac{d[\theta_{O_2}]}{dt} = -k_4 \left(\frac{k_1}{k_2 + k_3} \right)^{1/2} F_{h\upsilon}^{1/2} [\theta_{O_2}]$$

Photoexcitation Behavior Above F_{hv} (crit.) in Kinetic Regime B

$$h + T \xrightarrow{k_2} T^+$$

- **Upon saturation of hole traps above F_{hv} (crit.)**

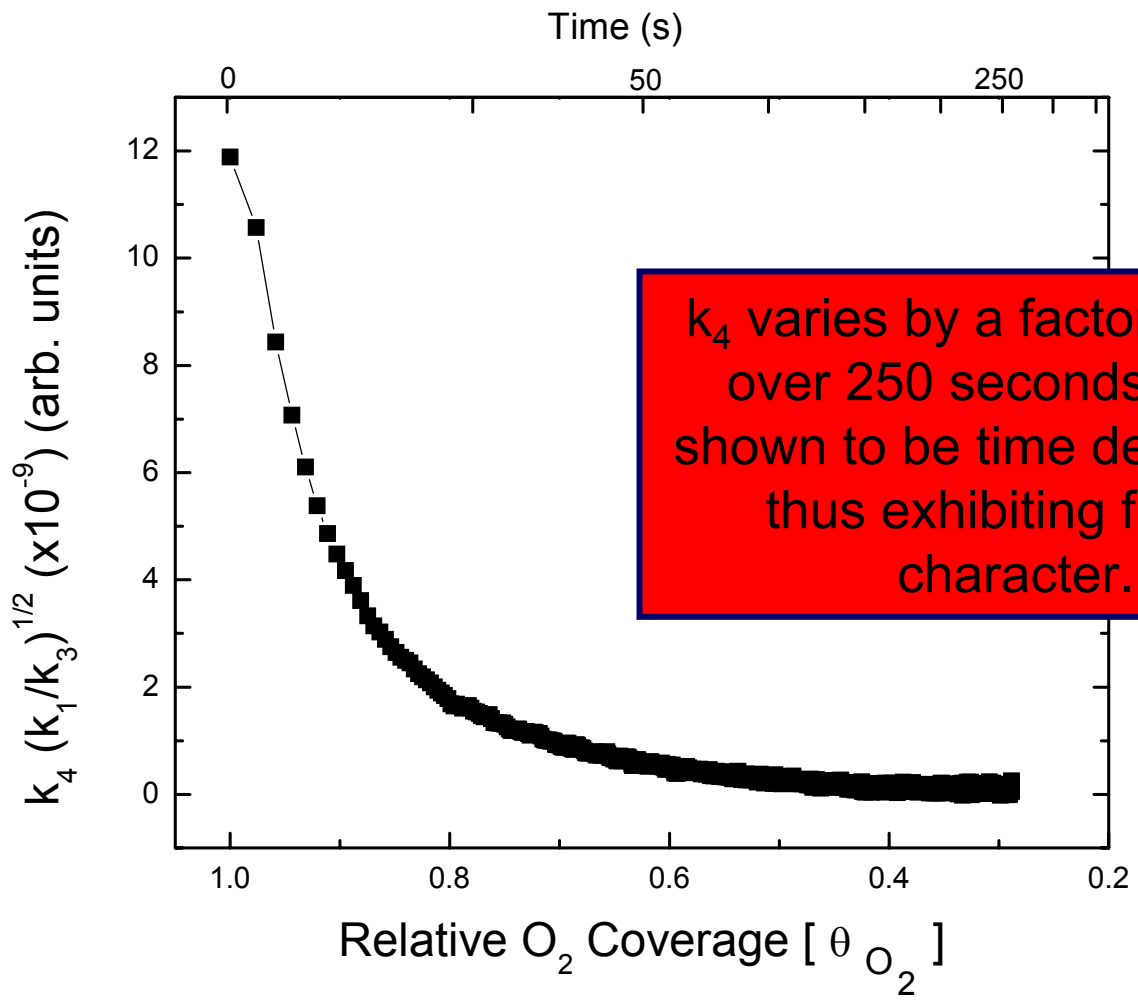
$$\mathbf{k_2 \longrightarrow 0}$$

$$\frac{d[\theta_{O_2}]}{dt} = -k_4 \left(\frac{k_1}{\cancel{k_2} + k_3} \right)^{1/2} F_{h\upsilon}^{1/2} [\theta_{O_2}]$$

$$\int \frac{d \ln[\theta_{O_2}]}{dt} = -\int k_4 \left(\frac{k_1}{k_3} \right)^{1/2} F_{h\upsilon}^{1/2}$$

$$\frac{1}{F_{h\upsilon}^{1/2}} \cdot \ln[\theta_{O_2}] = -k_4 \left(\frac{k_1}{k_3} \right)^{1/2} \cdot t$$

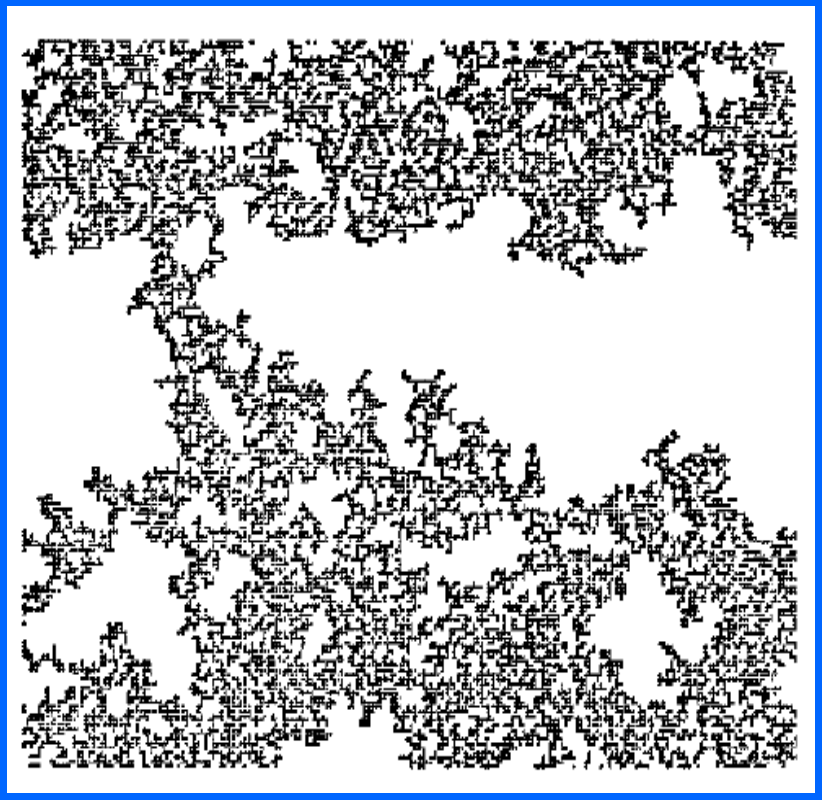
Range of Experimentally Measured Photodesorption Rate Constants



k_4 varies by a factor of ~100 over 250 seconds and is shown to be time dependent, thus exhibiting fractal character.

Time-dependent rate constants are described by a Fractal Kinetic Process

Rate Coefficient



"Percolation Cluster"

$$k = k_1 \, t^{-h} \quad where \;\; 0 \le h \le 1$$

instantaneous rate coefficient

fractal term

h = 0 – infinite mixing

h = ½ - one dimensional transport

R. Kopelmann, Science 241 (1988) 1620.

R. Kopelman in "Fractal Approach to Heterogeneous Chemistry" (1989) 295.

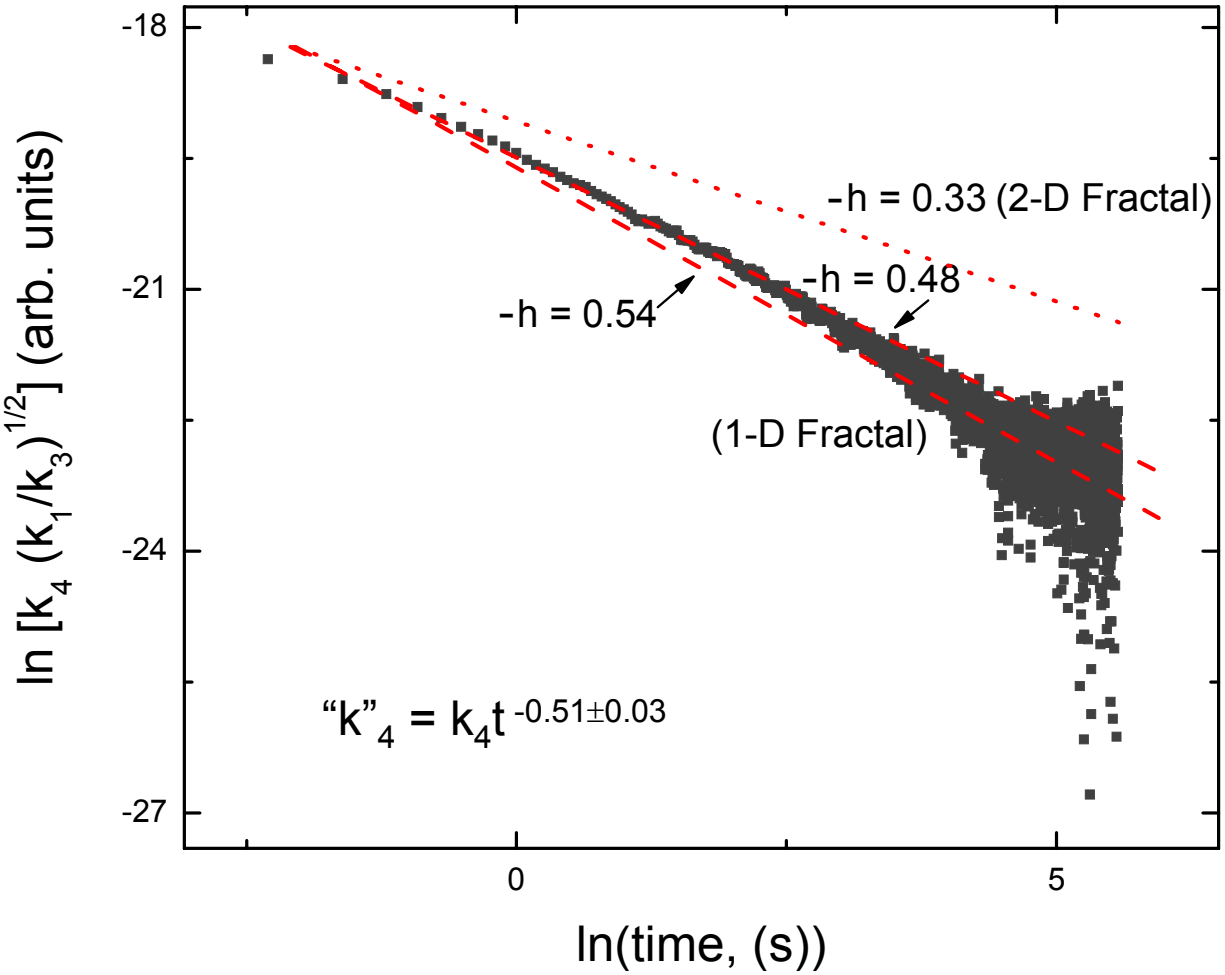
R. Kopelman, J. Stat. Phys. 42 (1986) 185.

