

Photocatalysis on Single Crystal TiO_2 Surfaces

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Outline

Motivation for modeling heterogeneous photocatalysis using single crystals

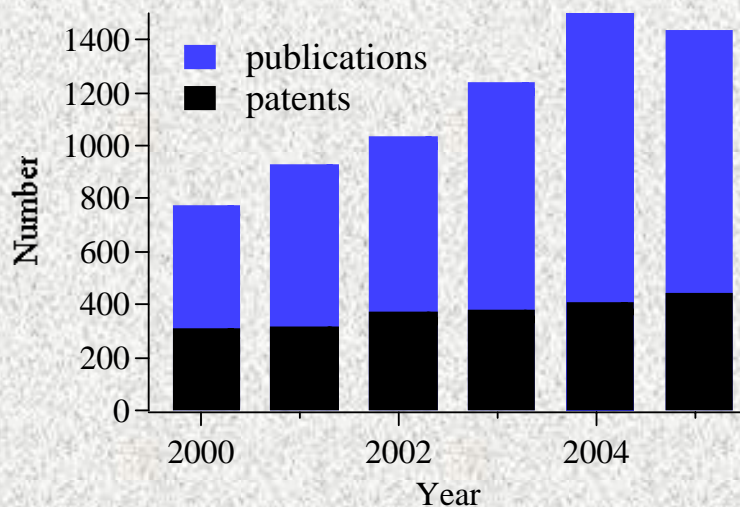
Examples studies on rutile $\text{TiO}_2(110)$

- oxygen and water
- trimethyl acetic acid
- acetone

Conclusions

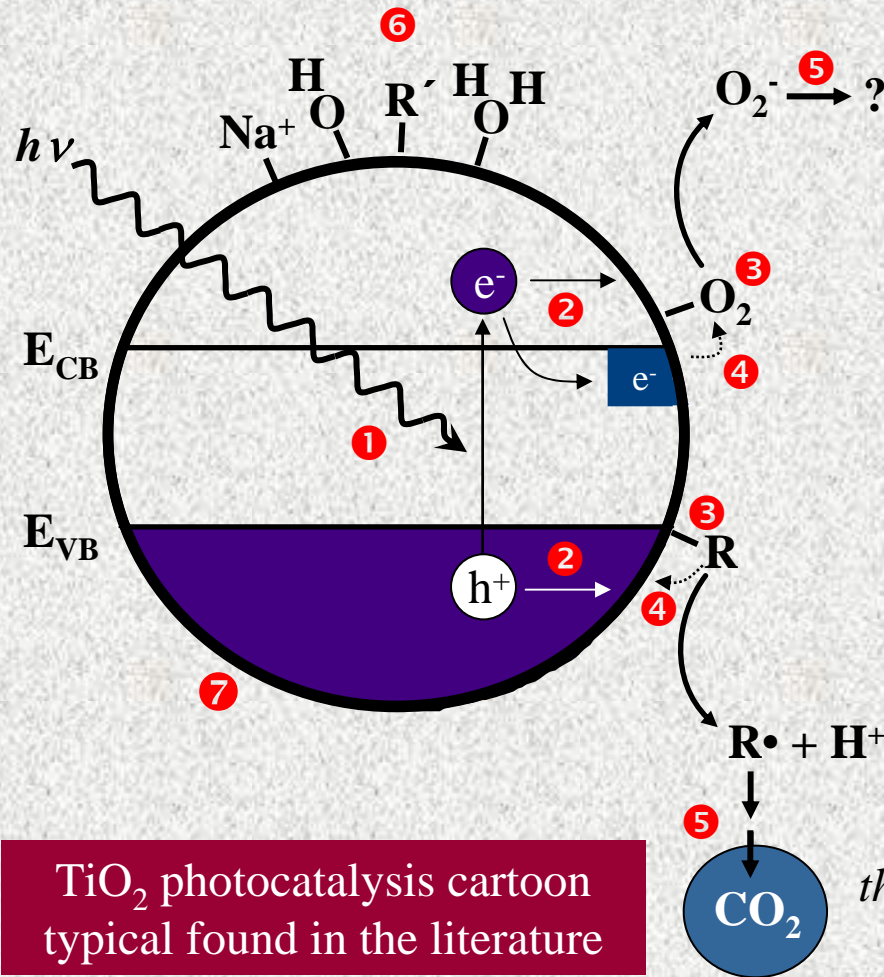
Growing Interest in TiO₂-Based Photocatalysis

Numerous companies market products or services involving use of TiO₂ as a photocatalyst (e.g., for self-cleaning glass, water treatment, air purification, disinfection, deodorization, etc.)



Large and growing numbers of patents and publications involving TiO₂-based photocatalysis (Source: SciFinder (Chem Abstracts) search on “TiO₂+photo-”)

Photocatalysis on TiO₂

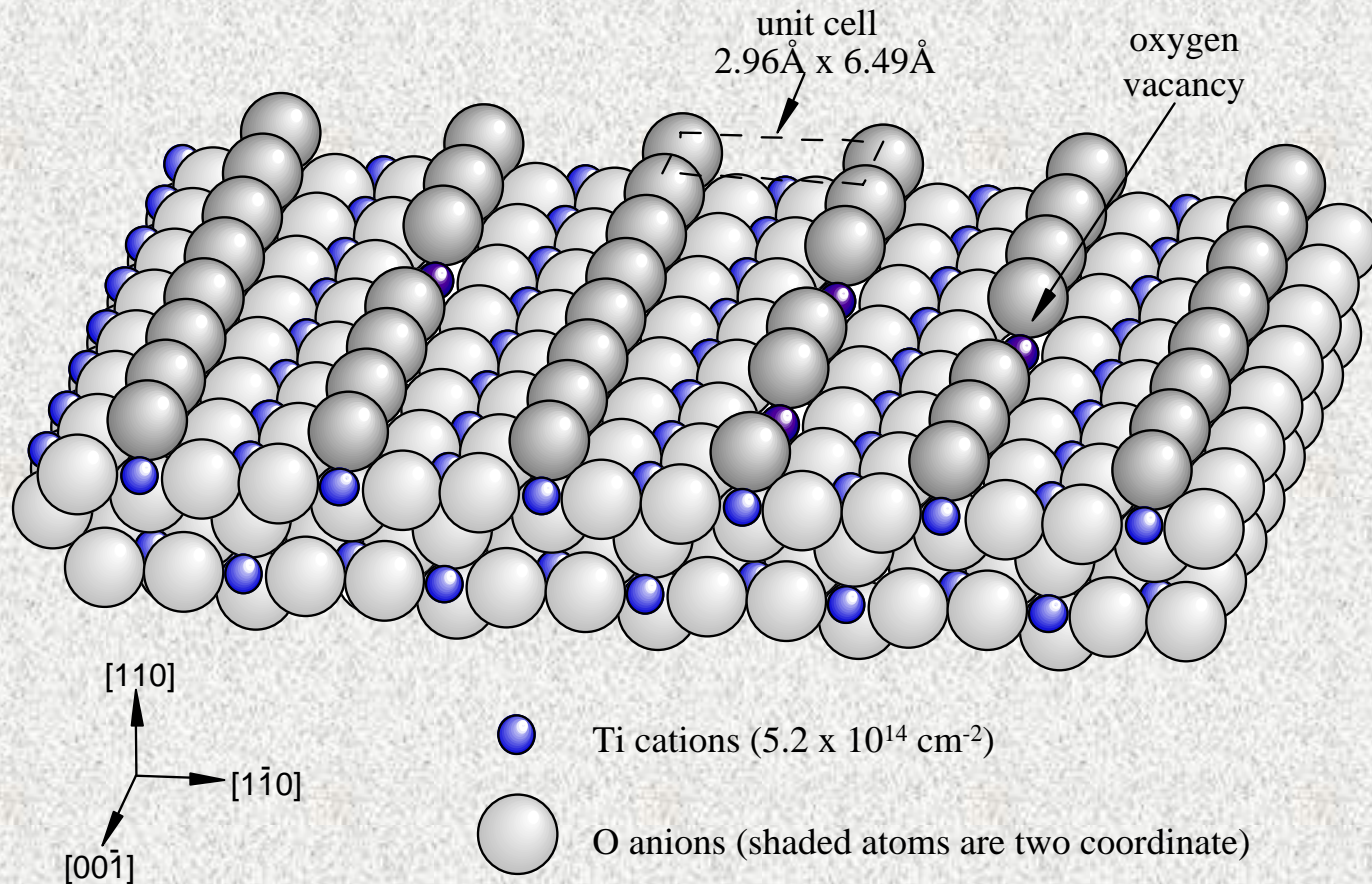


Important issues

- ① excitation (band structure and its modification)
- ② charge diffusion and trapping
- ③ molecular adsorption
- ④ charge transfer
- ⑤ reaction mechanism (coupled redox and thermal chemistries)
- ⑥ poisons, promoters and spectators
- ⑦ surface and material structure

the analytical focus of most photooxidation studies

Rutile TiO₂(110) single crystal surface



- Annealing TiO₂(110) in UHV results in creation of surface oxygen vacancy sites.
- Coverage of vacancies is linked to the concentration of bulk defects.
- Each vacancy is occupied by what is traditional referred to as 2 Ti³⁺ cations.

Outline

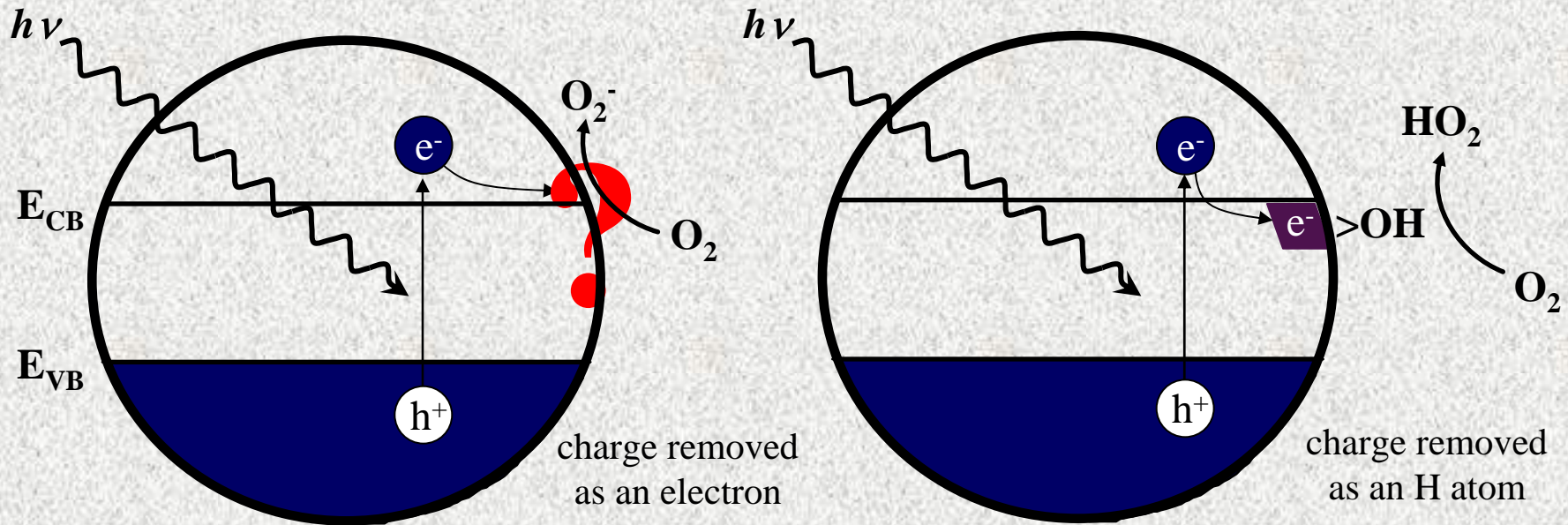
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- **oxygen and water**
- trimethyl acetic acid
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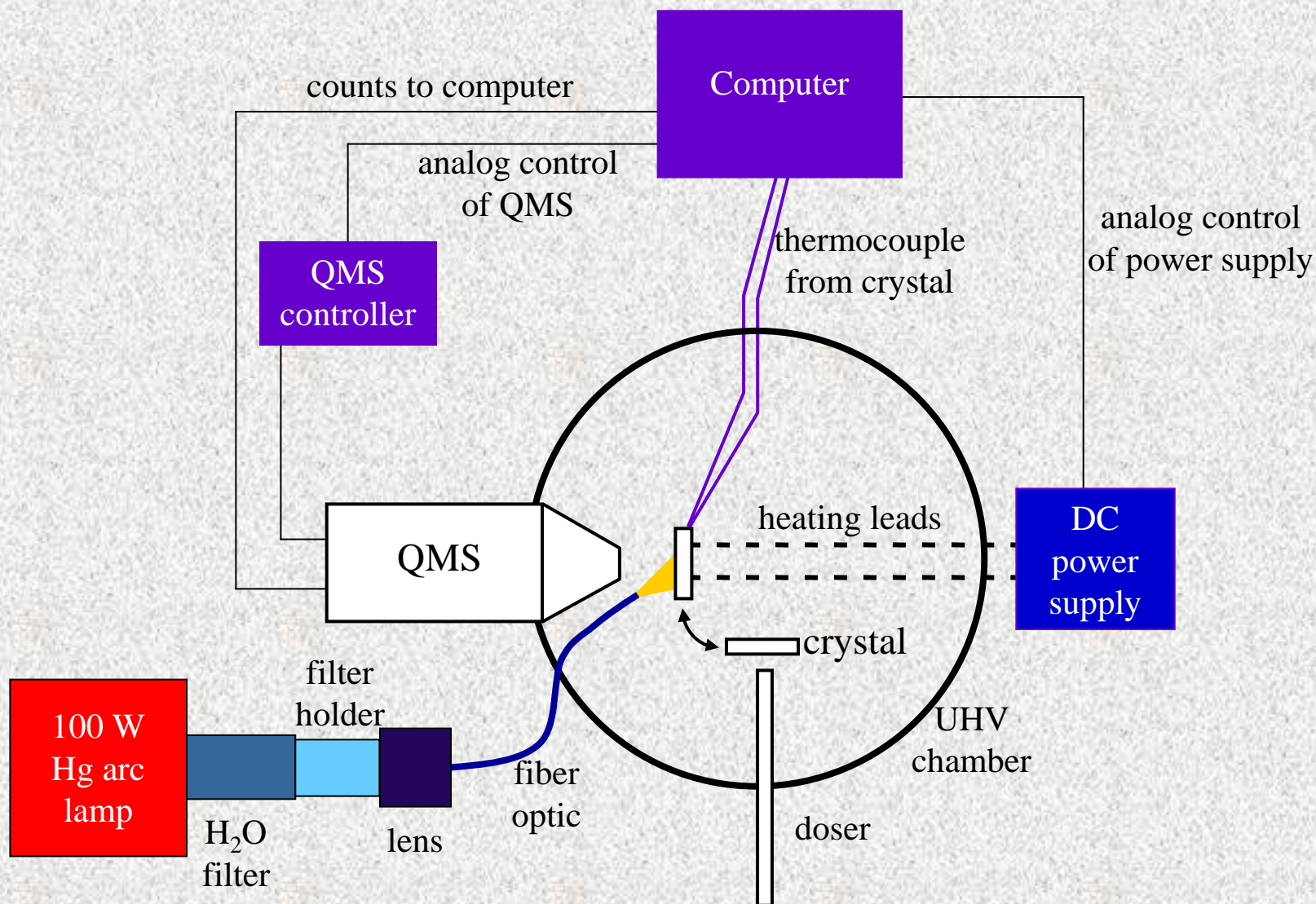
Conclusions