$$k = k_1 \cdot t^{-h}$$

$$\ln k = -h \ln t + const.$$

ln k versus ln t should give a straight line with slope = -h

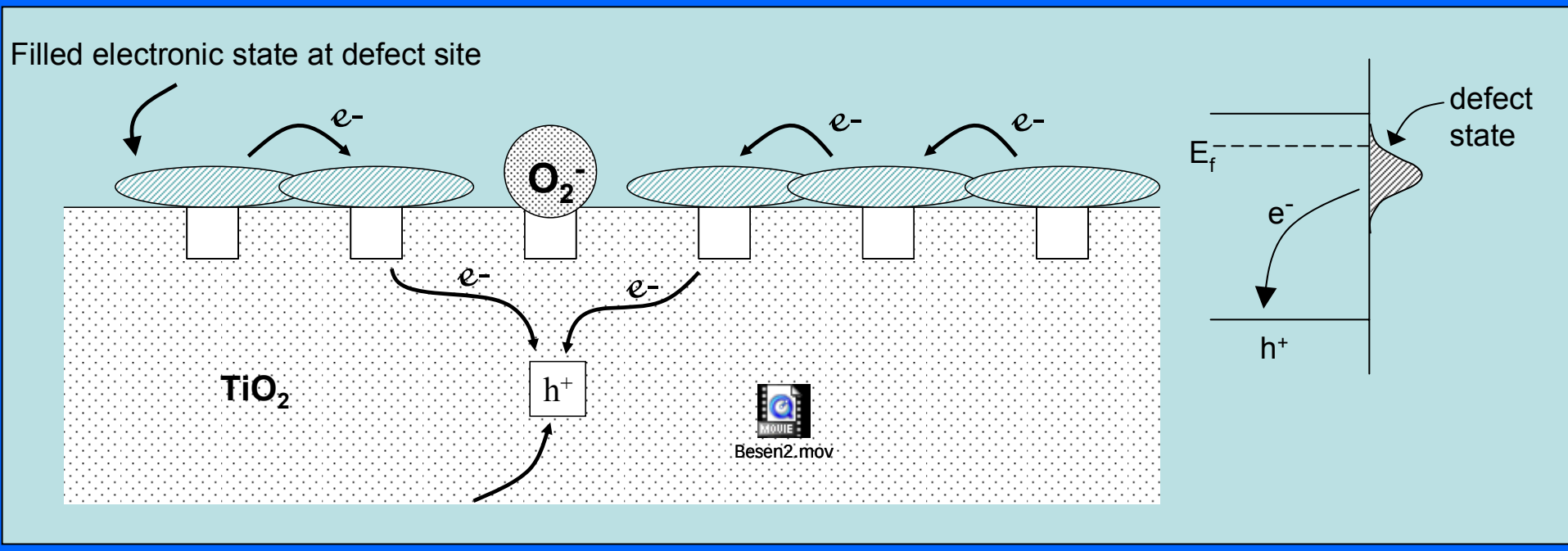
Fractal Kinetic Behavior of the Photodesorption of O_2 from $TiO_2(110)$



A tentative new model explaining the 1-D fractal O_2 desorption kinetics is proposed.

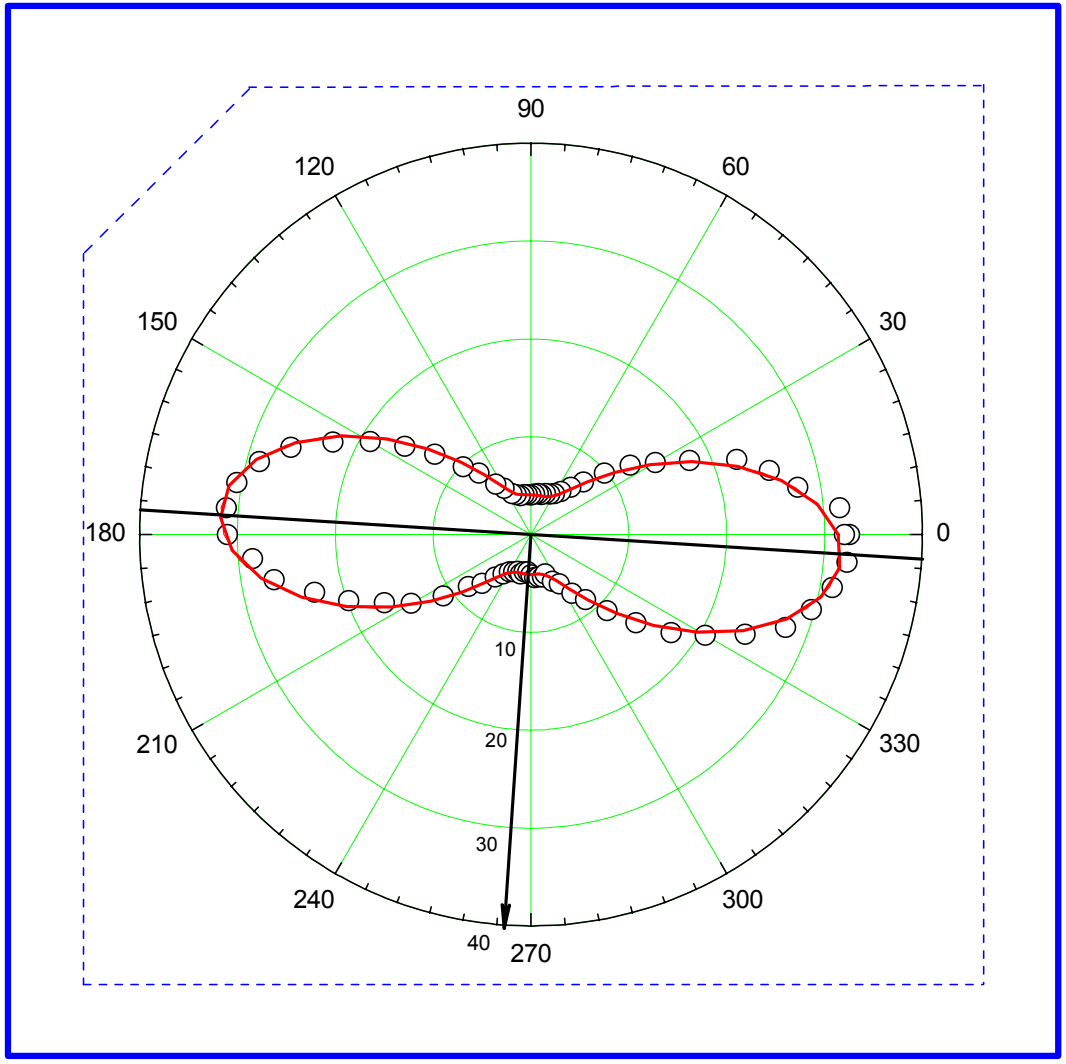
T. L. Thompson and J. T. Yates, Jr., "Control of a Surface Photochemical Process by Fractal Electron Transport Across the Surface: O_2 Photodesorption from TiO_2(110)," J. Phys. Chem. B 110, 7431 (2006).

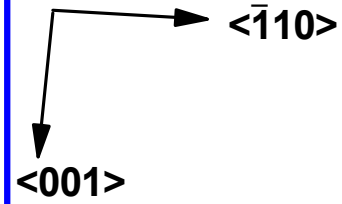
Fractal Electron Transport via O-Vacancy Sites



- **"Charge Cloud" associated with vacancy -** Vijay and Metiu, *J. Chem. Phys.* 118 (2003) 6536.
- **"Charge Cloud" causes enhanced electron transport across the crystal surface.**
- **Reduced efficiency of CT between photoproduced holes and adsorbed O_2^-.**

Anisotropy in the Bulk Resistivity of TiO_2(110) Crystal – Four-point Probe Measurements at 300 K





O. Byl and J. T. Yates, Jr. 2006

Summary and Conclusions:

- Charge clouds surrounding surface oxygen vacancies combine to form a percolation network for electron transport across the surface causing a decrease in the efficiency of photodesorption of O_2.

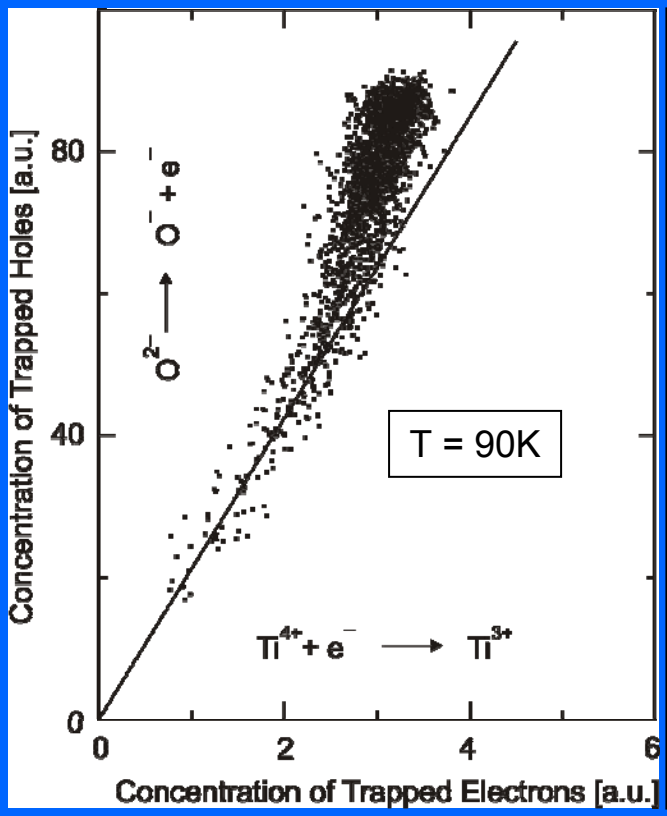
- A kinetic analysis of the O_2 photodesorption process reveals that the rate coefficient for photodesorption changes by a factor of > 100 over ~ 250 seconds.

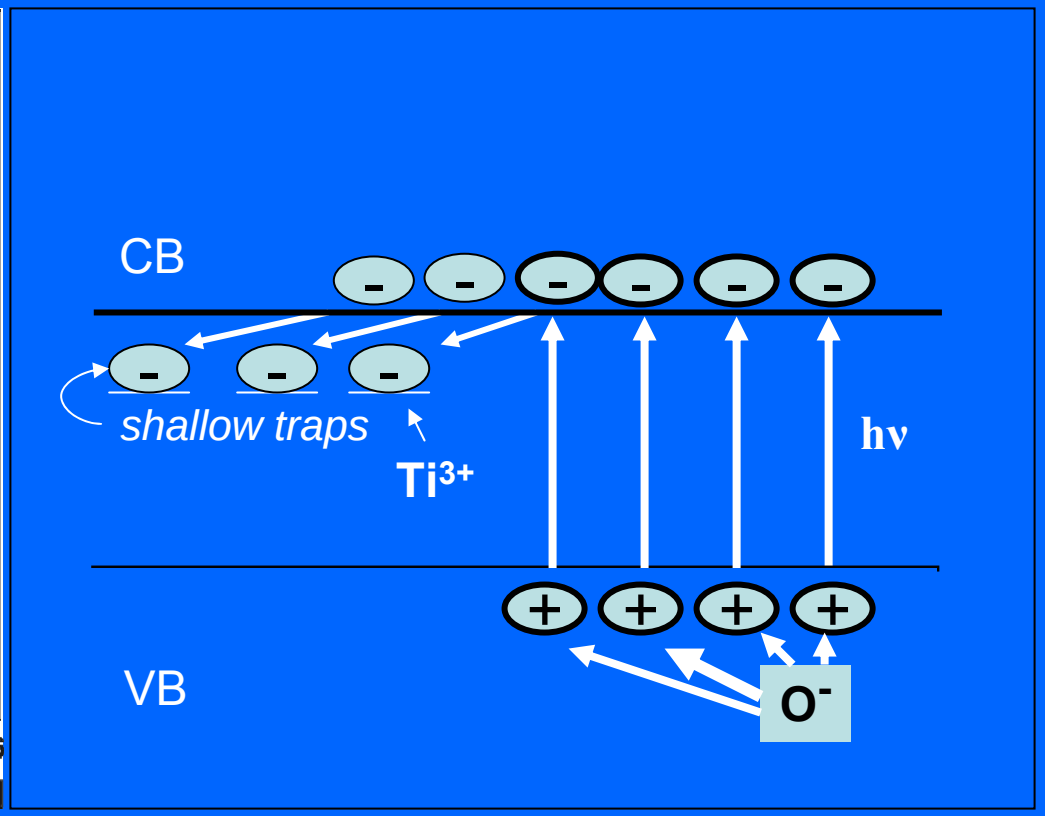
- Electron transport across the surface is likely to be one-dimensional, based on the fractal analysis. Significant anisotropy in conduction through TiO_2 has been observed in bulk measurements.

Studies on TiO_2 Powder

- ESR
- IR

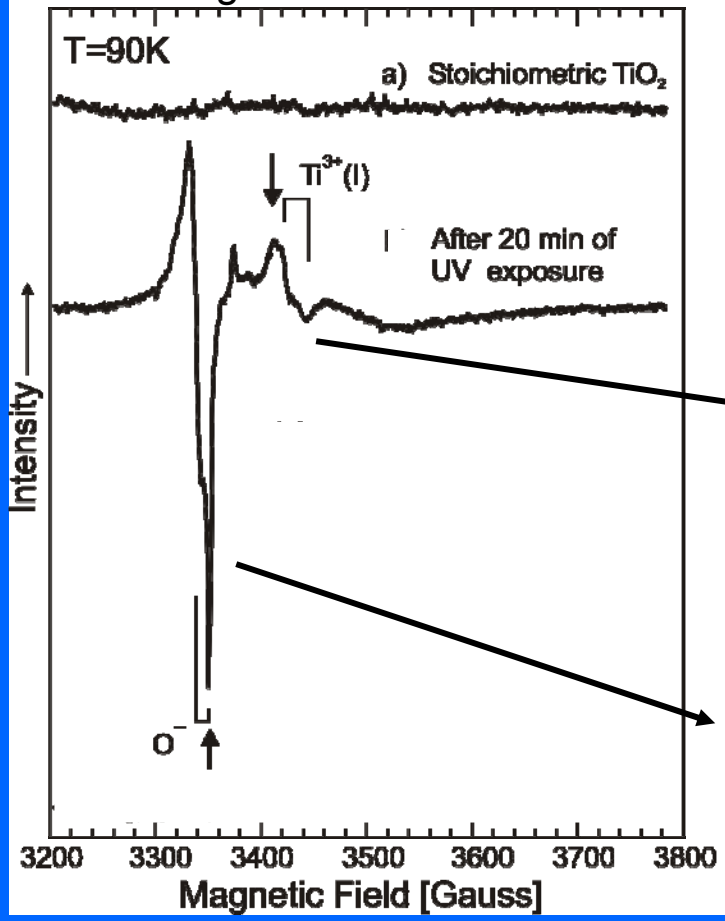
Correlation Between Photogenerated Electron and Hole Production at 77K in TiO_2 Powder

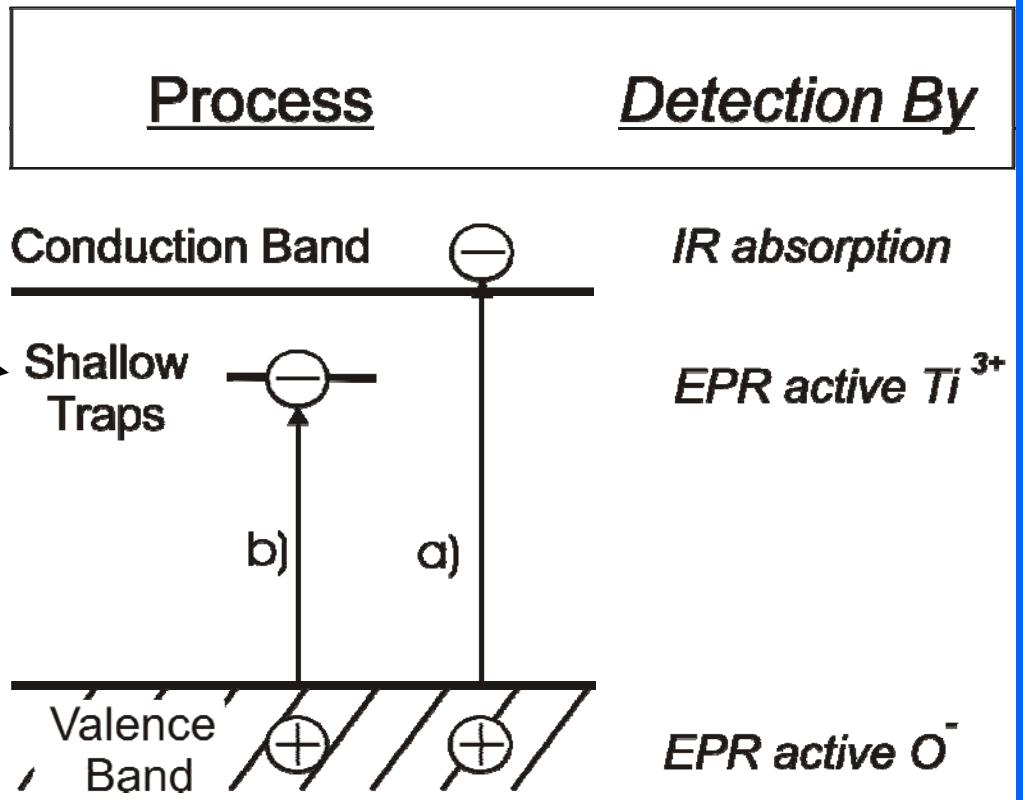




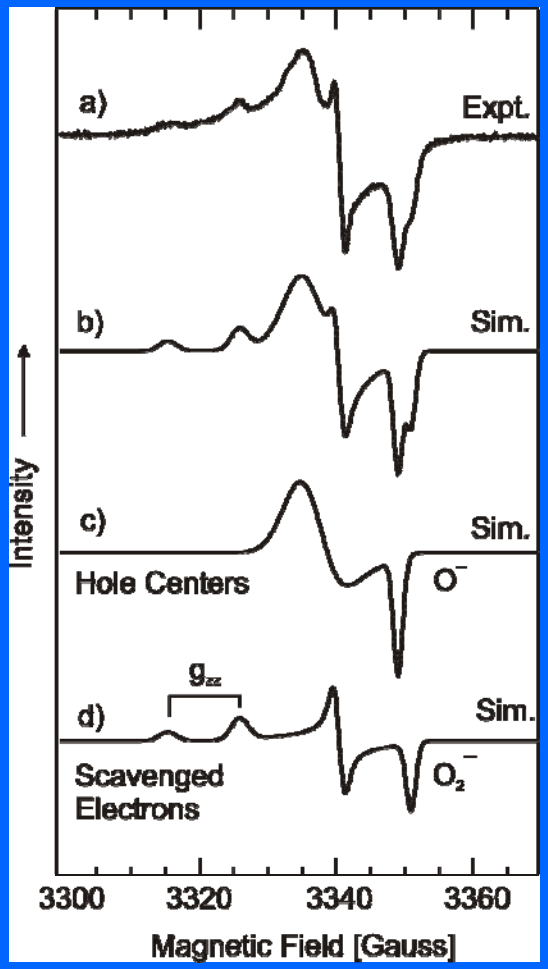
T. Berger, M. Sterrer, O. Diwald, E. Knözinger, D. Panayotov, T. L. Thompson and J. T. Yates, Jr. J. Phys. Chem. B 109, 6061 (2005)

EPR Signature for Ti^{3+} and O^{-}





O_2 (a) as an Electron Scavenger: Production of O_2^- (ads.)