O₂ as an electron scavenger

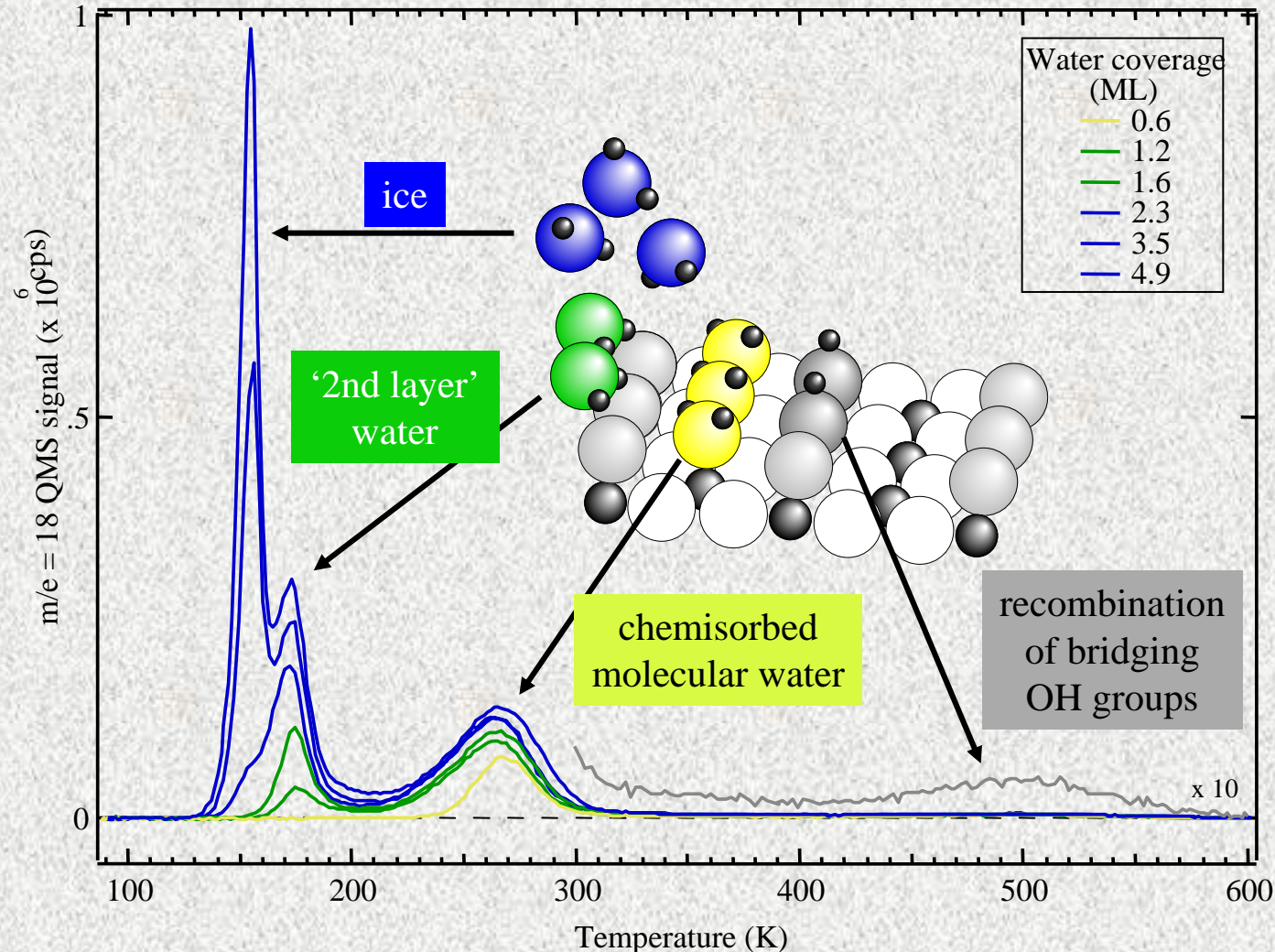


- Excited electrons trap at shallow band gap states on a sub-picosecond time scale. (*Colombo and Bowman, JPC 99 (1995) 11752 and 100 (1996) 18445*)
- Electrons trapped in surface states can have very long lifetimes (~minutes) depending on the concentration of electron scavenger present.
- Many surface trap sites are OH-related. (*Szczepankiewicz, et al. JPCB 106 (2002) 2922*)

Temperature programmed measurements



Thermal desorption states of water on TiO₂(110)



Desorption states fill sequentially.

Coverage in 500 K TPD peak is equal to the oxygen vacancy population.

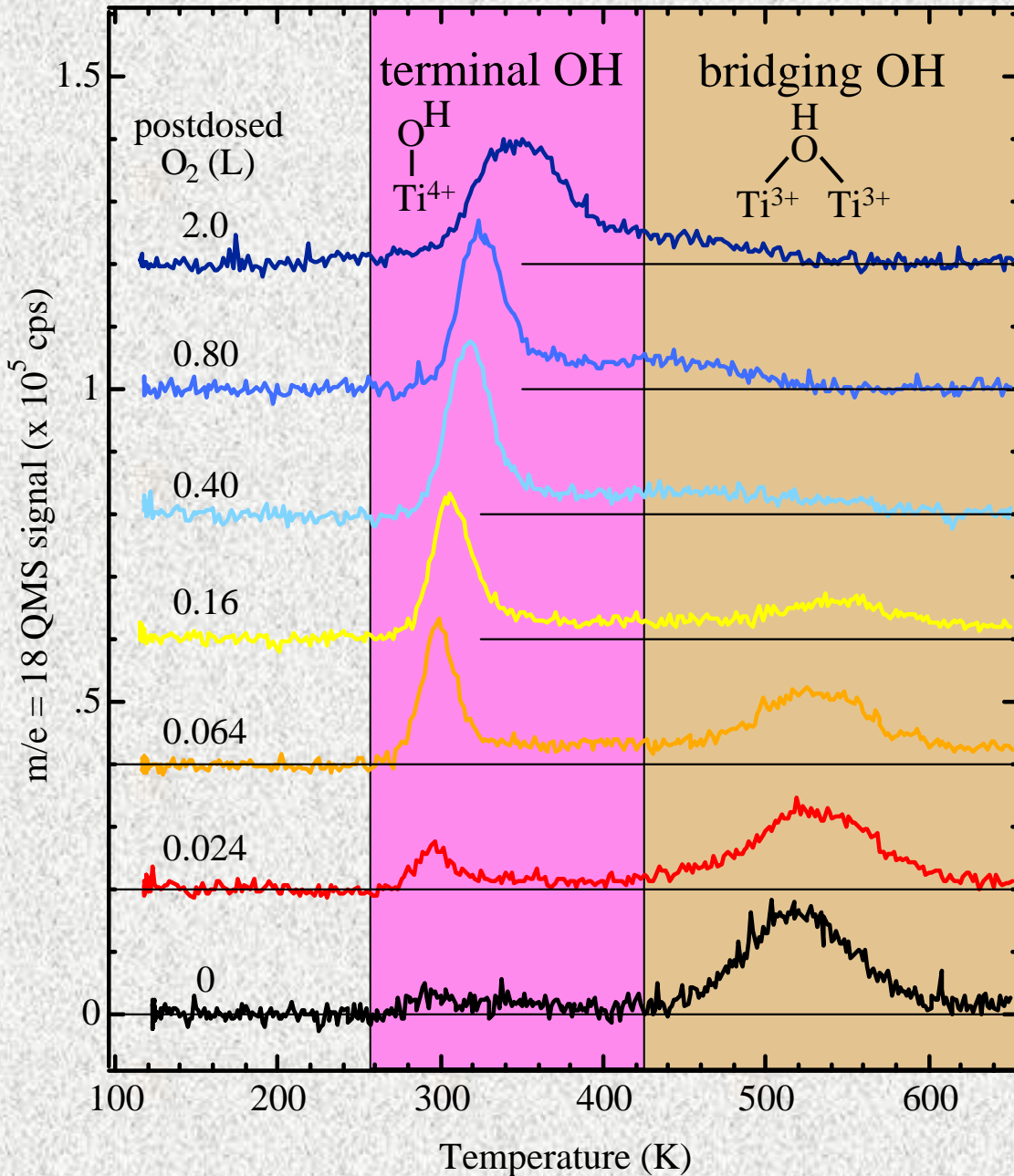
2nd layer is H-bonded to bridging O/OH sites

Multilayer fills with 'non-classical' coverage-dependent behavior.

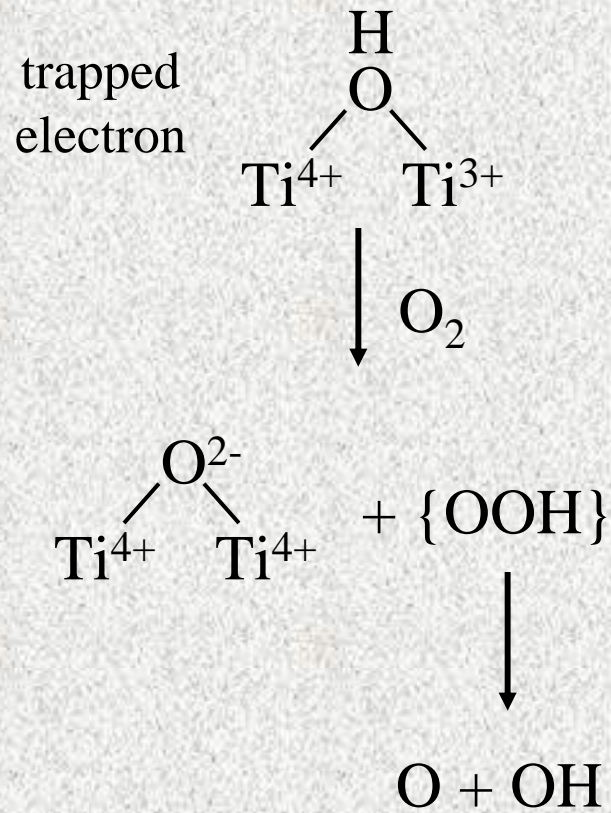
Hugenschmidt et al., Surf. Sci. 302 (1994) 329.

Henderson, Surf. Sci. 355 (1996) 151; Lang. 12 (1996) 5093.

Simulating the role of O₂ via reaction with OH groups at Ti³⁺ sites



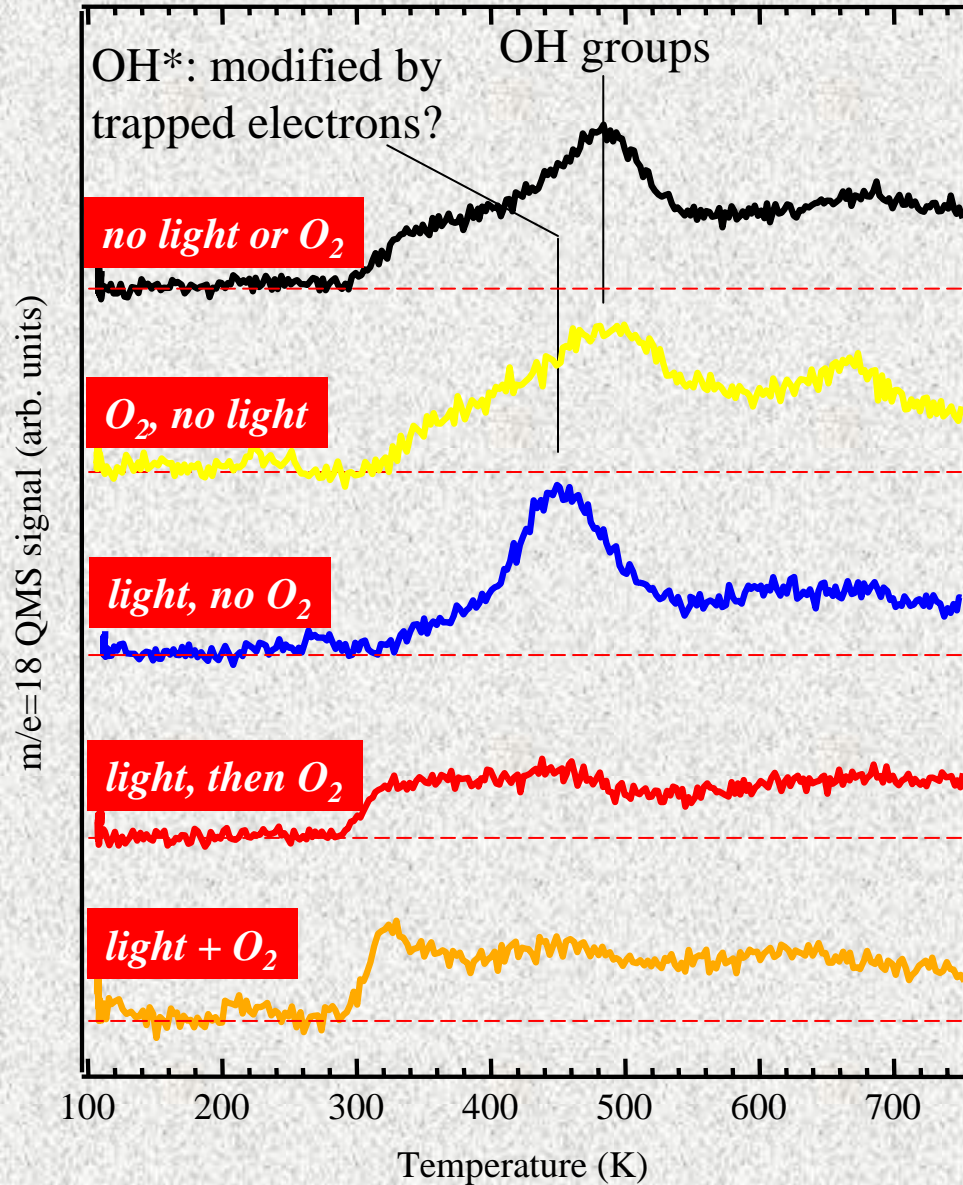
TiO₂(110) w/ 14% vac.



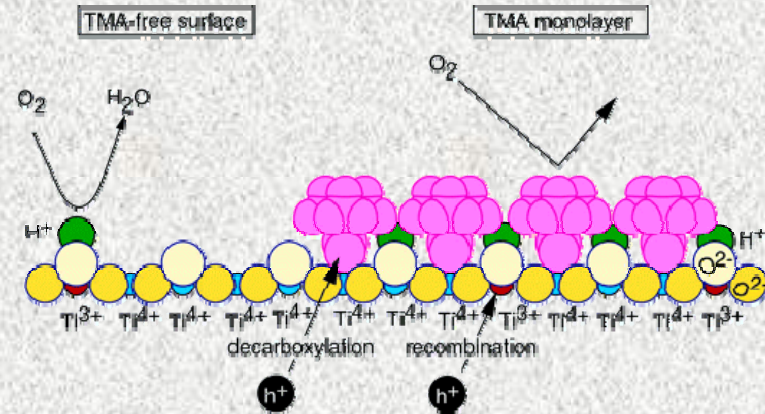
(Henderson, et al. JPC B 107 (2003) 534)

O₂ reaction with Ti(3+)-OH during TMAA photodecomposition

Water from TMAA on TiO₂(110) w/ 7% vac.



- TMAA alone (no UV or O₂)
- 300 L O₂ on TMAA
- UV irradiation in UHV (no O₂)
- 130 L O₂ after UV irradiation in UHV
- UV irradiation in 5x10⁻⁷ O₂

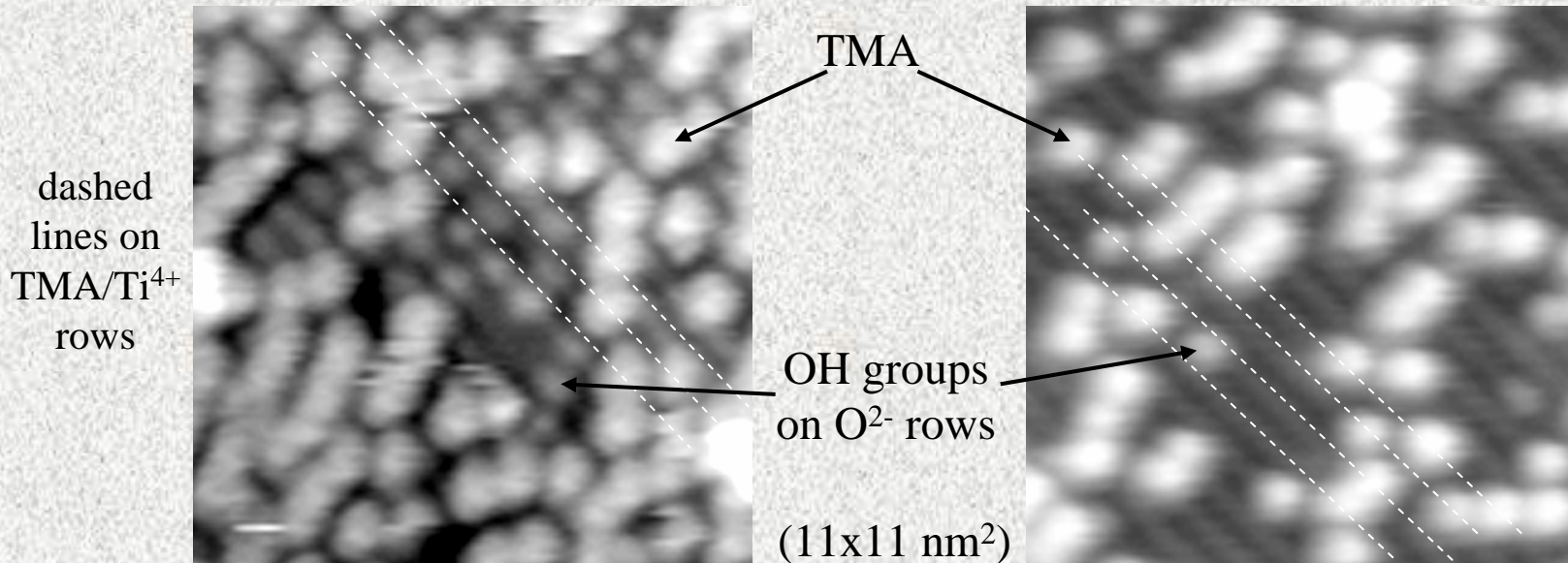


- Light generated Ti³⁺-OH groups behave toward O₂ like Ti³⁺-OH groups formed from water dissociation at oxygen vacancies

Titration of Ti(3+)-OH groups with O₂

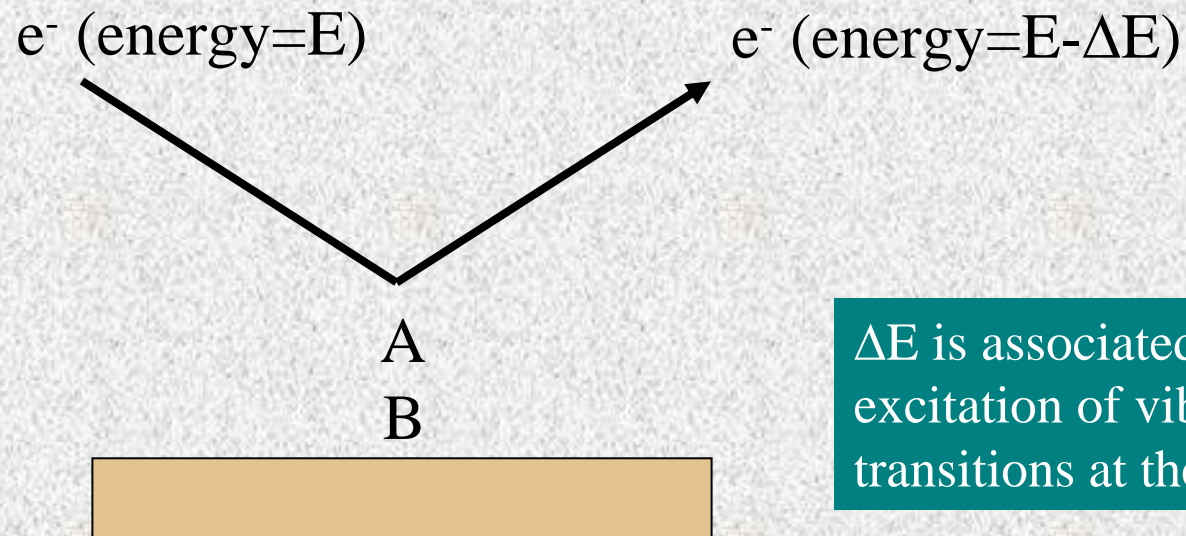
UV irradiation of TMA
in UHV (no O₂)

Exposure of UV-irradiated TMA
to 100 L O₂ in the dark



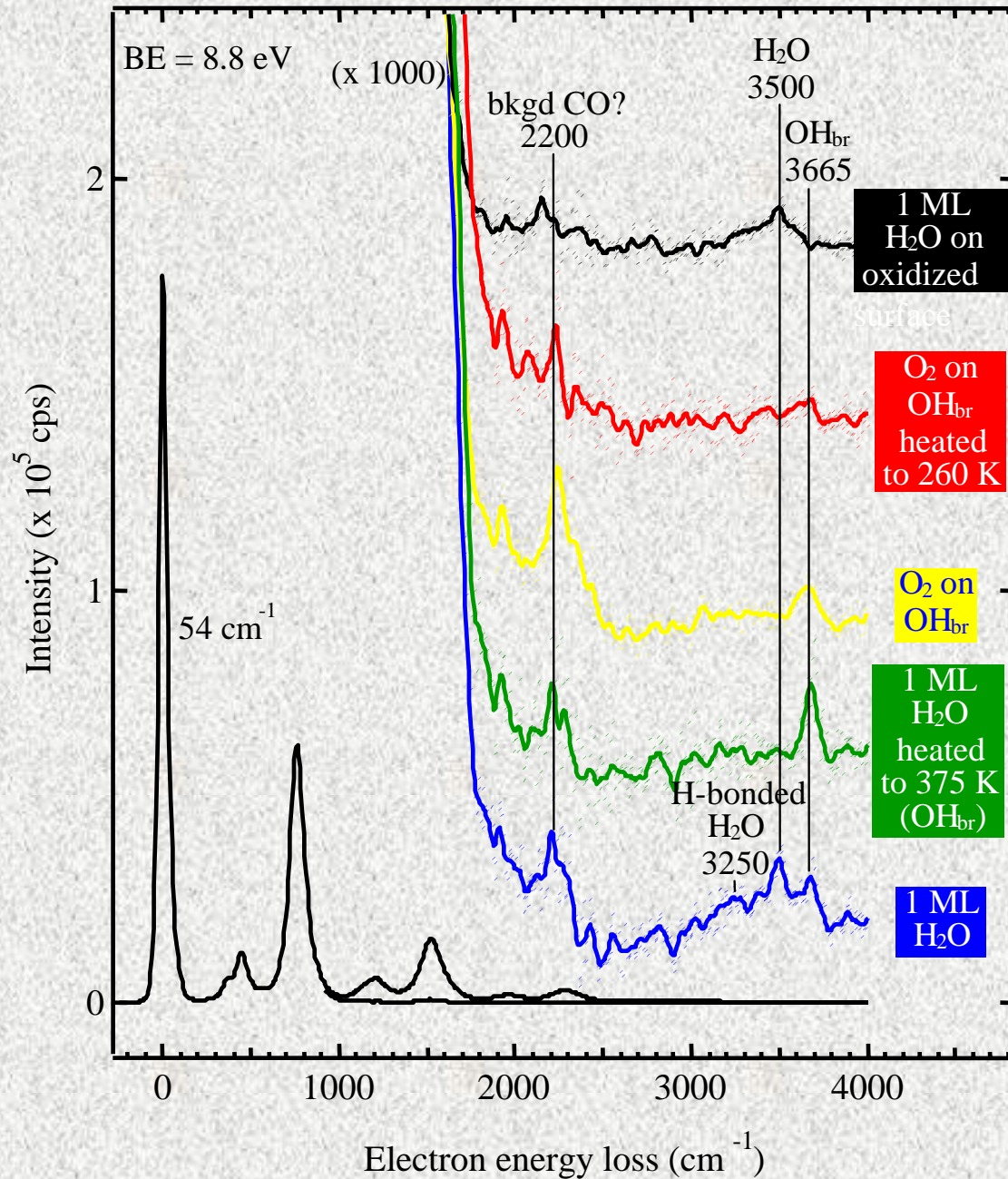
- Tunneling features located between TMA/Ti⁴⁺ rows before O₂ exposure are mostly absent after O₂ exposure at RT
- Assignment of spots on bridging O²⁻ rows to Ti³⁺-OH groups is consistent with STM literature:
 - water dissociation at vacancies (*Brookes et al., PRL 87 (2001) 266103/1; Schaub, et al. PRL 87 (2001) 266104/1*)
 - H atom exposure to the clean surface (*Suzuki, et al. PRL 84 (2000) 2156*)

Detecting surface electronic/vibrational modes using electron energy loss spectroscopy (EELS/HREELS)



ΔE is associated with electron excitation of vibrational/electronic transitions at the surface.

HREELS of H₂O and O₂ coadsorbed on vacuum annealed TiO₂(110)

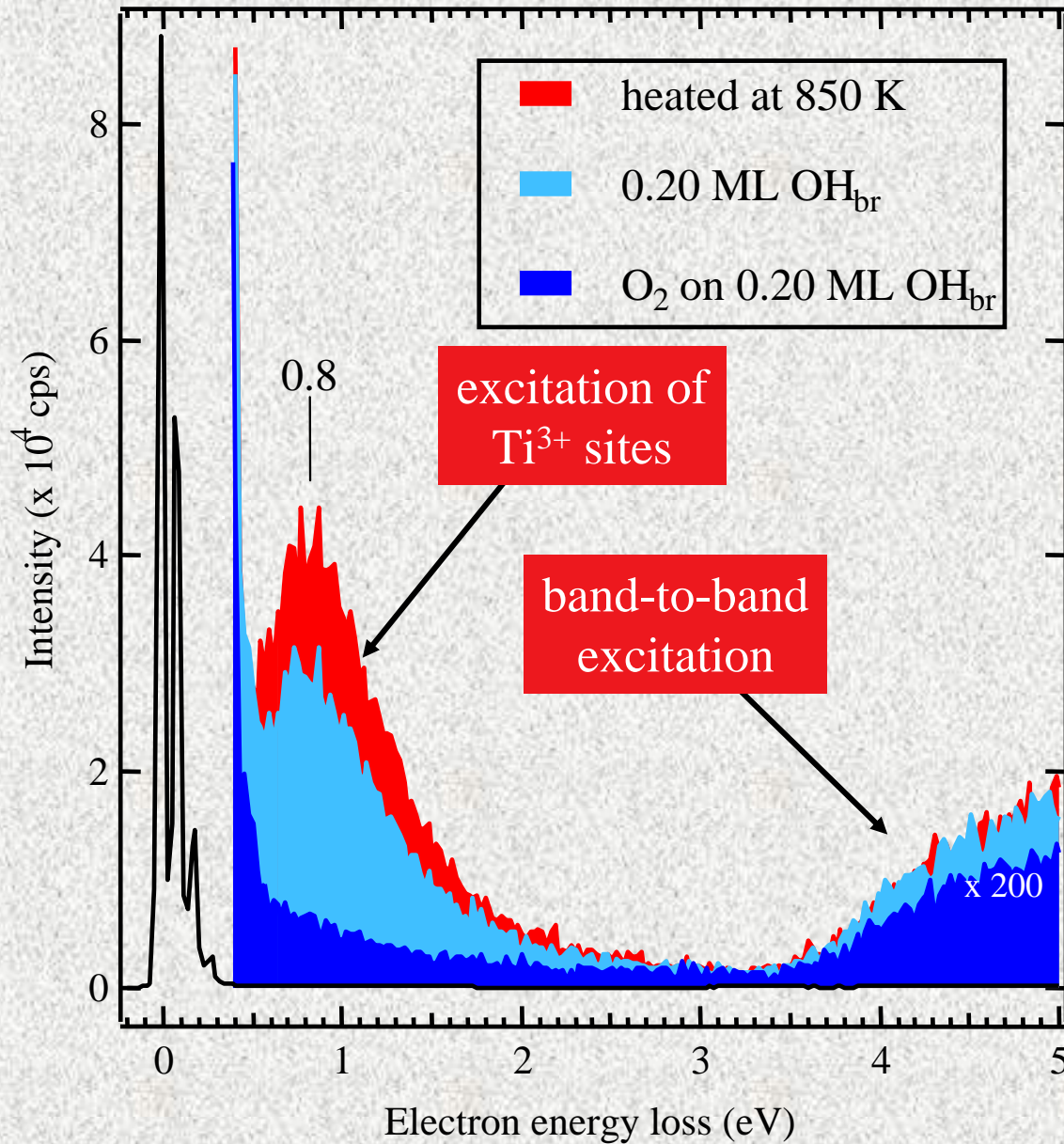


$\nu(\text{OH})$ mode at 3665 cm^{-1} is due to OH_{br} groups formed from water dissociation at vacancies.