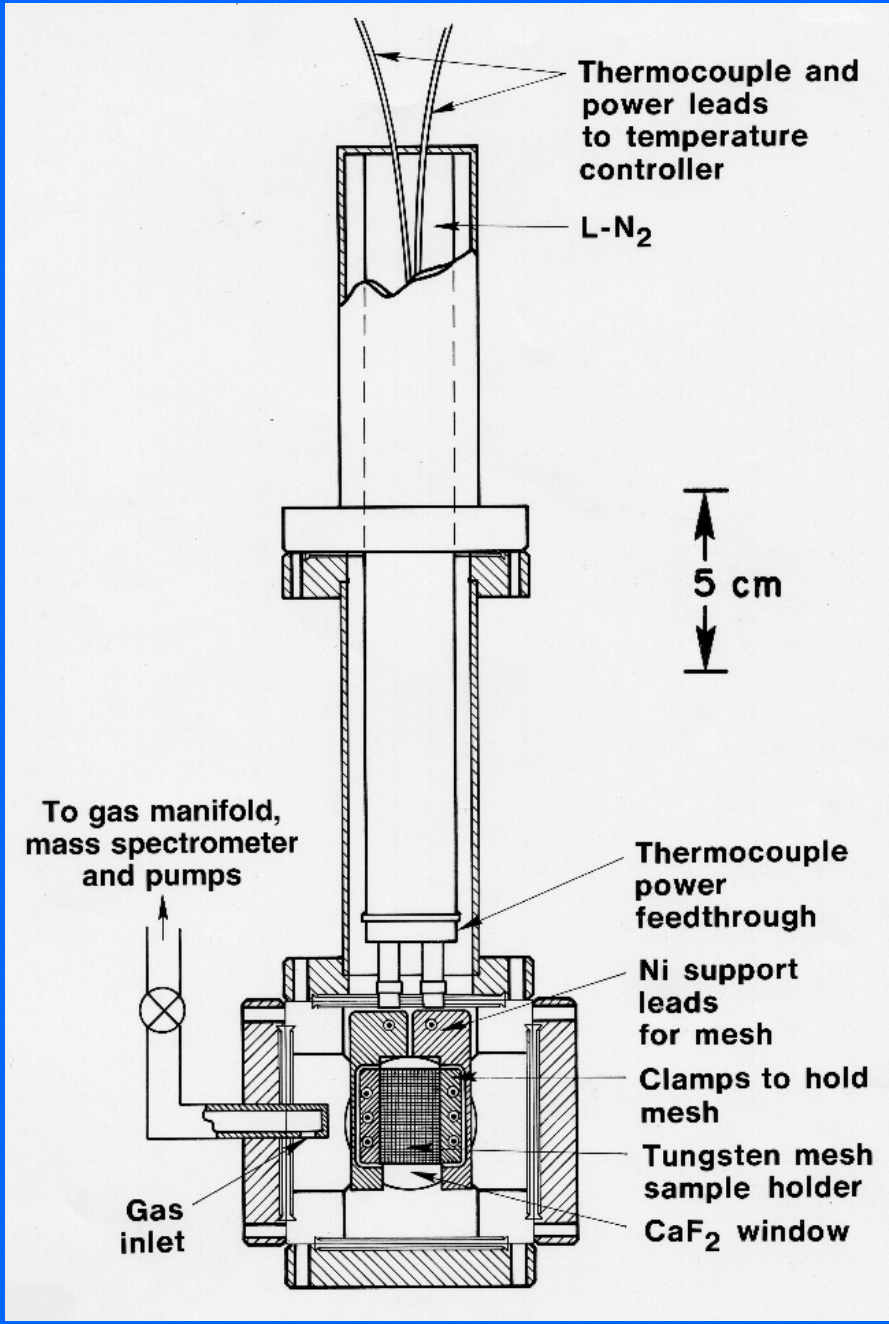


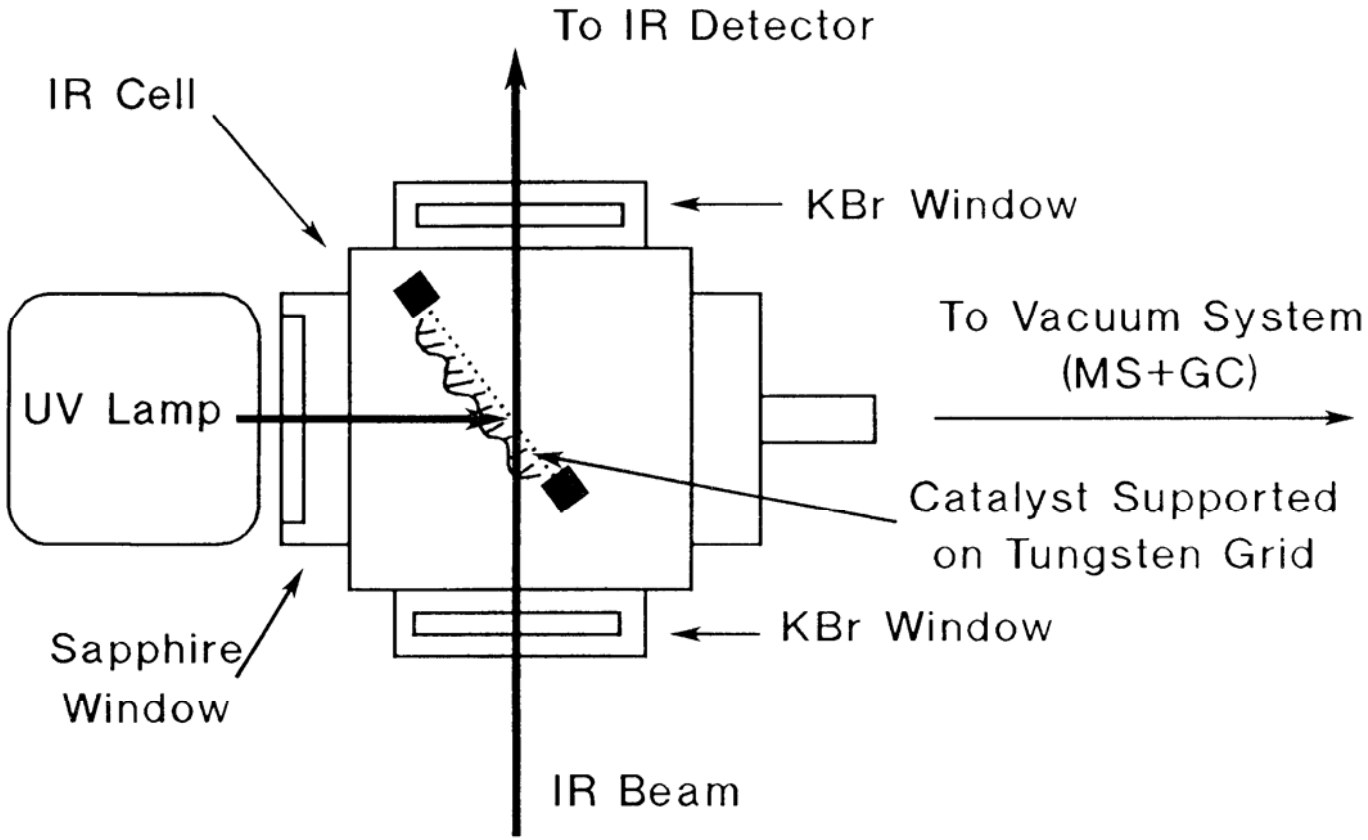
$TiO_2 + O_2(a)$

$\downarrow h\nu$

lattice O^- (hole)
+
scavenged e ($O_2^-(a)$)

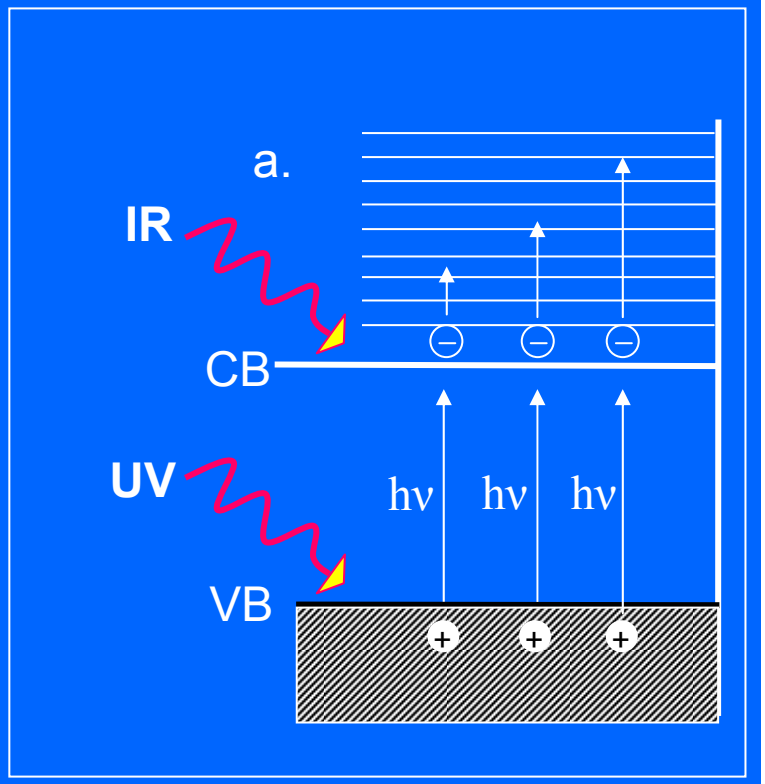
IR Spectroscopy Can Be Used To See Electrons Excited Into Conduction Band

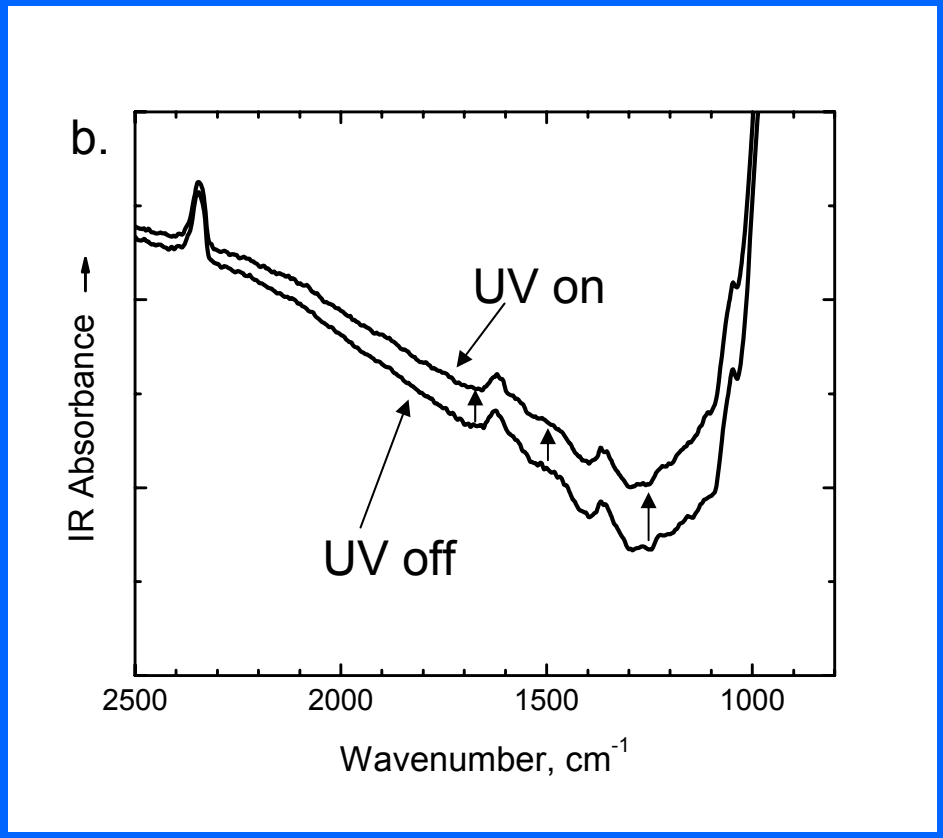

Thermocouple and power leads to temperature controller
L-N_2
5 cm
To gas manifold, mass spectrometer and pumps
Thermocouple power feedthrough
Ni support leads for mesh
Clamps to hold mesh
Tungsten mesh sample holder
CaF_2 window
Gas inlet



OPTICAL DESIGN OF CELL FOR SIMULTANEOUS PHOTOCHEMISTRY AND IR SPECTROSCOPY ON POWDERED CATALYST

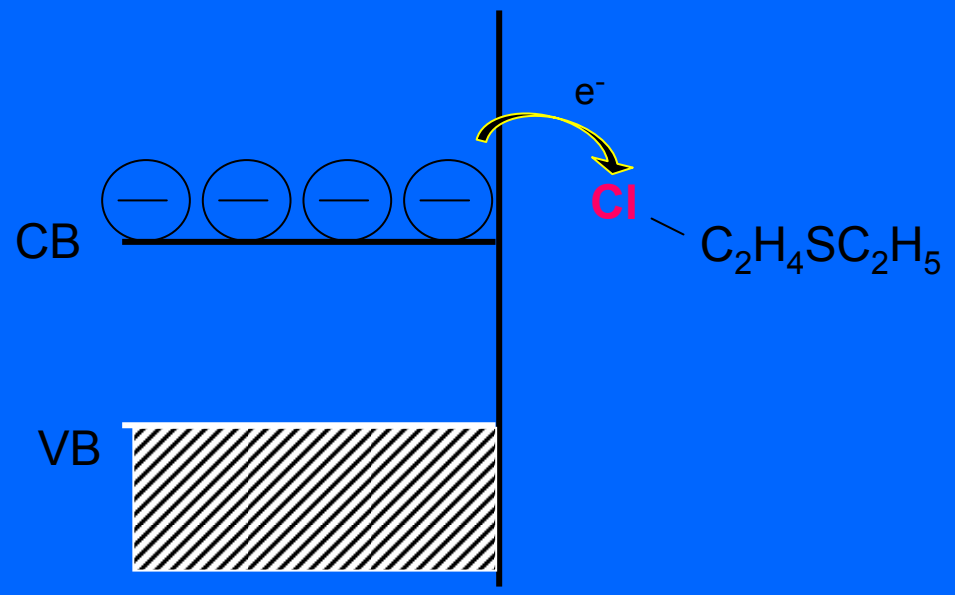
UV-Induced Increase of IR Background – CB Trapping