O-H product from the reaction of OH_{br} and O_2 is transparent in HREELS. (product is H-bonded and/or tilted?)

OH_{br} groups are not formed from water adsorption if vacancies are not available.

Vacancy oxidation from reaction between O_2 and OH_{br}



- Loss at 0.8 eV is due to a excitation of Ti^{3+} (not due to excitation into TiO_2 conduction band)
- Ti^{3+} cations, associated with the 0.8 eV state, are oxidized during the reaction of O_2 with OH_{br}

Outline

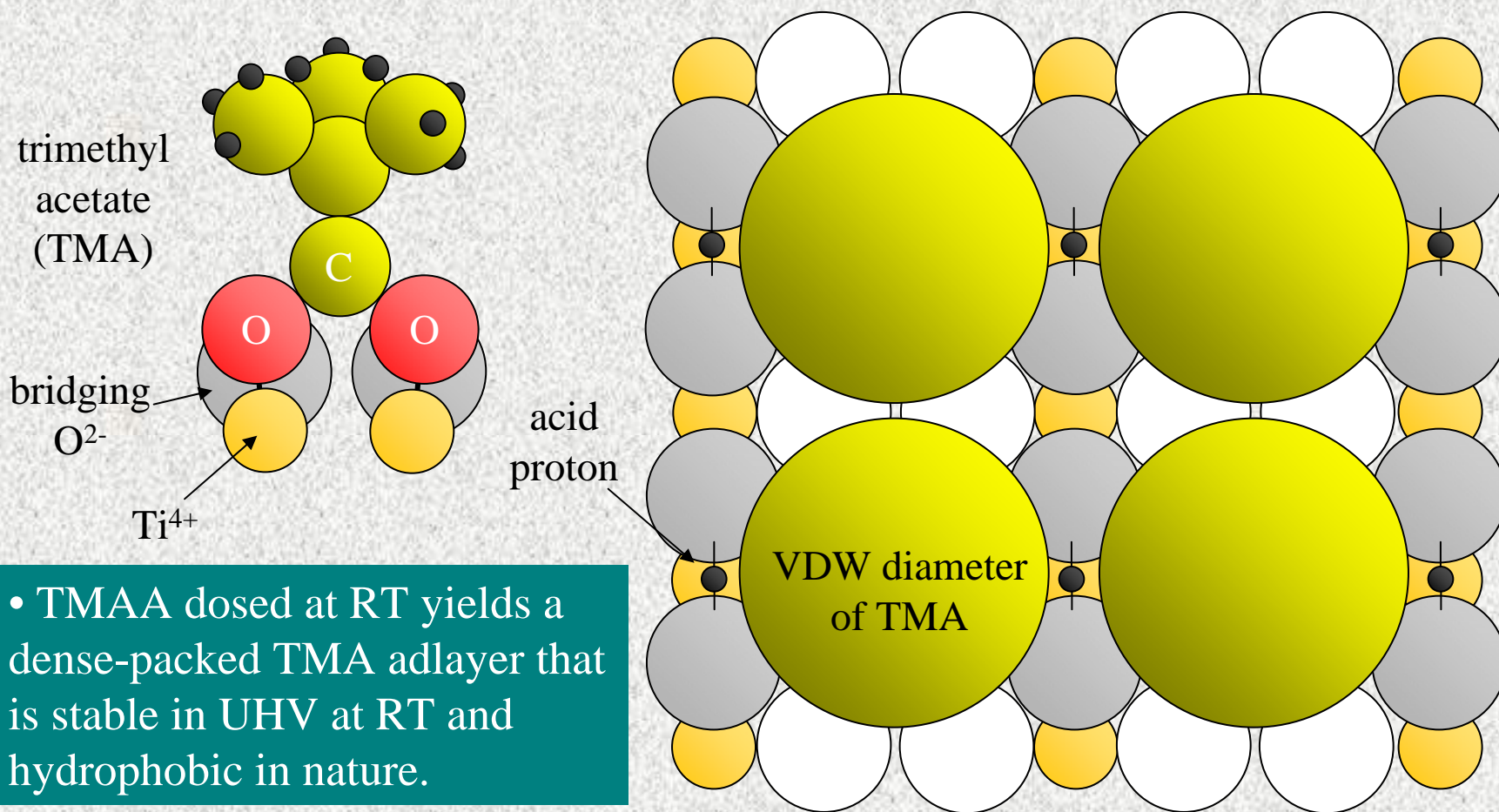
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Examples studies on rutile $\text{TiO}_2(110)$

- oxygen and water
- **trimethyl acetic acid**
- acetone

Conclusions

(2x1) overlayer of TMA on TiO₂(110)



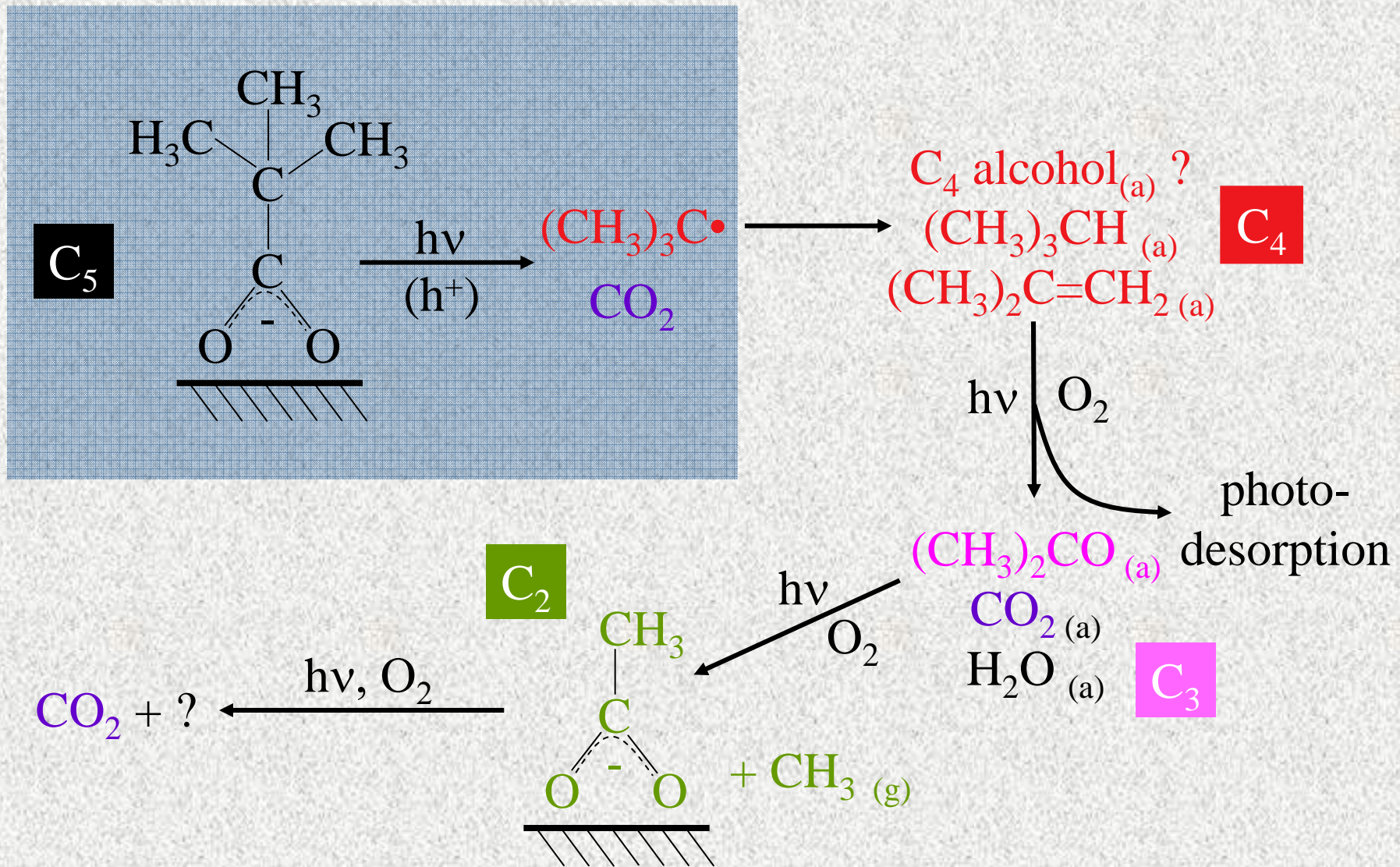
Review of carboxylic acids on TiO₂(110): H. Onishi, Springer Ser. Chem. Phys., 70 (2003) 75.

Photo-induced hydrophilicity on TiO₂: J.M. White, et al. JPCB 107 (2003) 9029.

Photochemistry of TMAA on TiO₂(110): M.A. Henderson, et al. JACS 125 (2003) 14974.

Photochemical rate changes due to 'hydrophobic-to-hydrophilic' transition: H. Uetsuka, et al. JPCB 108 (2004) 10621.

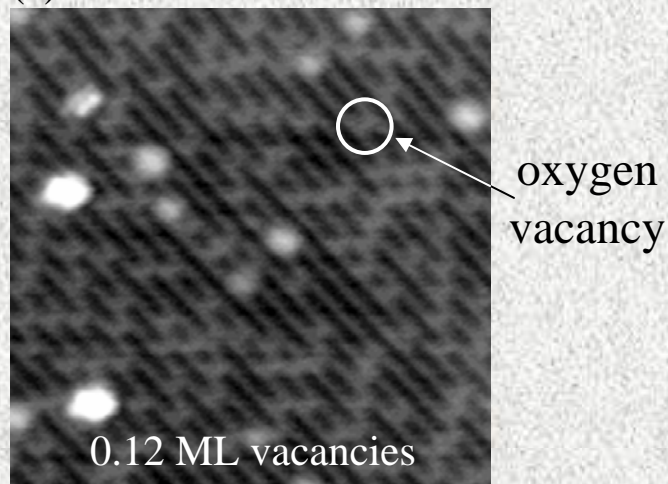
TMA photodecomposition pathway on TiO₂(110)



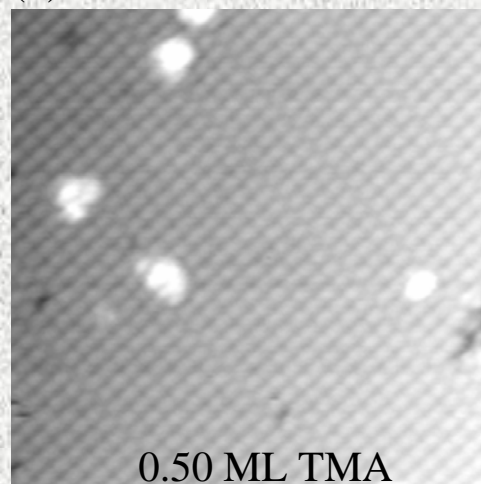
Henderson, et al. JPC B 107 (2003) 9029; 108 (2004) 3592; 108 (2004) 10621; 108 (2004) 18932; 109 (2005) 12062; 109 (2005) 12417; Langmuir 21 (2005) 3443; JACS 125 (2003) 14974; J. Catal. 238 (2006) 111, 153.

STM of TMAA dosed on TiO₂(110) at RT

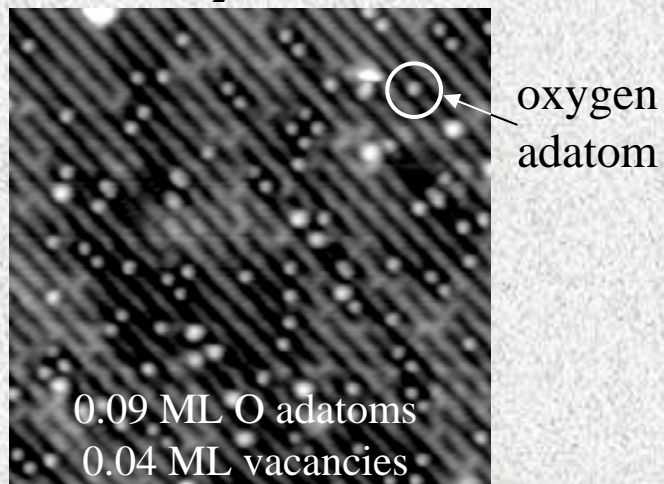
(a) vacuum annealed surface



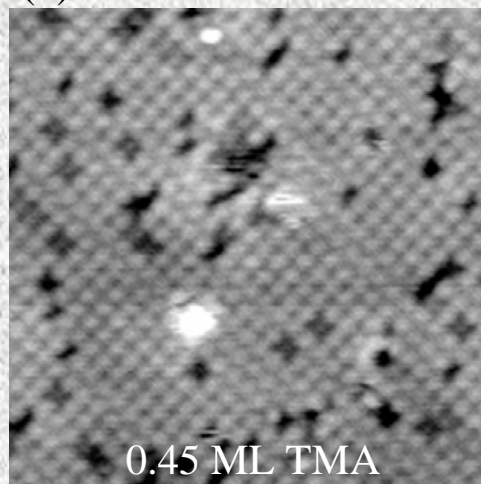
(b) satn. TMA on 'a'



(c) 100 L O₂ on 'a' (16 x 16 nm²)



(d) satn. TMA on 'c'



On the clean surface:

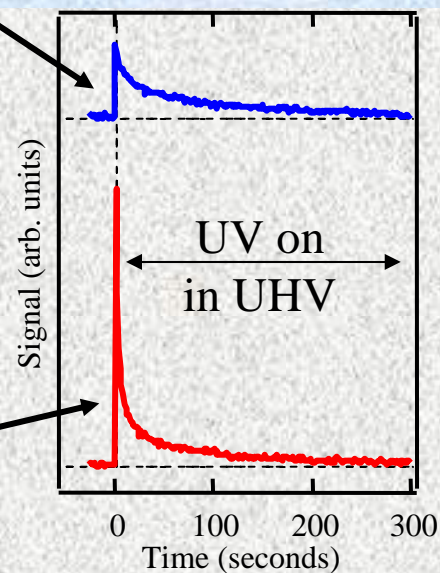
- bright rows = Ti⁴⁺

- dark rows = O²⁻

(U. Diebold, SSR 48 (2003) 53.)

Pre-oxidation affects both
TMA order and rate of TMA
photodecomposition.

CO₂ photodesorption

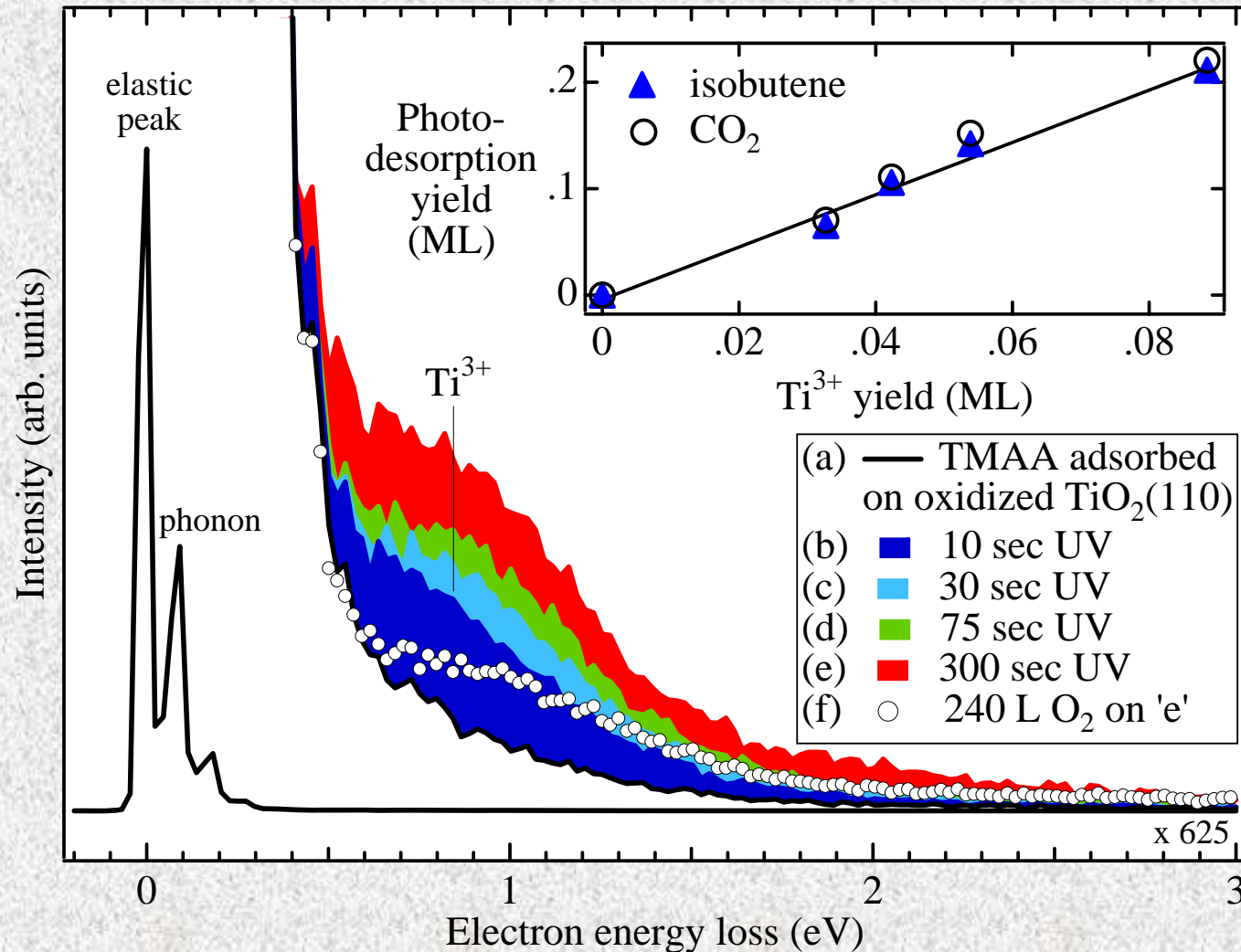


M.A. Henderson, et al. JACS 125 (2003) 14974.

H. Uetsuka, et al. JPCB 108 (2004) 10621.

Photo-excited electron trapping on TMAA-covered TiO₂(110)

no O₂; UV irradiation at RT



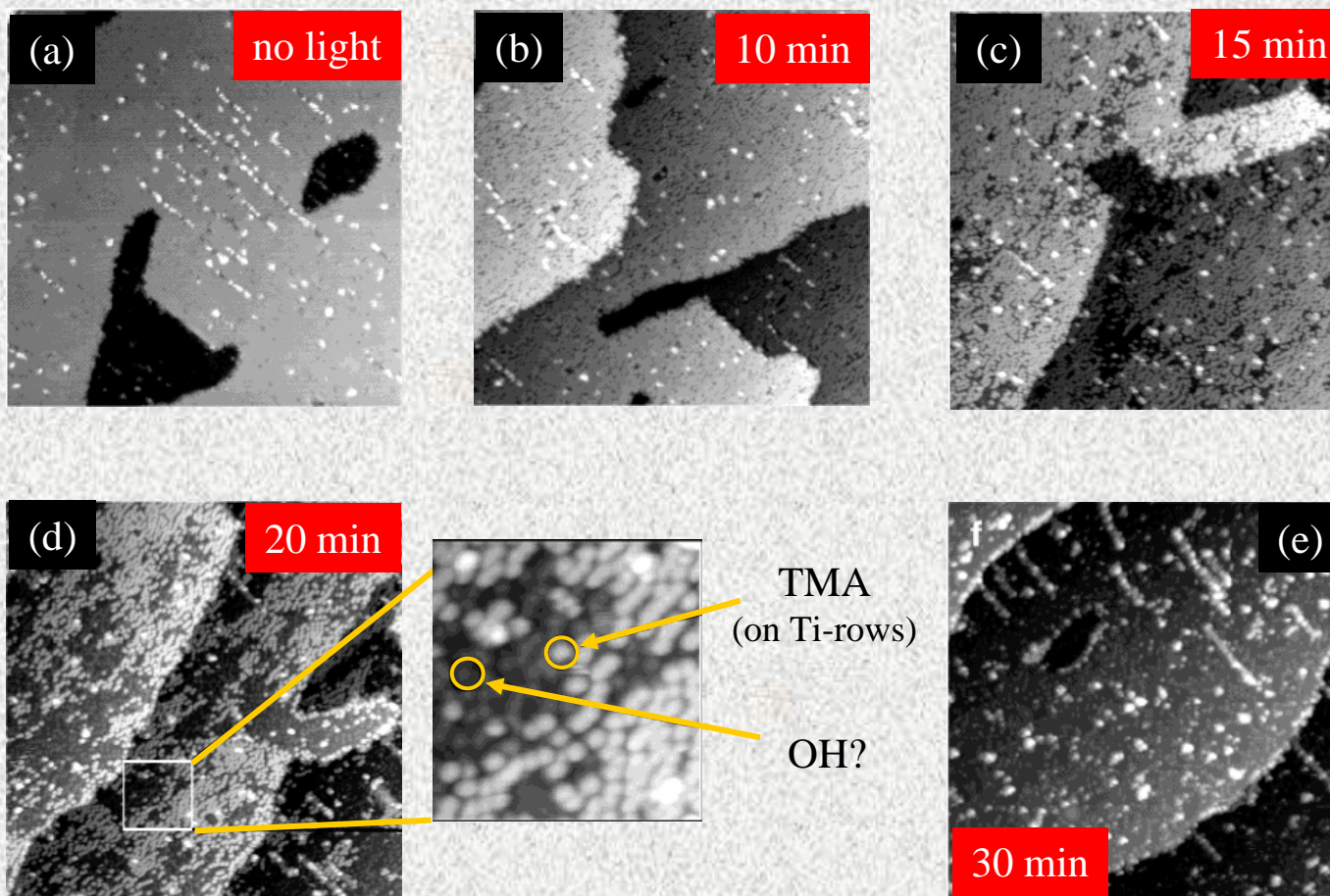
- Ti³⁺ feature same as that observed from vacancies

- Electron trapping not observed on the clean surface

- Electron trapping yield correlates with the photo-desorption yields from hole transfer; both are needed!

- O₂ titrates trapped electrons

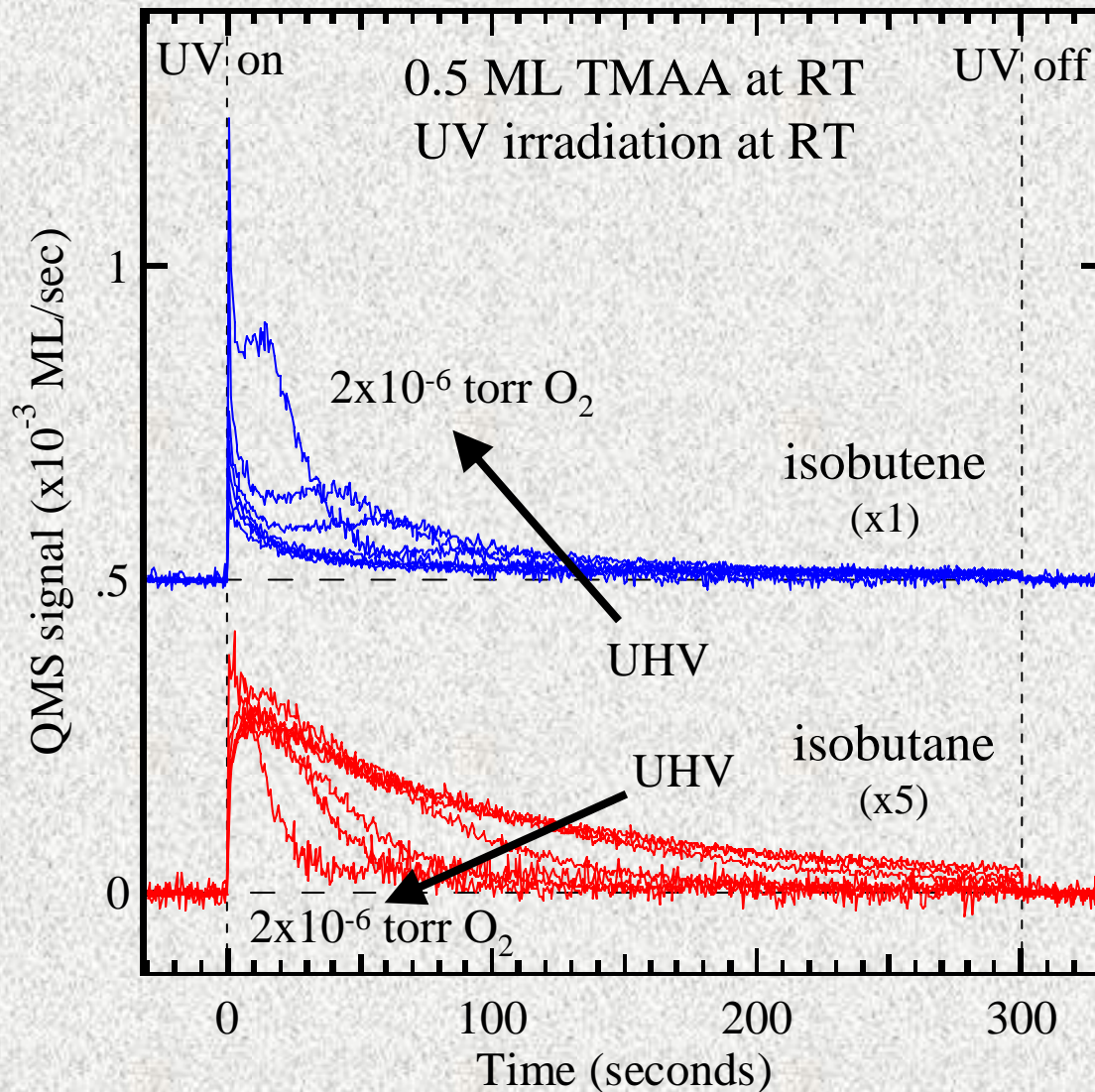
STM during photodecomposition of TMA



- Voids develop in TMA layer at an accelerated rate during photolysis
- Voids possess weak spots attributable to OH groups
- TMA groups on steps show lower reactivity than those on terraces.