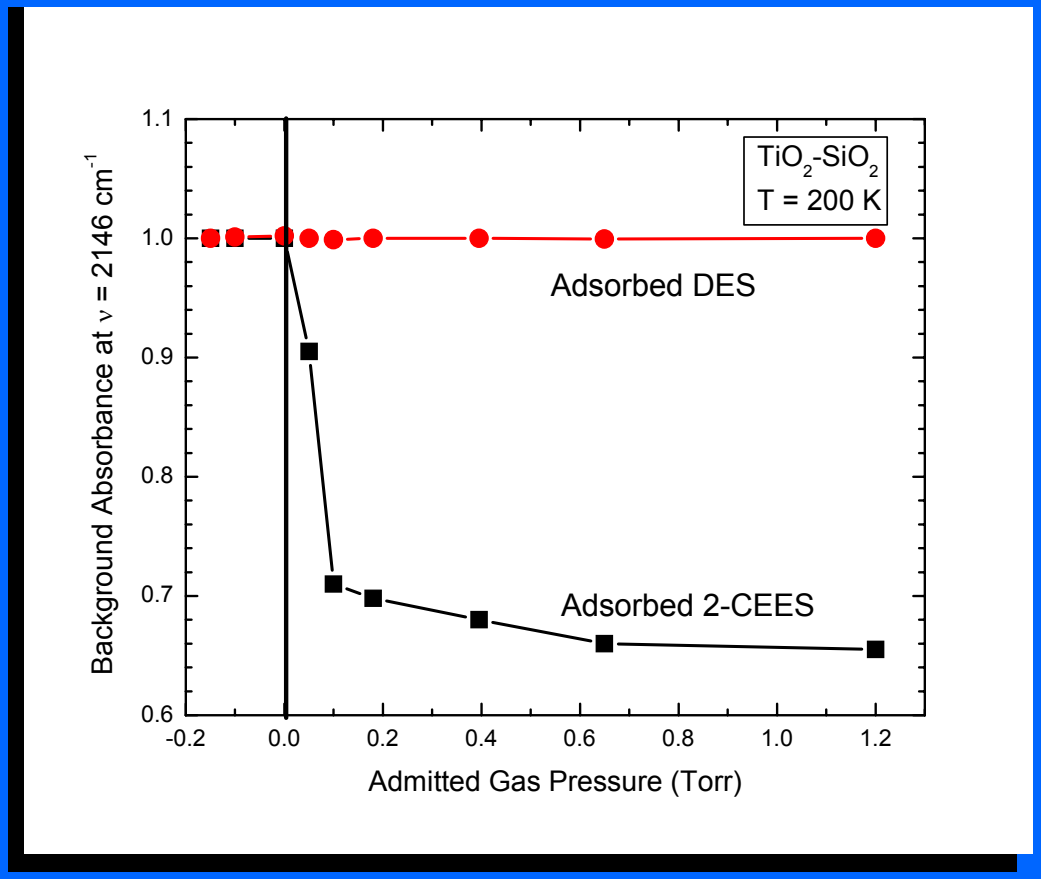


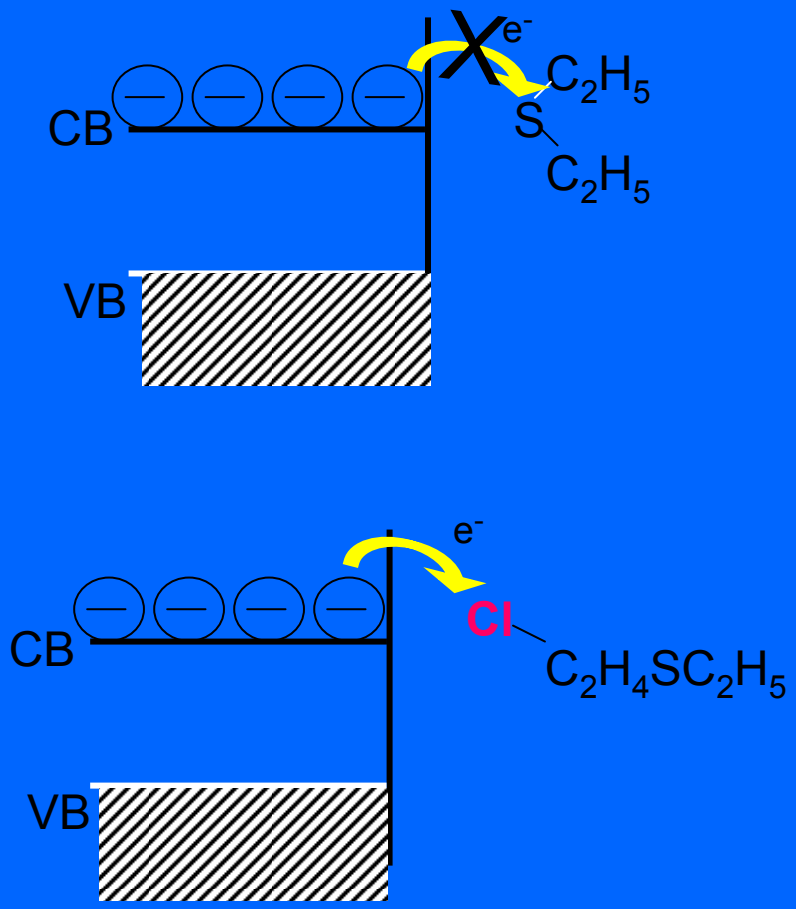
T. Berger, M. Sterrer, O. Diwald, E. Knözinger,
D. Panayotov, T. L. Thompson and J. T. Yates, Jr.
J. Phys. Chem. B 109, 6061 (2005)

Conduction Band Electrons Transfer to Adsorbed Organic Molecules



Preferential Electron Transfer: TiO_2 CB Electrons to Electrophilic Molecules





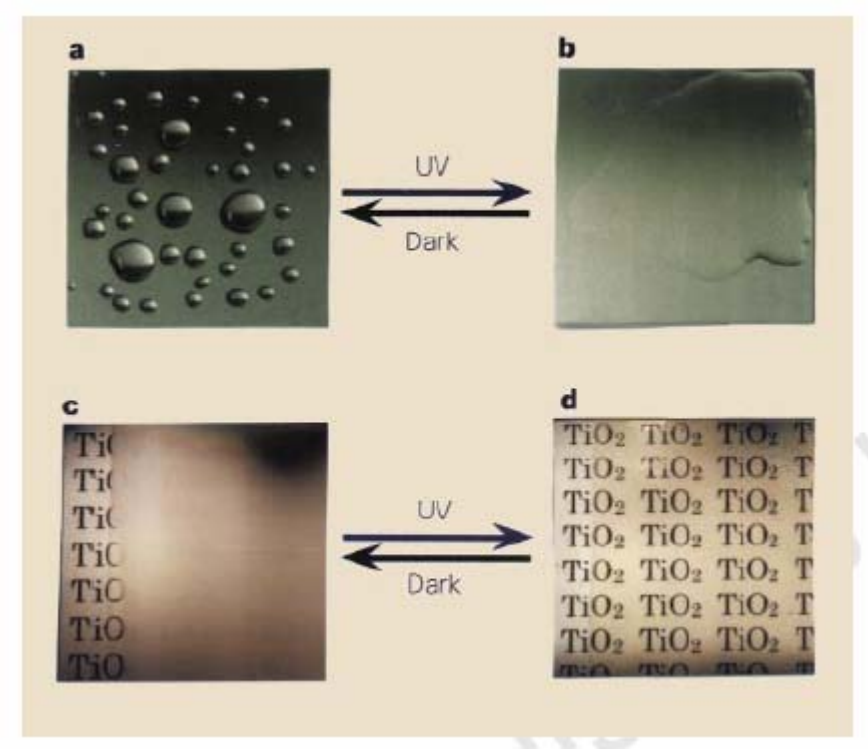
- **CB electron transfer to electrophilic <u>atom</u> in adsorbed molecules**

SUMMARY

- Oxygen Vacancy Defects – Made by Heating Above 700 K
- O_2 Adsorbs on Vacancies
- Hole Traps Retard Photochemistry of O_2
- ESR and IR Effective Tools for Detection of Holes [O^{-1}] and CB Electrons in TiO_2 Powders
- CB Electrons Populated by UV at 130 K as Seen by IR Background Shift
- CB Electrons Depopulated by Electrophilic Organic Adsorbates – need electronegative atom

A Recent Development- Explanation of UV-Induced TiO_2 Hydrophilicity

“Light-Induced Amphiphilic Surfaces”

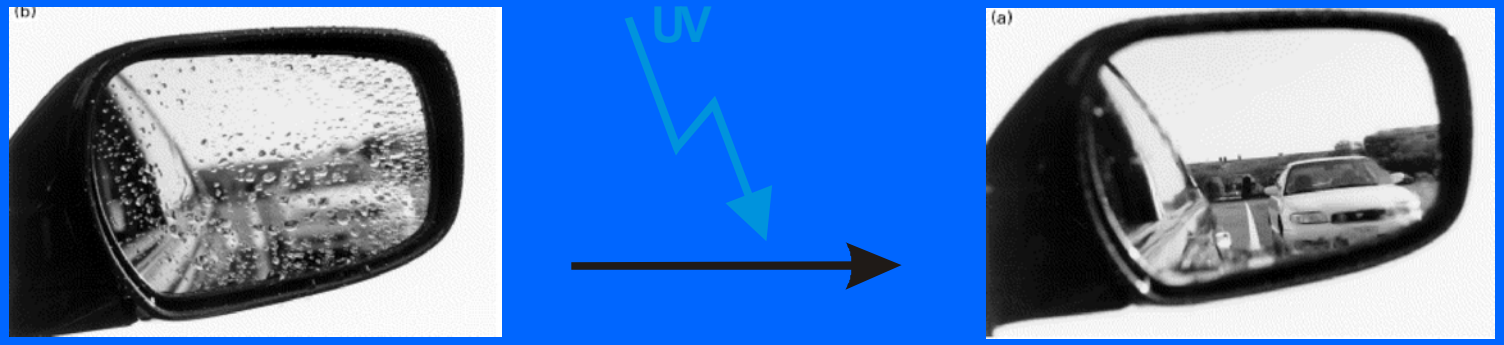


Rong Wang, Kazuhito Hashimoto, Akira Fujishima, Makota Chikuni, Eiichi Kojima, Atsushi Kitamura, Mitsuhide Shimohigoshi, Toshiya Watanabe

Nature, **388** (1997) 870-873.

TiO_2 - UV-induced Hydrophilicity - Applications
Anti-fogging

Taken from: Fujishima, Hashimoto, Watanabe, "TiO_2-Photocatalysis, Fundamentals and Applications", BKC Inc. Tokyo, 1999



Taken from: Hata, Kai, Yamanaka, Oosaki, Hirota, Yamazaki, JSAE Review 21, 97-102, 2000

60% of Toyota automobiles already use this technology today.

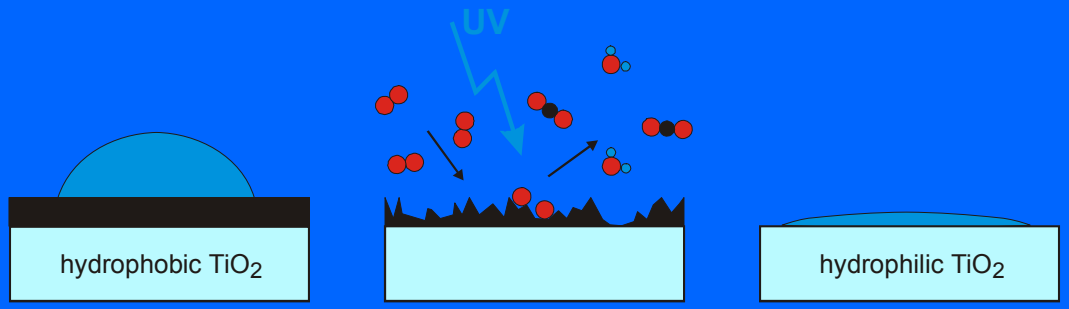
SUNCLEAN™
Self-Cleaning Glass by PPG

SunClean self-cleaning glass by PPG is designed to...
MAKE YOUR LIFE EASIER.

What causes TiO_2 to become hydrophilic in UV?

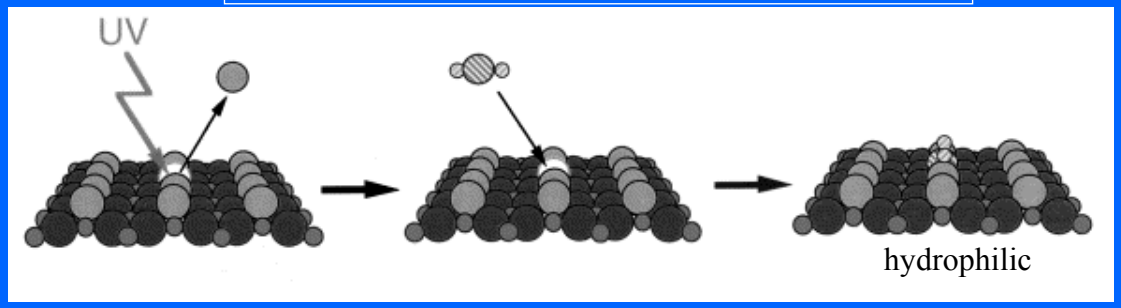
3 Models:

- Photocatalytic removal of organic compounds ?



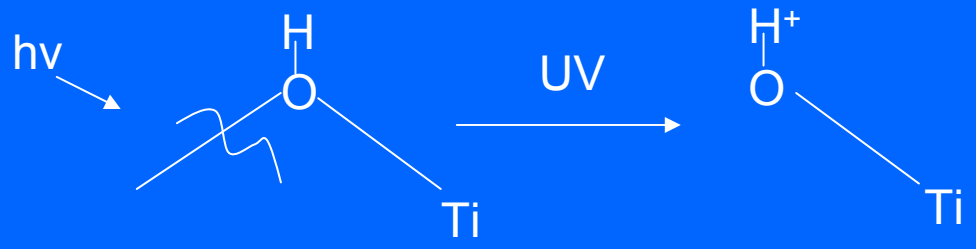
Fujishima, Rao, Tryk, J. Photochem. Photobio C **1**, 1 2000.

- UV induced oxygen vacancies ?



Nakajima, Koizumi, Watanabe, Hashimoto, J. Photochem. Photobiol. A **146**, 129-132, 2001

- UV-Induced bond breaking?



Sakai, Fujishima, Watanabe, Hashimoto, J. Phys. Chem. B **103**, 2188, 1999.

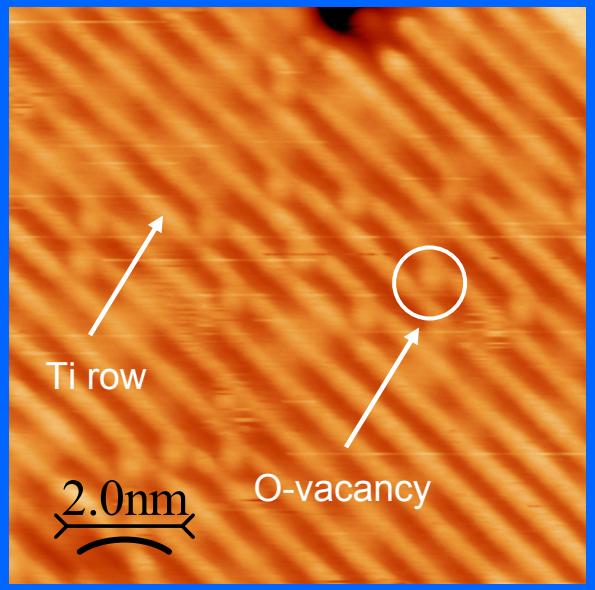
Problems with Existing Understanding of the UV-Induced Hydrophilicity Phenomena on TiO_2

- All current contact angle measurements have been made in the ambient atmosphere on surfaces which are not atomically clean. Hydrocarbon (and other organic contamination) effects are uncontrolled.

- Problem needs a <u>clean</u> <u>surface</u>-<u>ultrahigh</u> <u>vacuum</u> approach and atomic resolution of surface atoms.

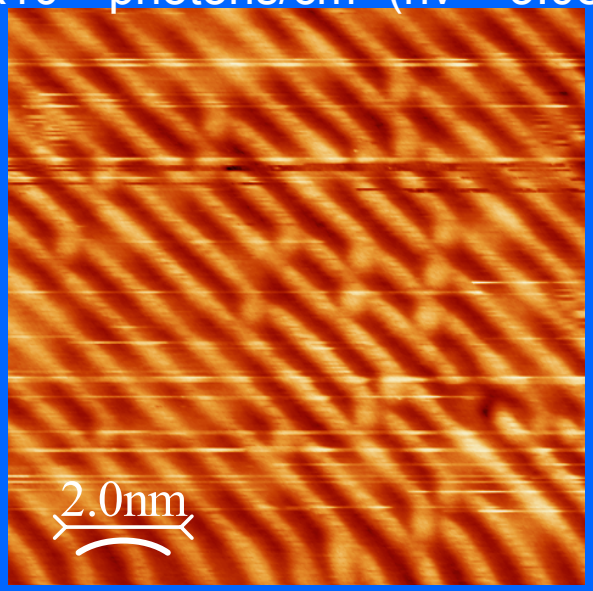
STM Investigation of Vacancy Formation by Intense UV Irradiation – TiO_2(110)-(1x1)

No Irradiation



UV Exposure:

5.4×10^{21} photons/cm^2 (hv > 3.0eV)

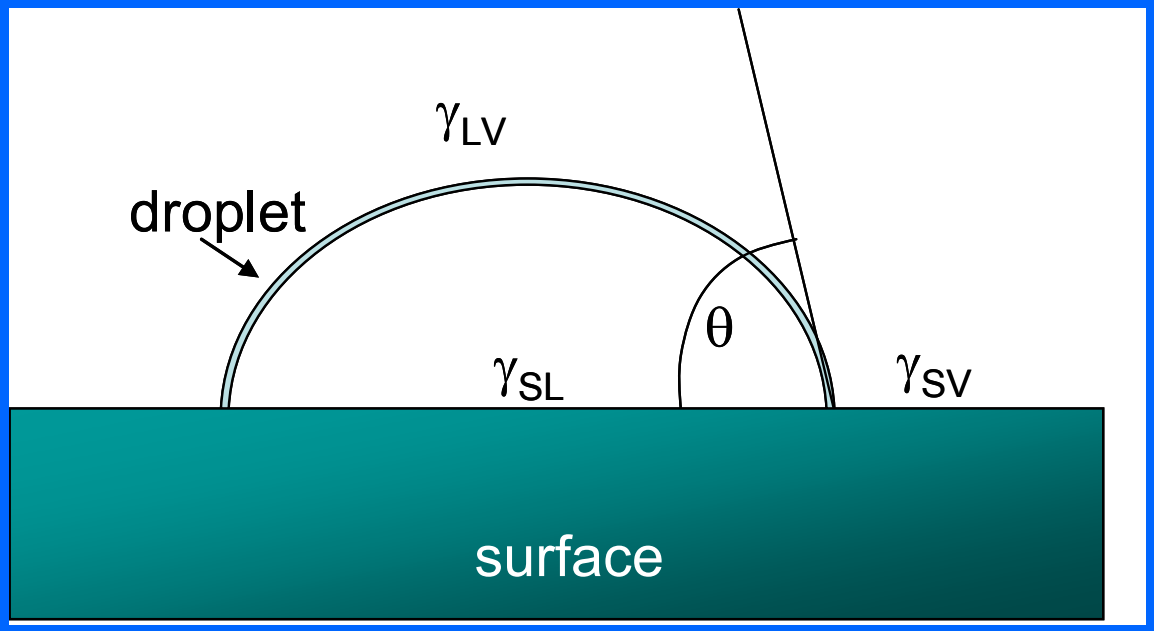


$$Q \leq 10^{-23.5 \pm 0.2}\ \text{cm}^2$$

Implies that ~10^8 photons/site do not produce O vacancy defects!