(a) TMA monolayer on a vacuum-annealed TiO₂(110) surface, and after UV irradiation at 280 K in 1×10^{-7} torr of O₂ for (b) 10, (c) 15, (d) 20, and (e) 30 min. (Image size: $88 \times 88 \text{ nm}^2$; Xe lamp)

Influence of O₂ on TMA photodecomposition selectivity

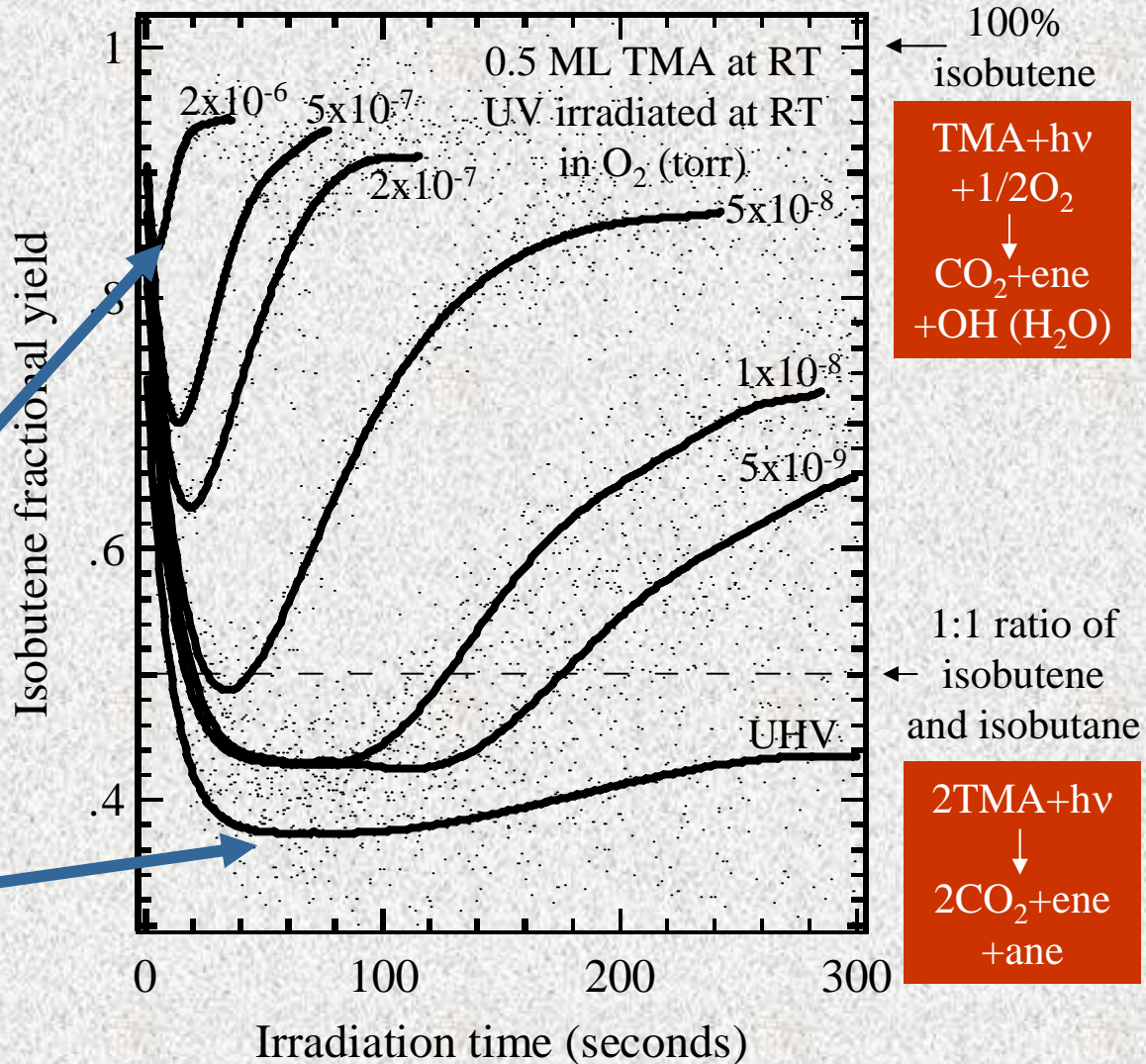
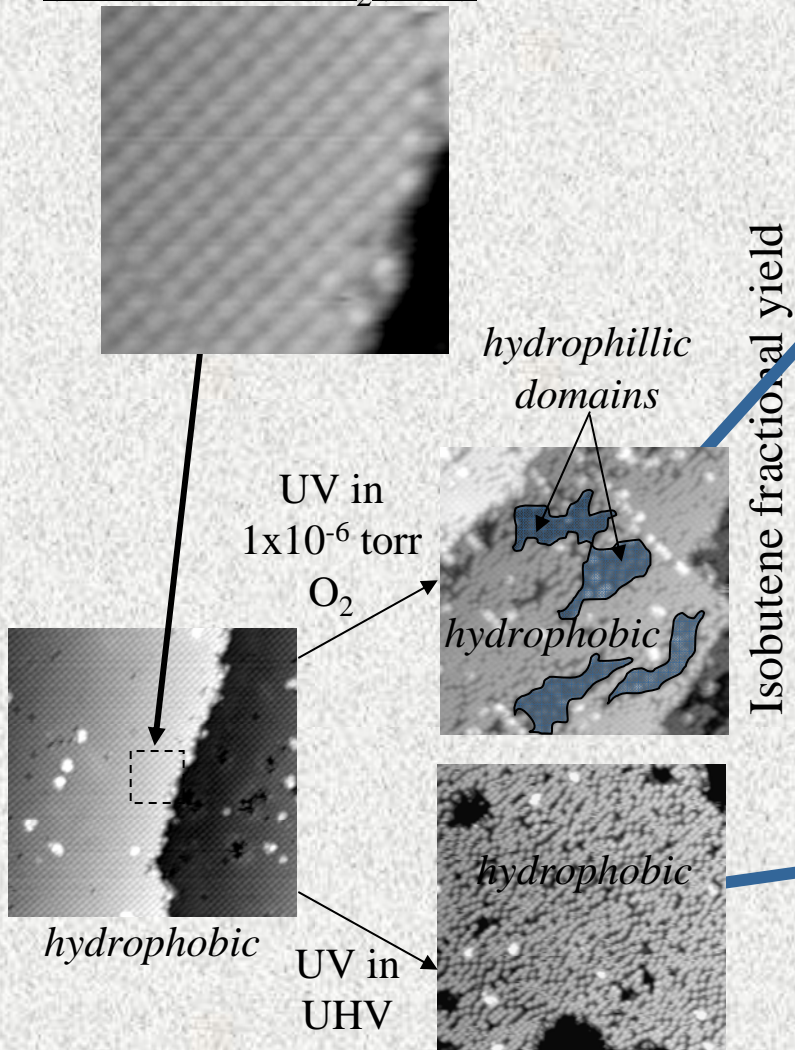


- Selectivity in the first step of TMA photooxidation shows strong O₂ pressure dependence
- Temporal changes in the selectivity are linked to coverage dependence in TMA photodecomposition

(Henderson et al.
J. Catal. 238 (2006) 153)

Photocatalytic selectivity and adlayer phase dynamics

(2x1) TMA/TiO₂(110)



Outline

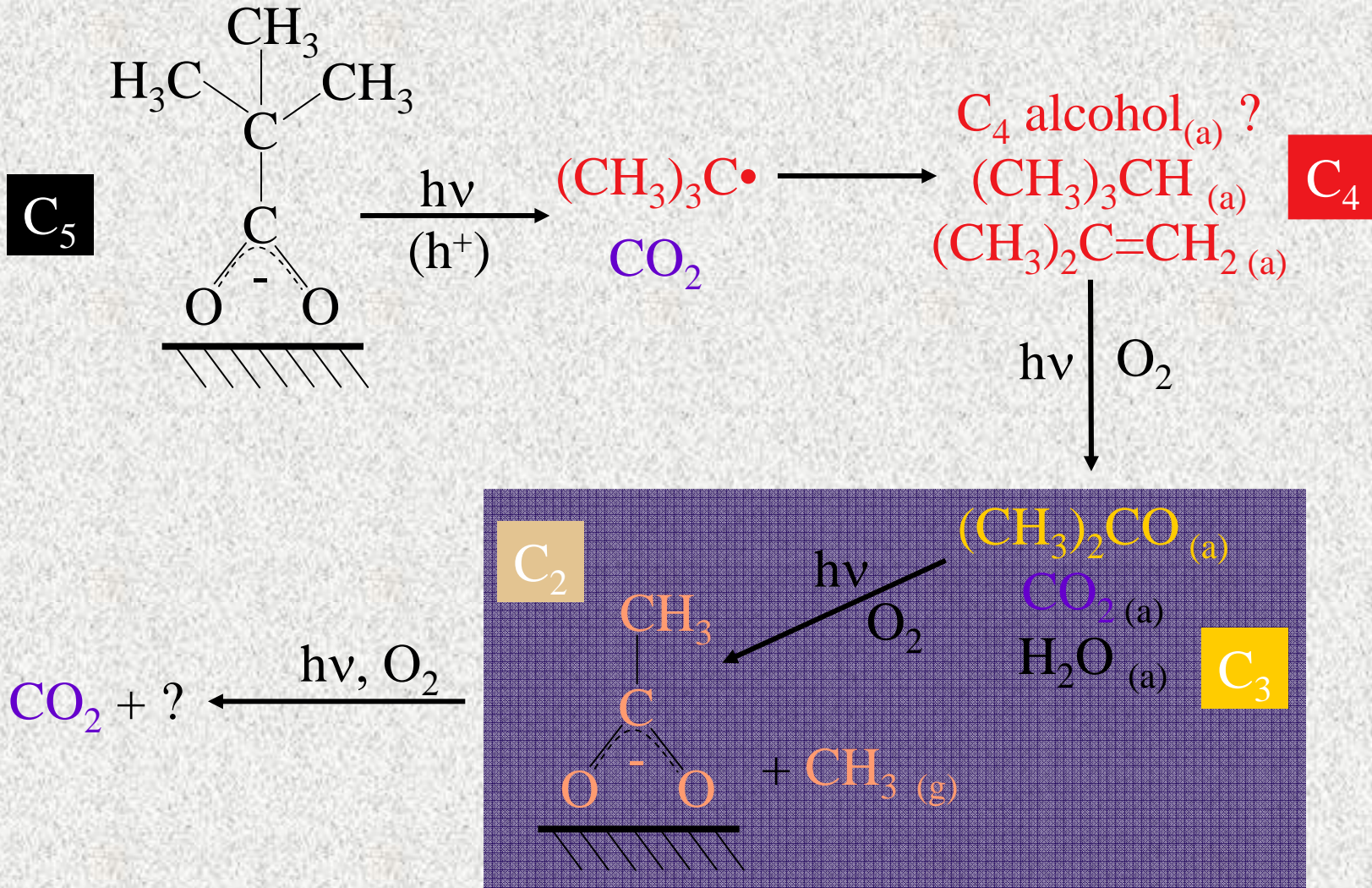
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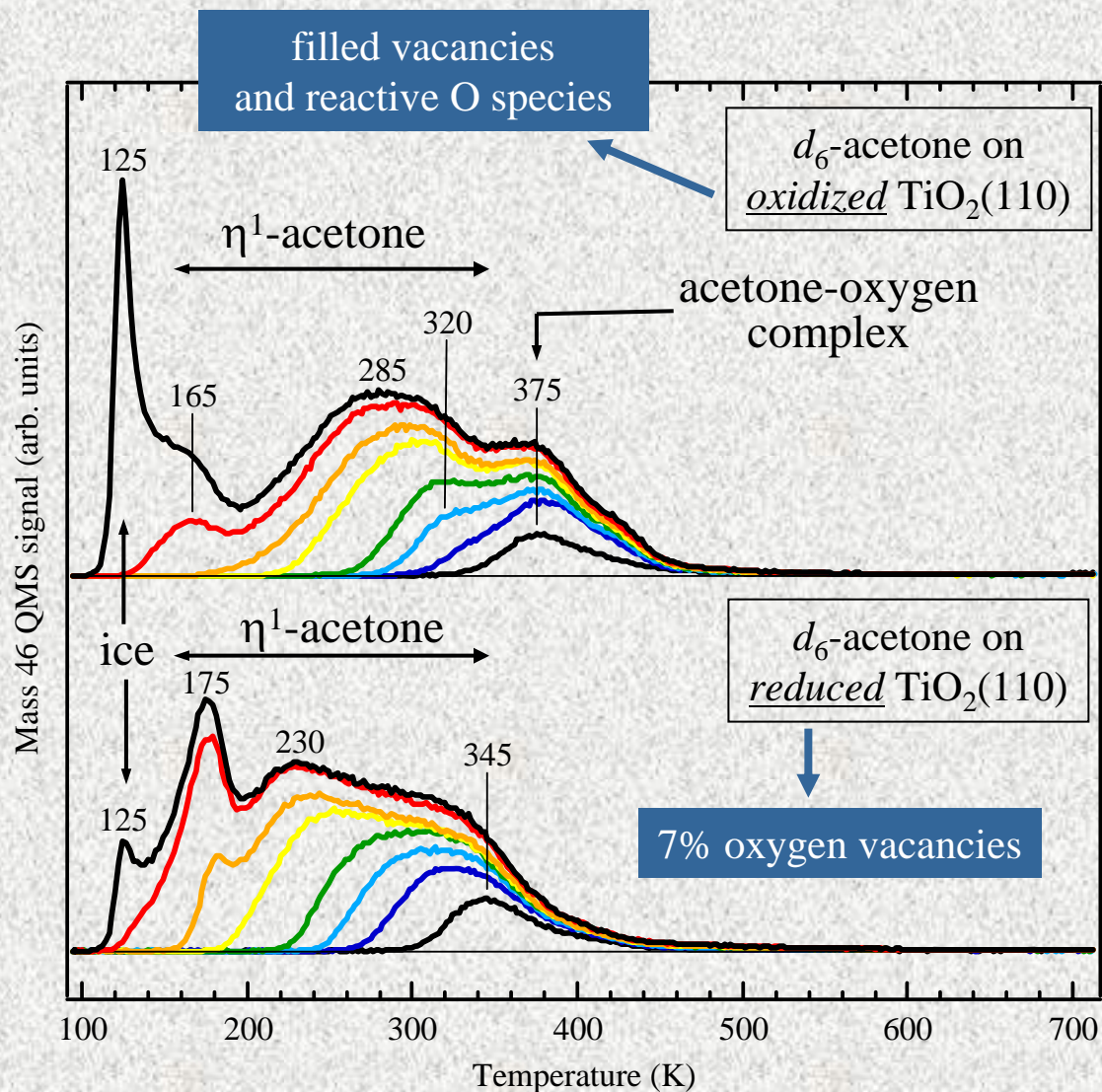
- oxygen and water
- trimethyl acetic acid
- **acetone**

Conclusions

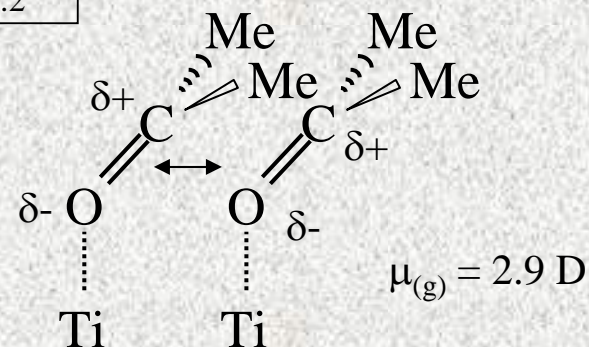
TMA photodecomposition mechanism for photolysis at 100 K