*Sergey Mezhenny, Peter Maksymovych, Tracy L. Thompson, Oliver Diwald, Dirk Stahl and Scott D. Walck, Chemical Physics Letters, **369** (2003) 152-158.*

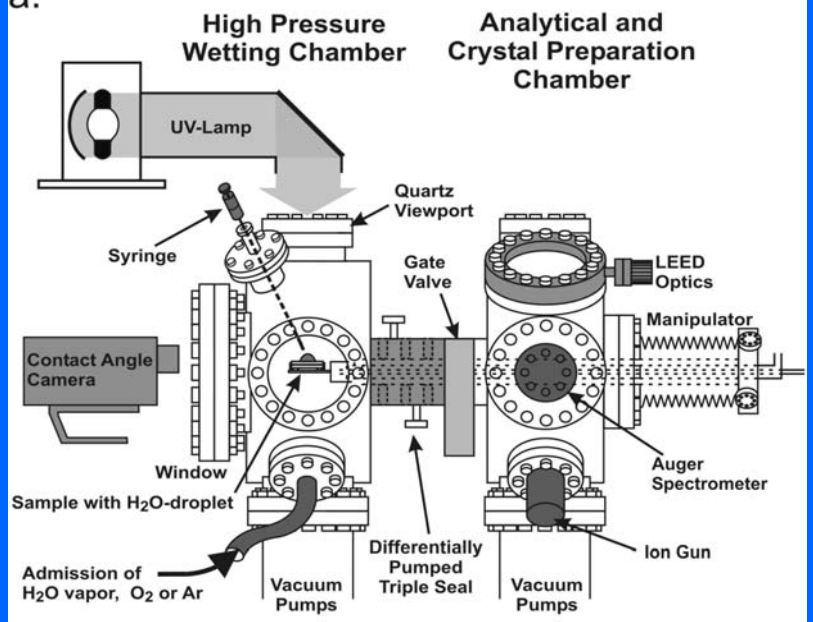
Liquid-Solid Contact Angle Measurements



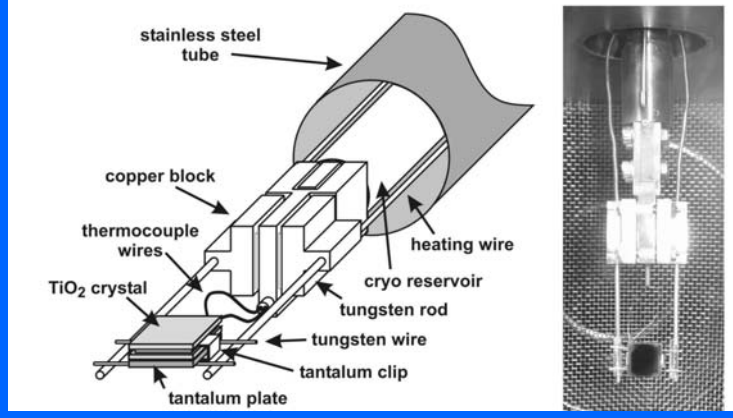
→ A γ_{SV} increases, θ decreases

Apparatus for H_2O Contact Angle Measurements on $TiO_2(110)$

a.



b. $TiO_2(110)$ Crystal Mount

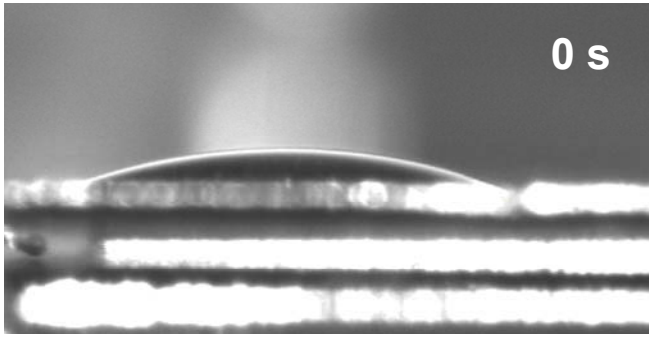


This technology allows study of contact angle for pure H_2O under conditions of:

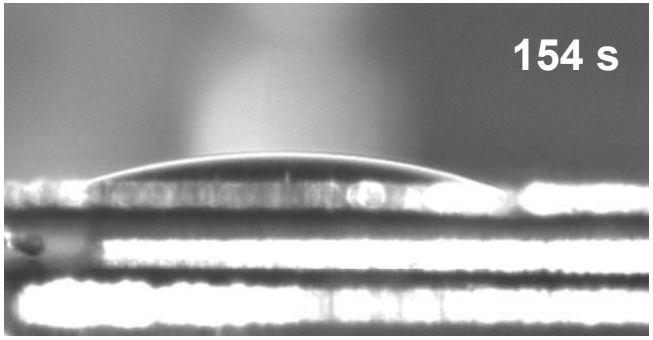
- well controlled initial surface cleanliness
- well controlled atmosphere
- well controlled photon flux