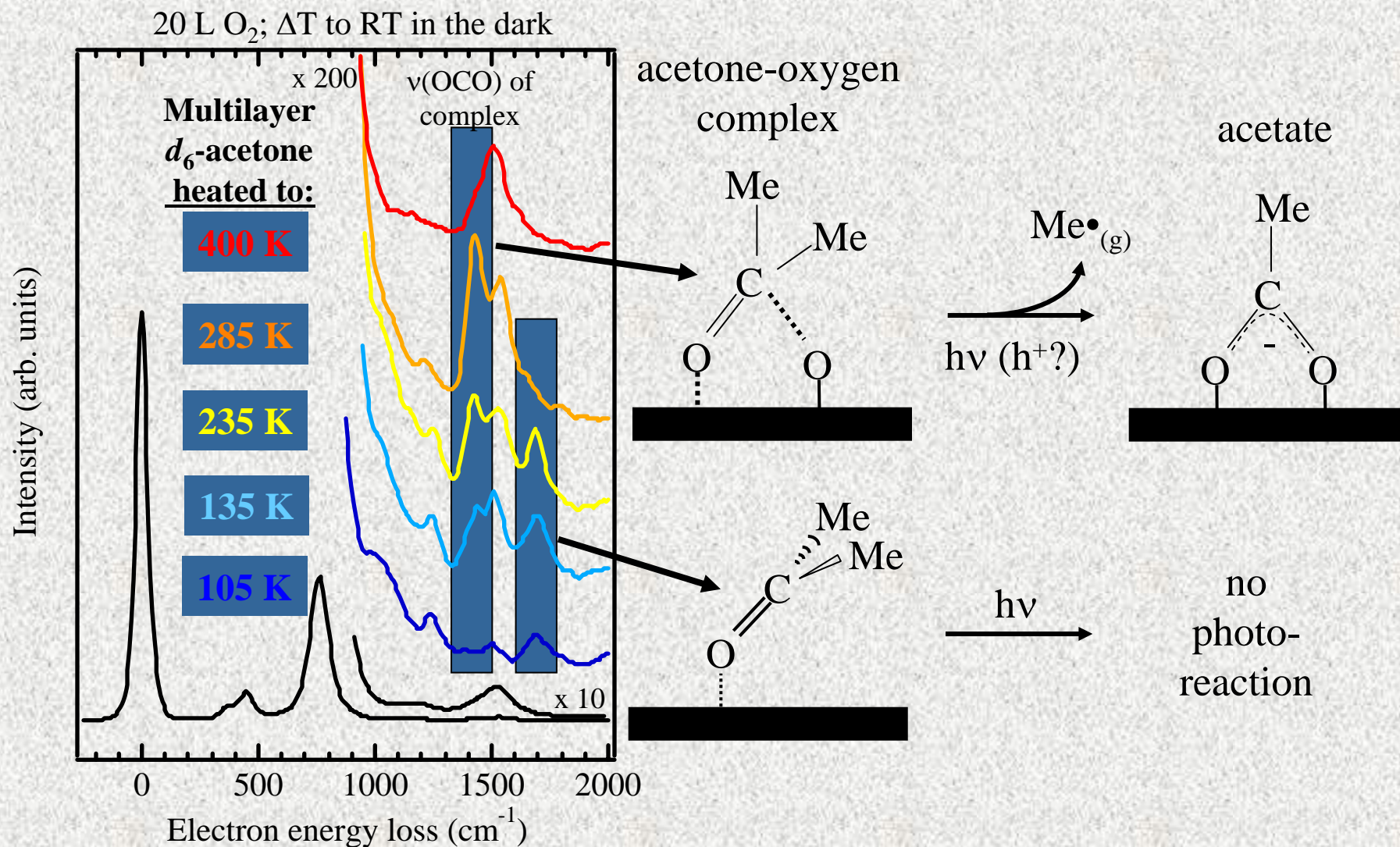
Acetone thermal chemistry on TiO₂(110)



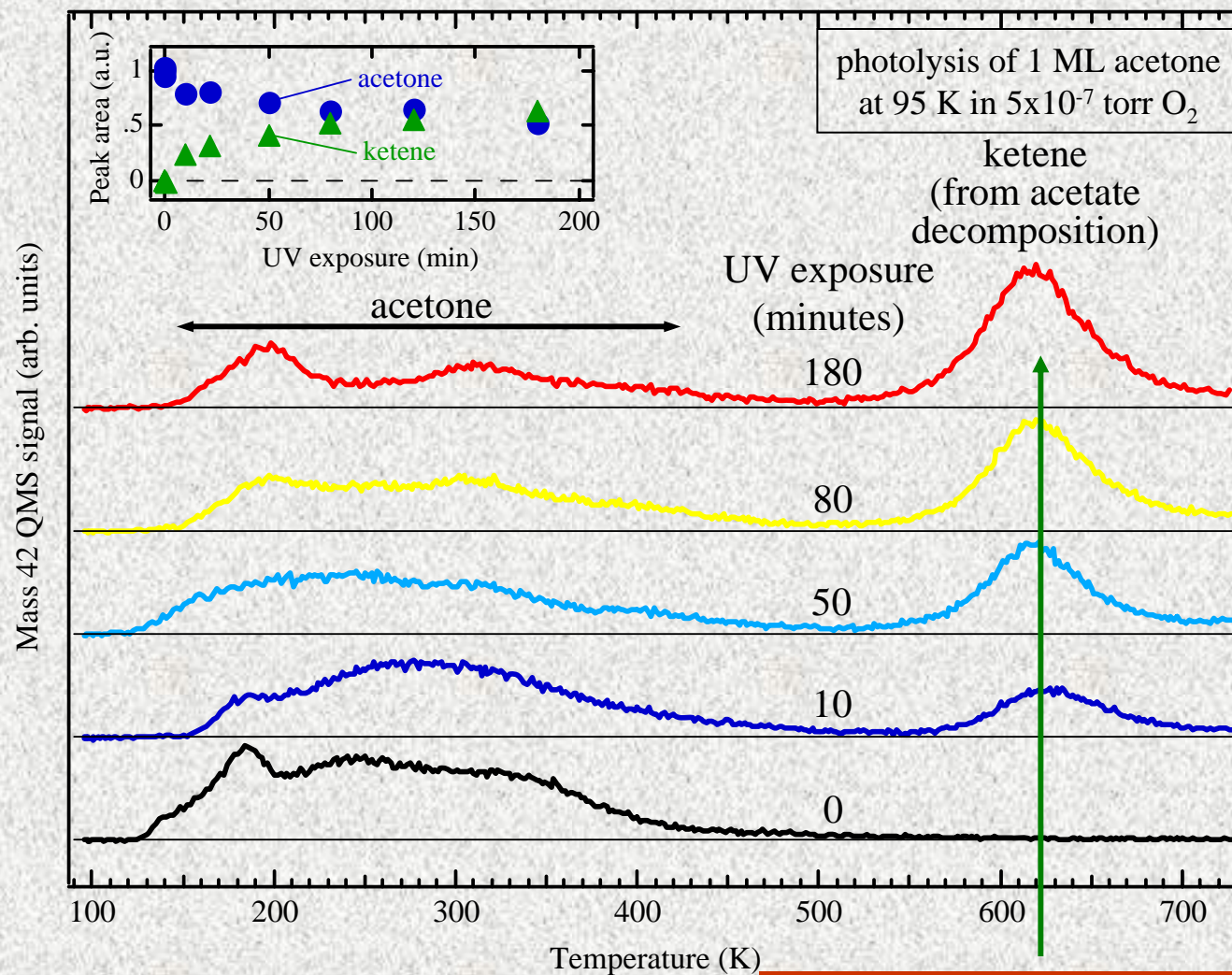
- Little or no thermal decomposition
- Acetone desorption is influenced by coverage and the surface redox condition
- Pre-oxidation stabilizes acetone and minimizes acetone-acetone repulsions



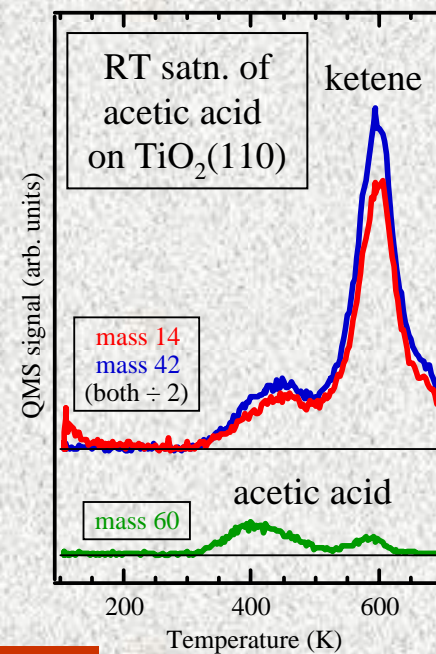
Organic and O₂ thermal chemistry: Conversion of a photo-inactive species to a photo-active species



Photodecomposition of 1 ML acetone on TiO₂(110)

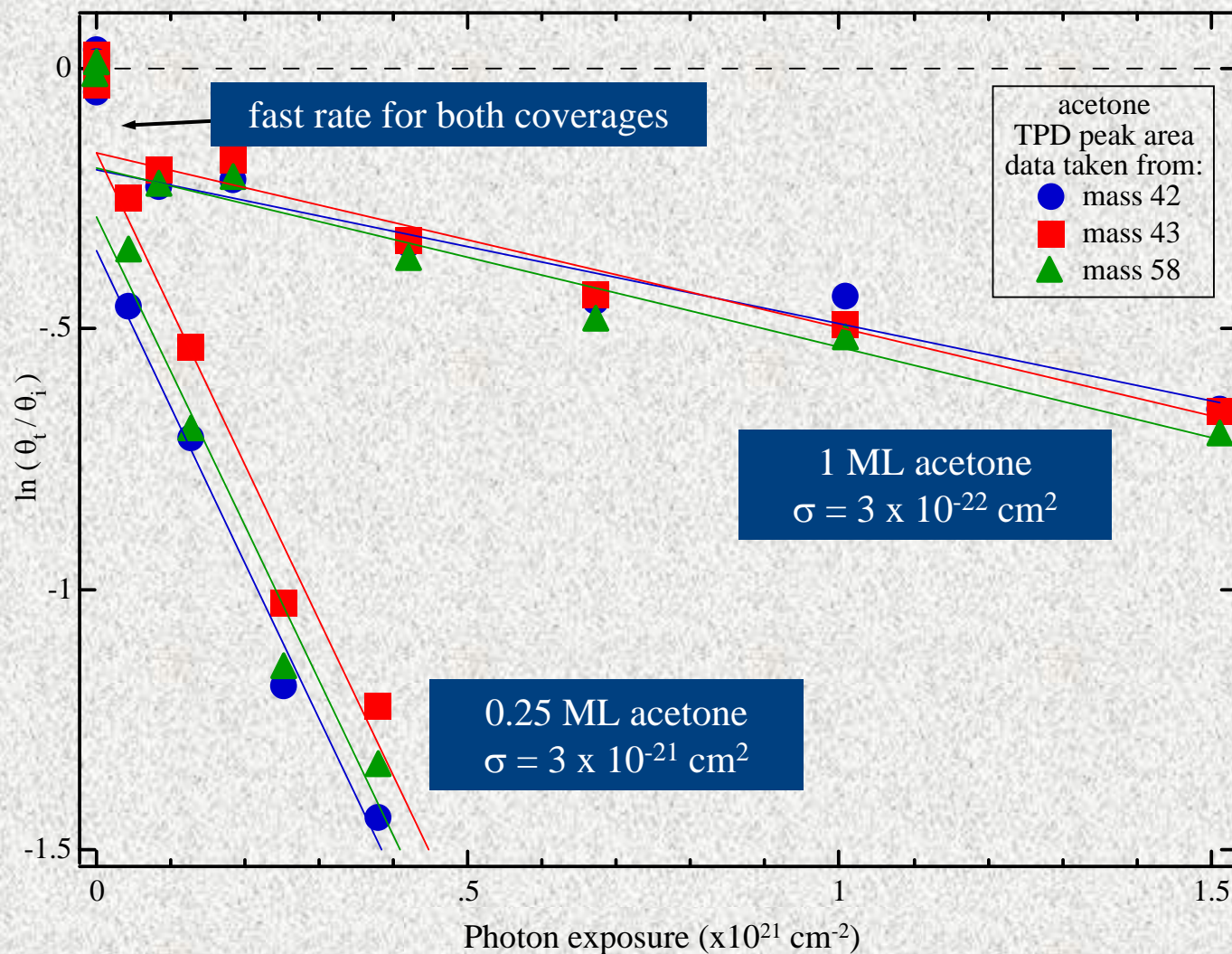


- Acetone is photo-decomposed to acetate, which thermally decomposes to ketene at 620 K.



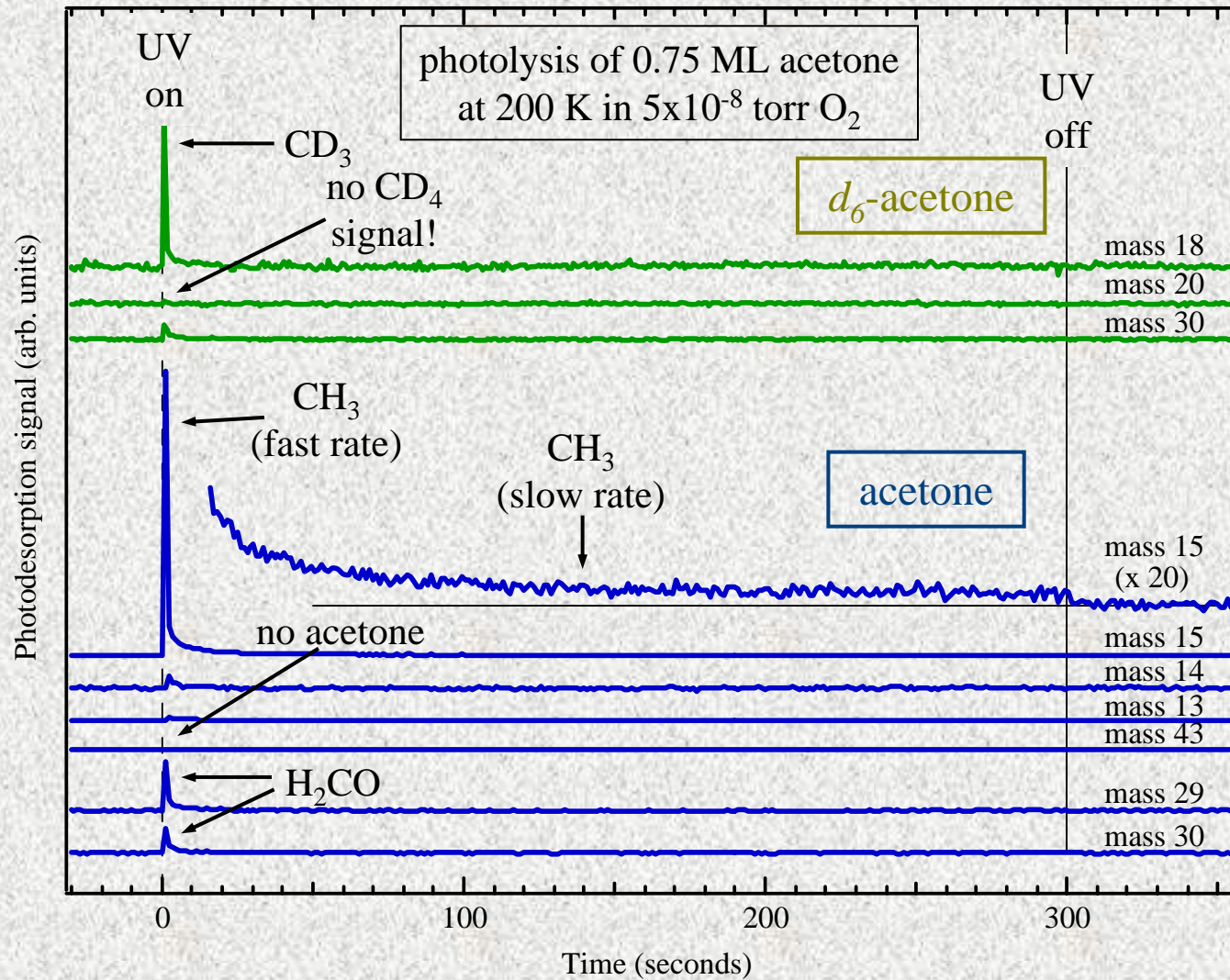
Immediate reaction product does not leave the surface!

Cross sections for acetone photodecomposition from TPD



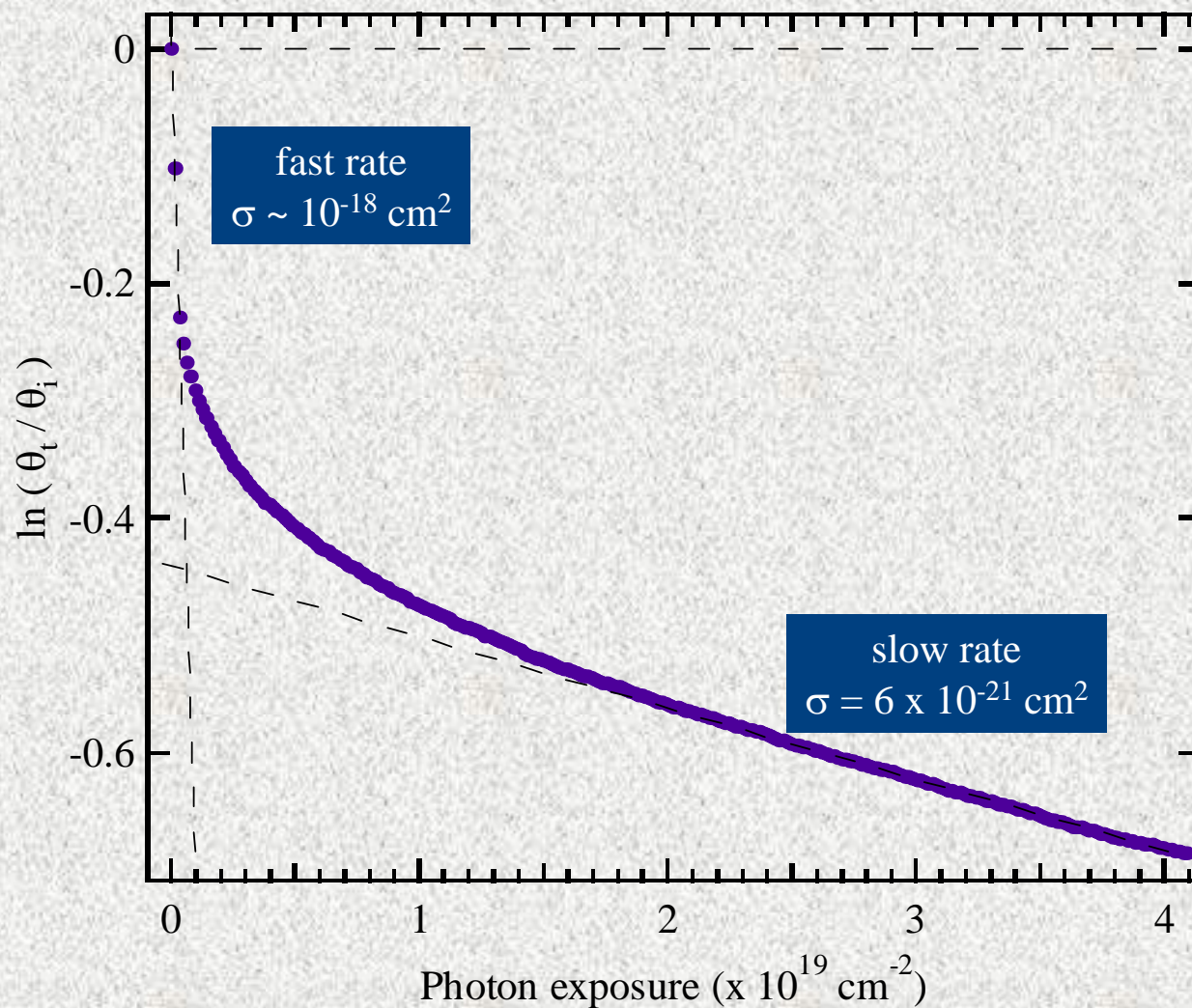
- Cross section of acetone photo-decomposition is coverage dependent; greater for lower coverages
- Fast initial and slow subsequent photo-decomposition rates
- Cross sections resemble gas phase values

Photodesorption during UV irradiation of acetone on TiO₂(110)



- Methyl radicals ejected from the surface during photolysis
- Fast and slow evolution of methyl radicals
- H₂CO is formed from reaction of methyl radical on the walls of the mass spectrometer. (H₂CO in powder studies from ejected CH₃ radicals?)

Cross sections for methyl radical ejection

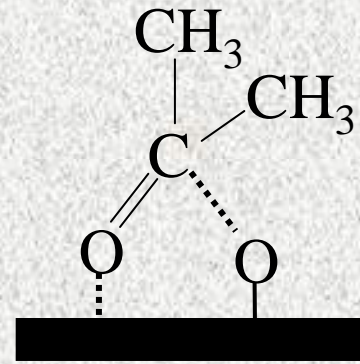
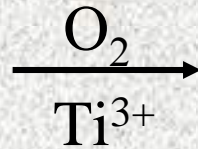
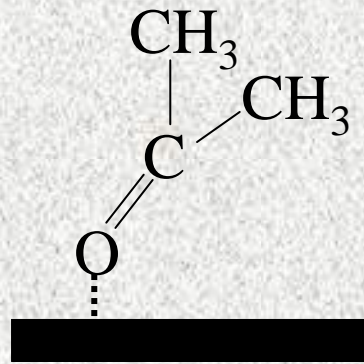


- Cross section for fast rate is two orders of magnitude greater than the slow rate

- Cross section for slow rate ($\sim 6 \times 10^{-21} \text{ cm}^2$) matches that obtained by TPD ($\sim 3 \times 10^{-21} \text{ cm}^2$); this suggests conversion of acetone to acetate and methyl radical ejection are mechanistically linked.

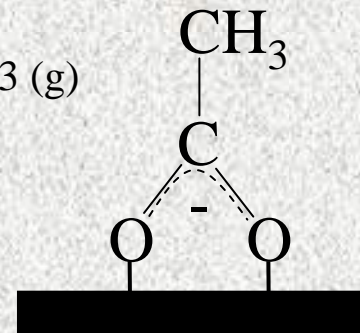
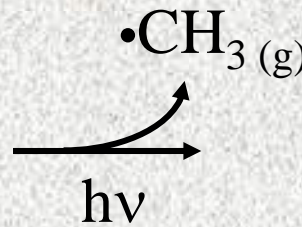
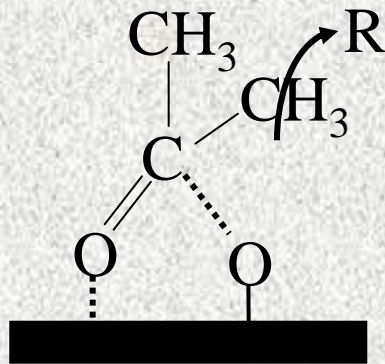
Proposed acetone photodecomposition mechanism

in the dark



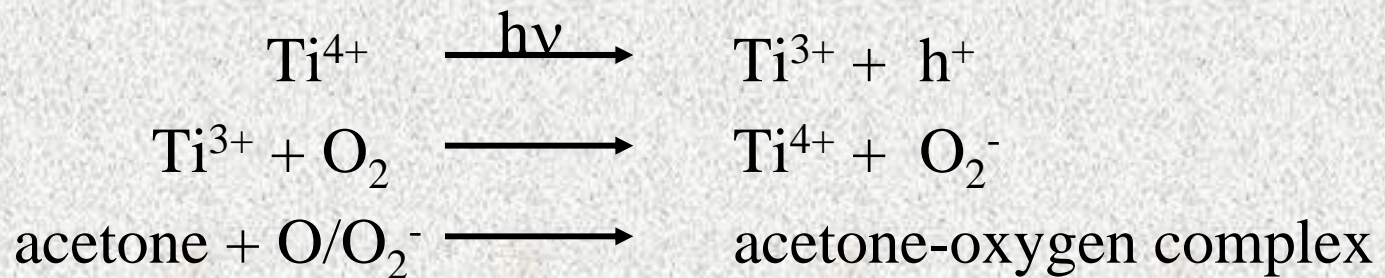
acetone-oxygen complex

UV fast process

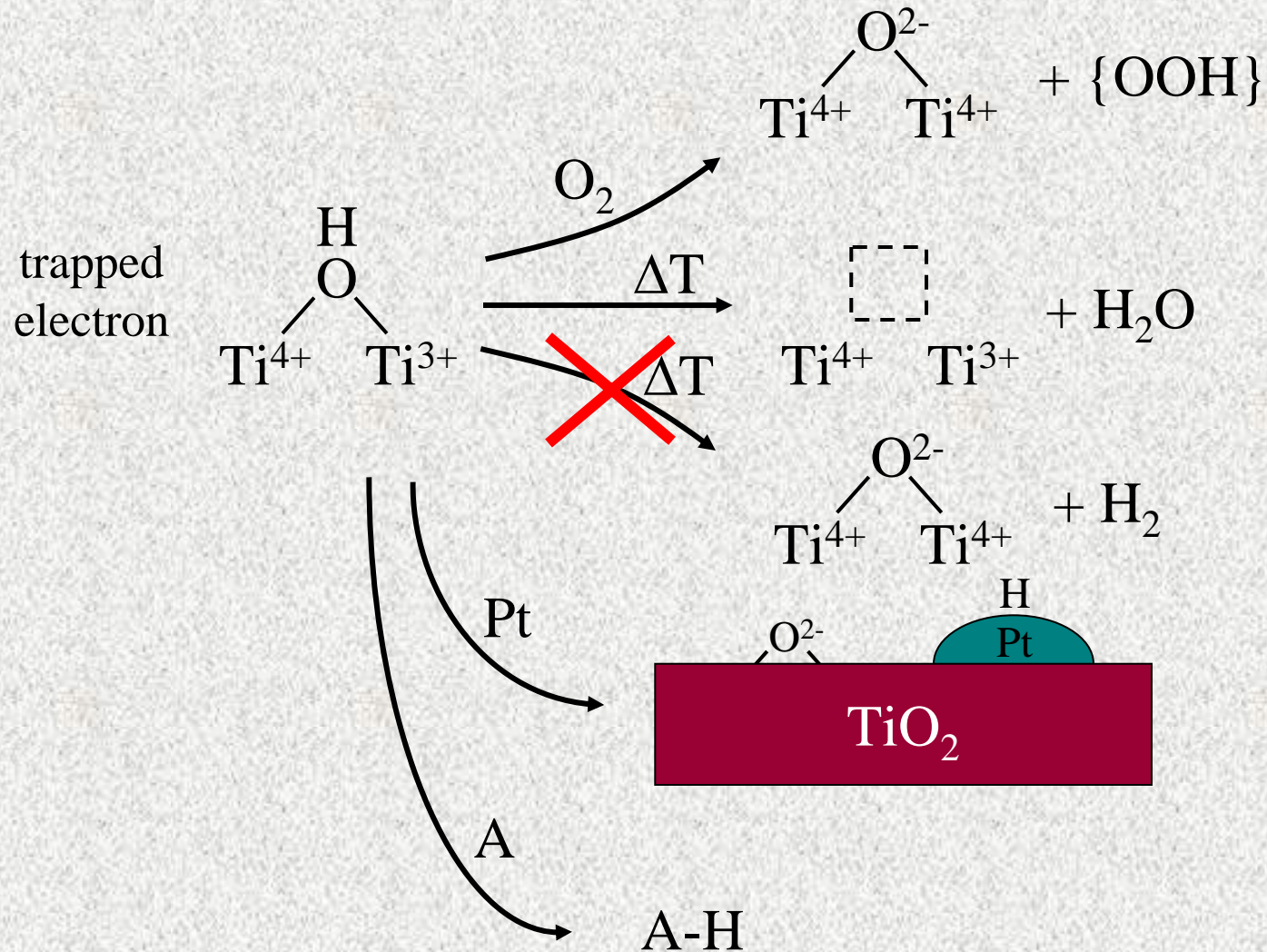


acetate

UV slow process
(O_2 flux dependent)



Hydrogen production on TiO₂



What about the holes?

Conclusions

Meaningful insights into the molecular-level details of heterogeneous photocatalysis can be obtained from model studies.

- Identification of charge transfer and trapping sites
- Detection of adsorbed and photodesorbed intermediates
- Determination of reaction pathways and selectivities
- Measurement of cross sections (rates)
- Observation of spatial effects such as evolution of hydrophobic and hydrophilic domains

Acknowledgements

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