Typical H_2O Contact Angle Showing Sudden Onset of Wetting of $TiO_2(110)$

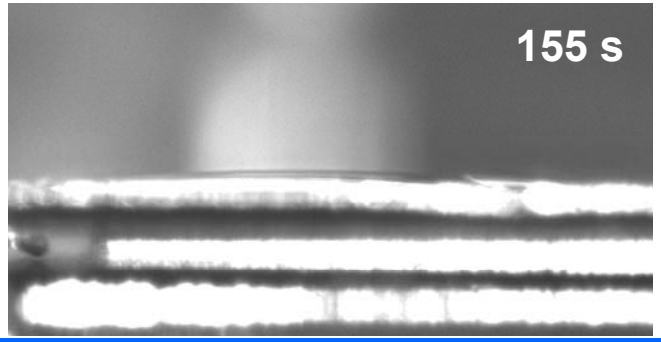
P_{O_2} = 1 atm; hexane = 120 ppm



a

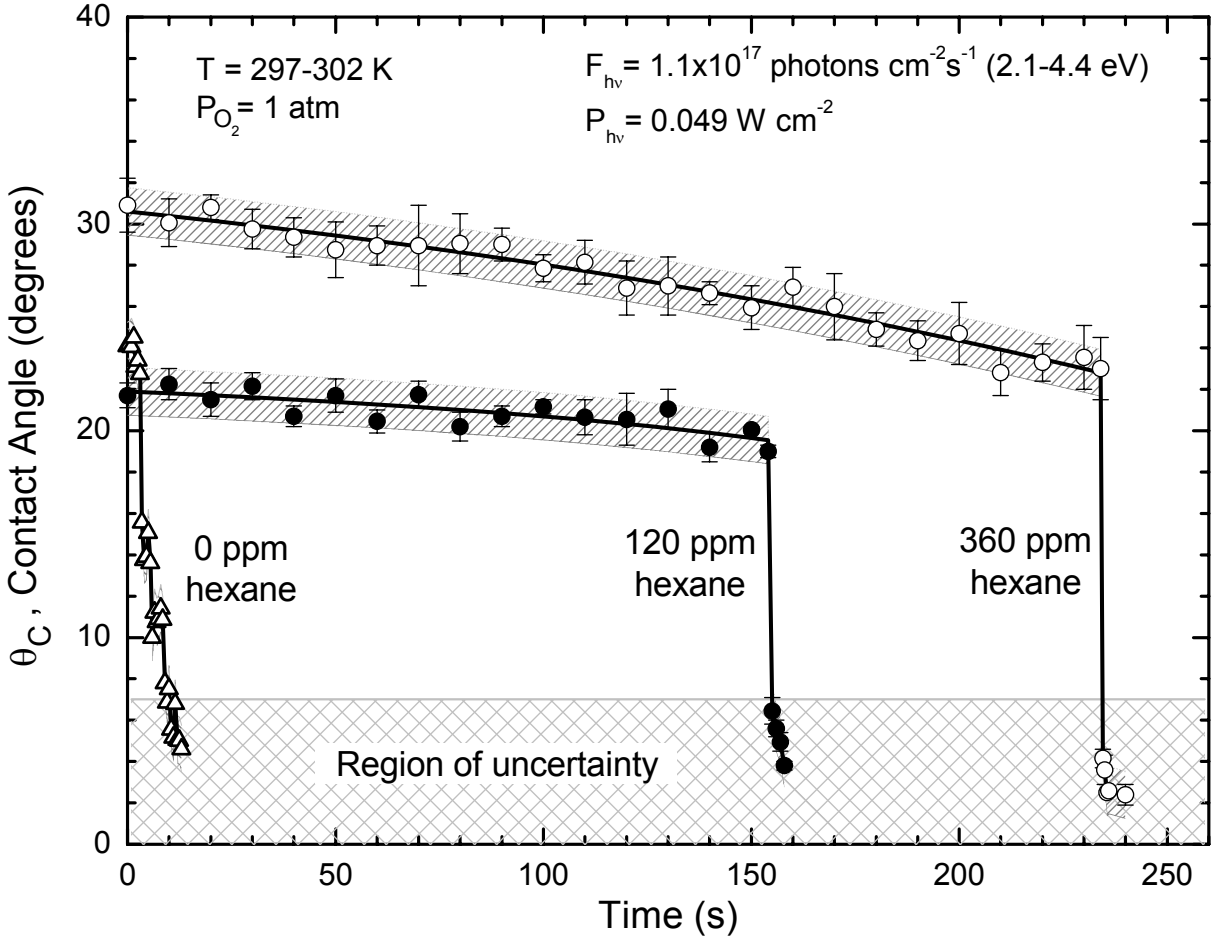


b

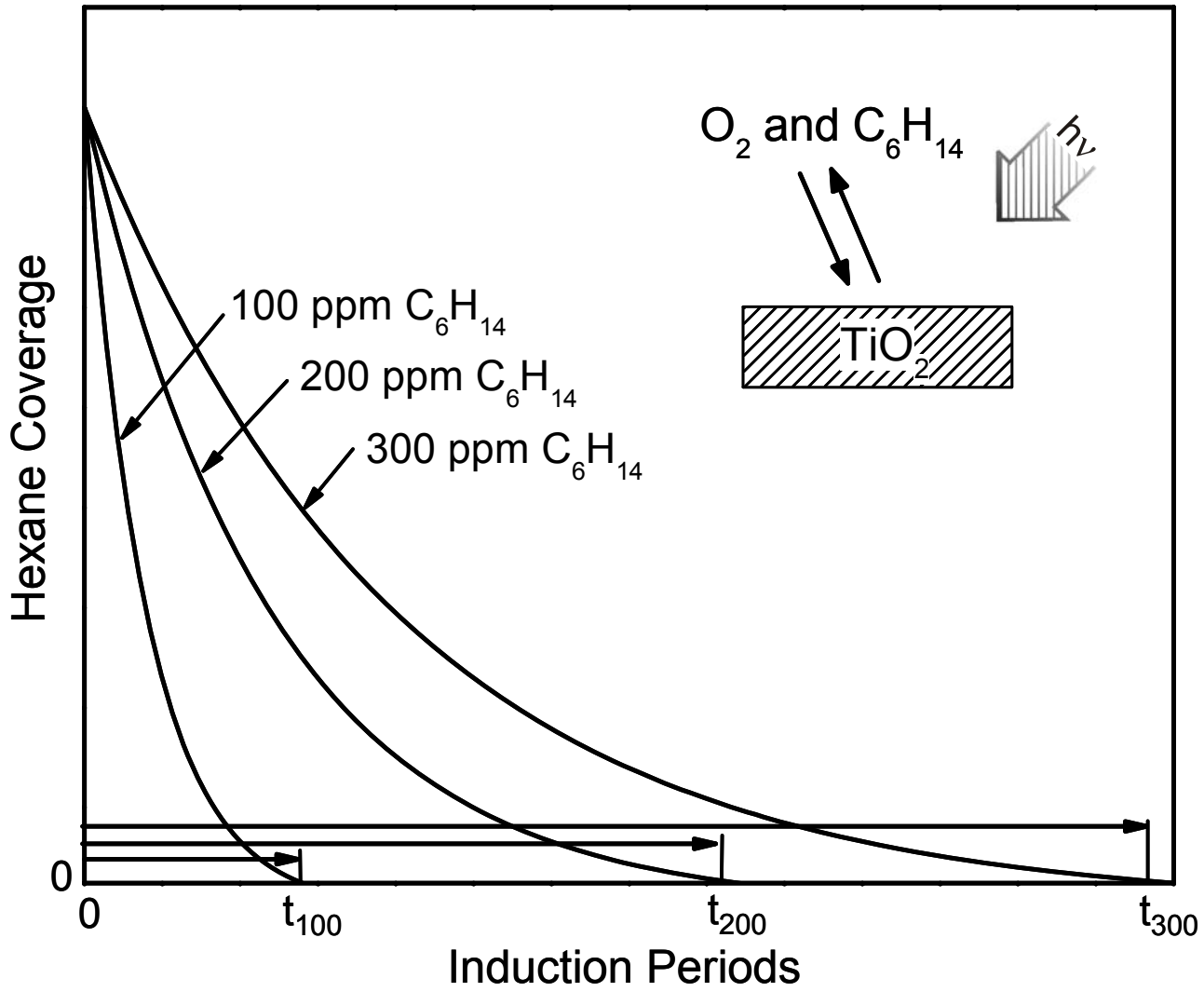


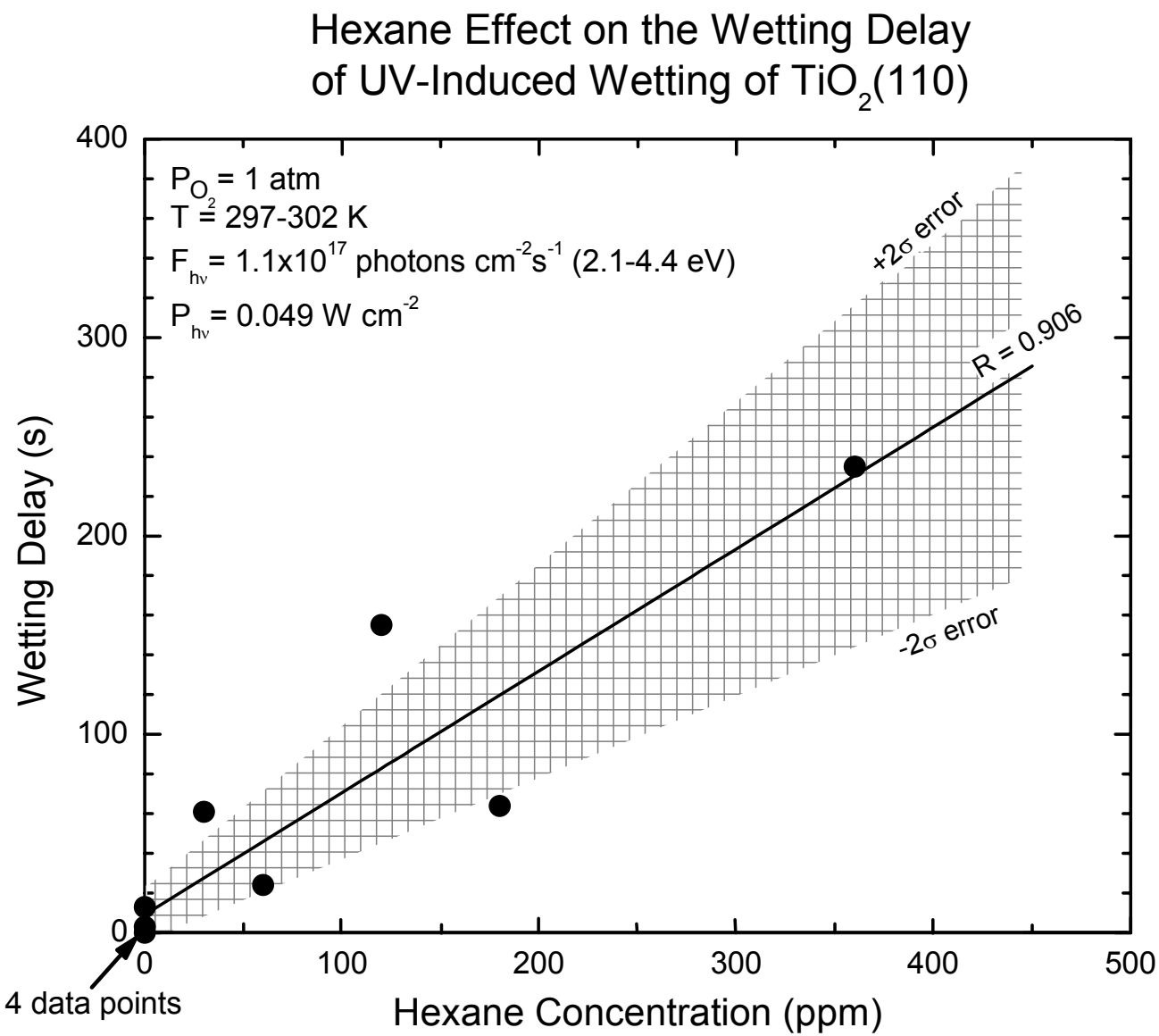
c

Hexane Vapor Effect on the UV-Induced Wetting of TiO_2(110)

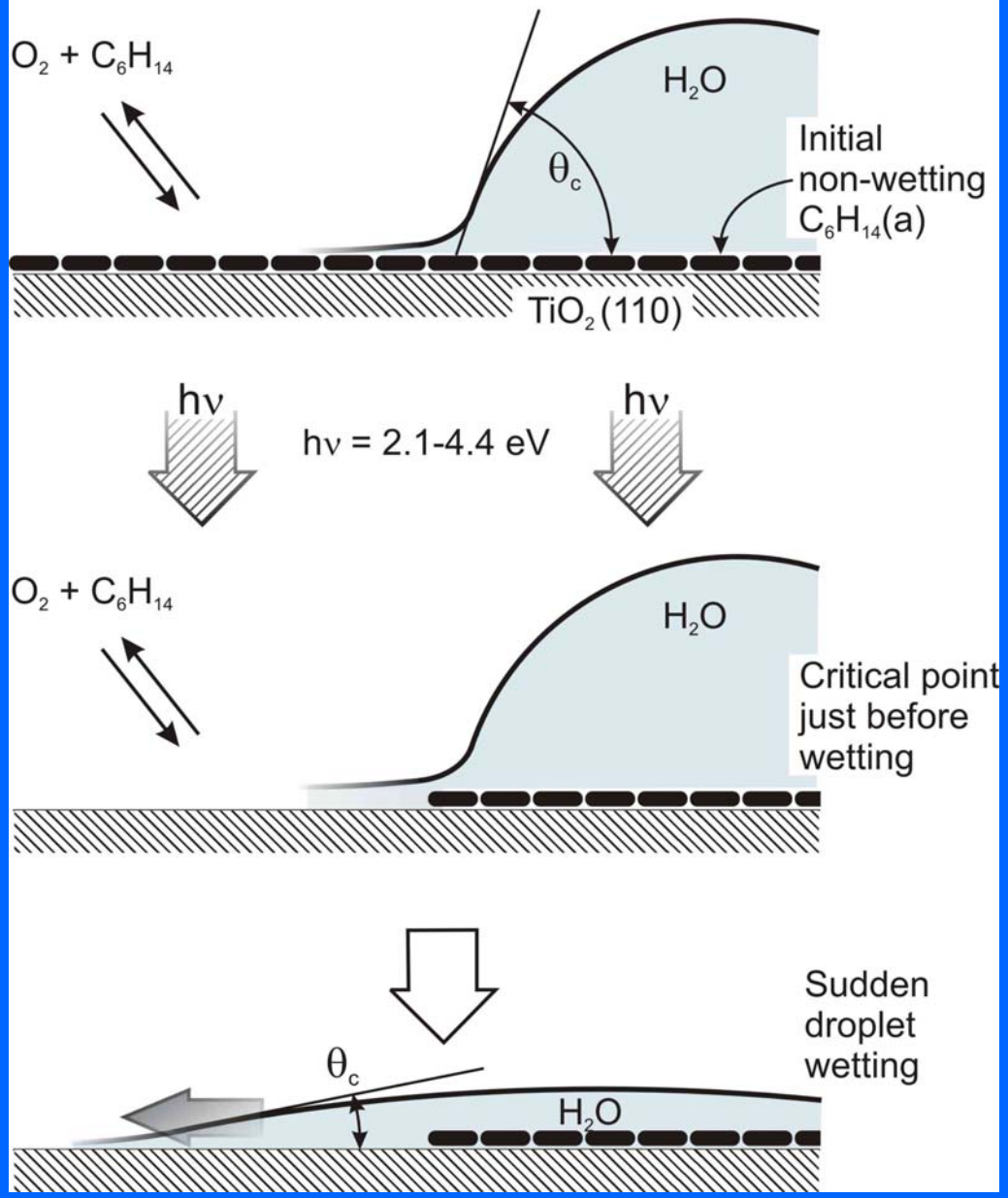


Schematic Origin of Wetting Delay Period




Hexane Effect on the Wetting Delay
of UV-Induced Wetting of TiO2(110)
PO2 = 1 atm
T = 297-302 K
Fhν = 1.1x10^17 photons cm^-2s^-1 (2.1-4.4 eV)
Phν = 0.049 W cm^-2
+2σ error
R = 0.906
-2σ error
Wetting Delay (s)
Hexane Concentration (ppm)
4 data points
0
100
200
300
400
500

Sudden Hydrophilic Effect due to Hydrocarbon Photooxidation on TiO_2



Conclusions

- Hydrophilicity model involving UV production of O-vacancy defect sites is unlikely based on STM results.

- Hydrophilicity model involving hydrocarbon photooxidation to produce clean wettable TiO_2 is likely to be true.
  - Induction period scales with ppm concentration of hexane in O_2.

What Have We Learned?

- Photochemistry on semiconductors occurs by e-h pair production in the substrate, accompanied by charge transfer to adsorbed species
- Defect sites are important
  - On surface for adsorption of molecules
  - In bulk-promoting charge-carrier recombination
- Second-order e-h recombination can give $F_{h\upsilon}^{1/2}$ dependence of photochemical kinetics
- Hole traps reduce photochemical efficiency
- Fractal photodesorption kinetics – controlled by anisotropy in crystal electrical conductivity

- EPR – detects e & h states sensitively

  e = Ti^{3+}

  h = O^{-}

- IR detects CB electrons – delocalization gives continuous optical absorption in IR region

- Hydrophilicity induced by UV on TiO_2 – caused by photooxidation of organic layers in equilibrium with hydrocarbons in atmosphere, causing cleanup of TiO_2 surfaces

- Don't believe STM images unless you know you have chemical control

Acknowledgements

Tracy L. Thompson	University of Pittsburgh
Peter Maksymovych	University of Pittsburgh
Dimitar Panayotov	University of Pittsburgh; Bulgarian Academy of Sciences
Sergey Mezhenny	University of Pittsburgh → University of Maryland
Tykhon Zubkov	University of Pittsburgh→ PNNL
Dirk Stahl	University of Pittsburgh→ Leitz
Oliver Diwald	University of Pittsburgh→ T. U. Wien, Austria
Professor Erich Knözinger	T. U. Wien, Austria
Thomas Berger	T. U. Wien, Austria
Martin Sterrer	T. U. Wien, Austria

This work has been supported by the Army Research Office under Dr. Stephen Lee and DARPA; Also by PPG Industries