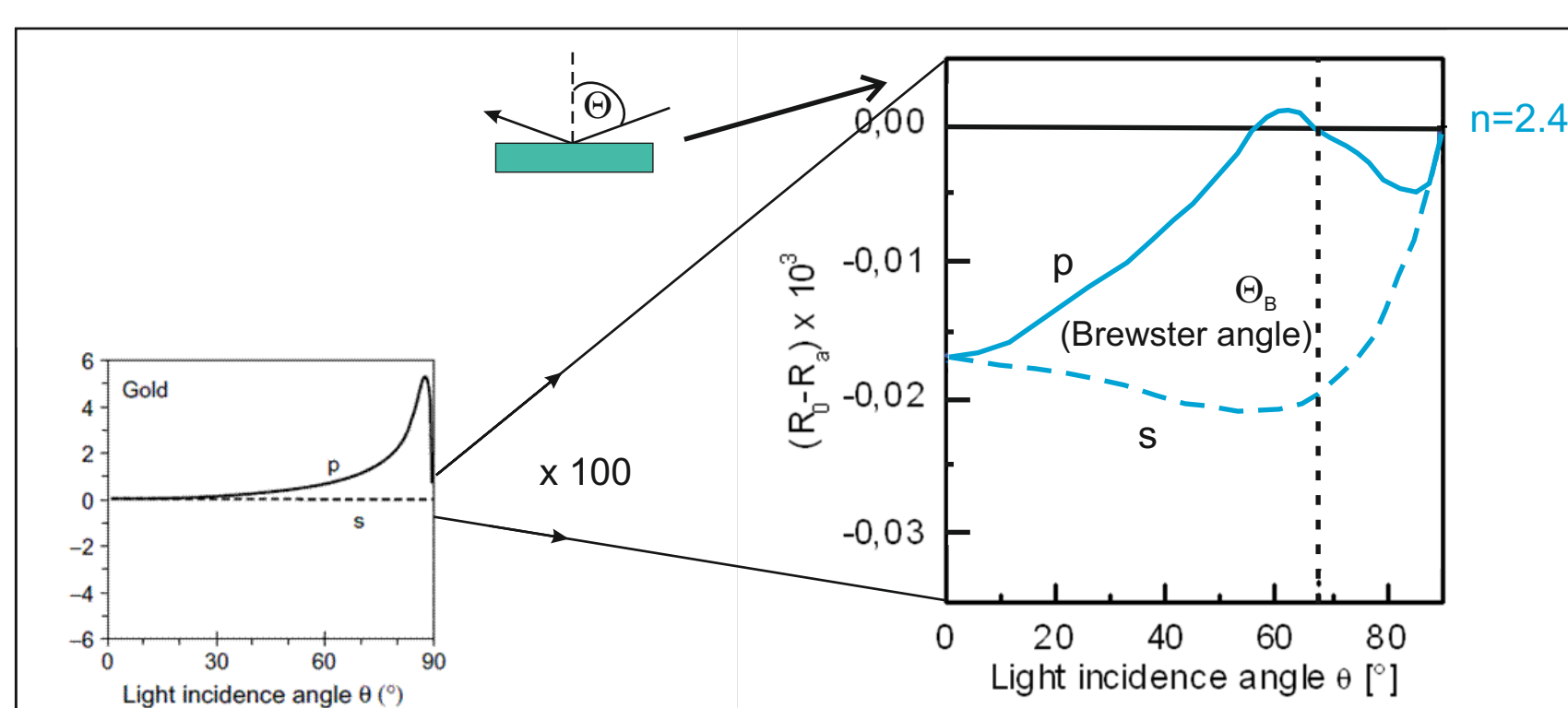


Photocatalytic Activity of TiO₂ Anatase (101) and Rutile (110) Single Crystals

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FTIR- and IRRA - spectroscopy of oxide surfaces

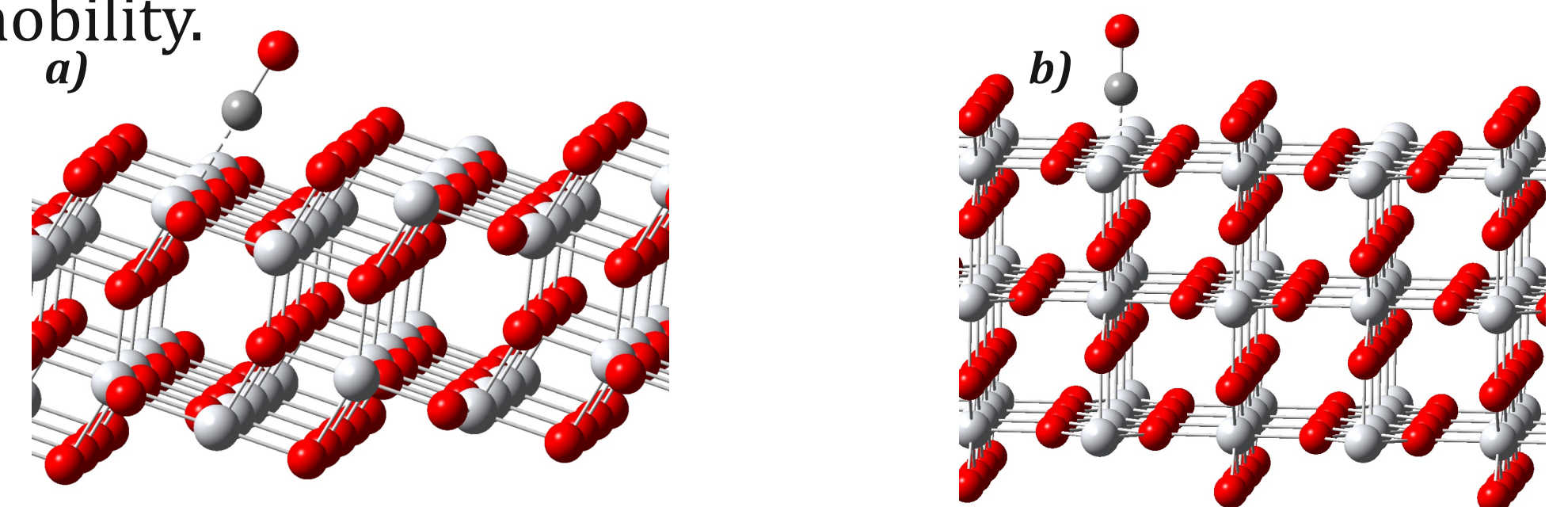
- To understand the complex IR spectra recorded for oxide powder, it is necessary to obtain data for well-defined model systems with reduced complexity, e. g. single-crystal surfaces.
- Metal surface selection rule:** Vibrational modes with a transition dipole moment (TDM) orientated parallel to the surface cannot be seen.
- Dielectric surfaces:** both s- and p-polarized light couple to adsorbate Vibrations - metal surface selection rule is invalid.
- Absorption bands of molecular adsorbates can lead to a reduction in reflectivity (positive bands), but also to an enhancement of reflectivity (negative bands).



Calculated reflectivity differences between the clean substrate (R_s) and the adsorbate covered substrate (R_p) for different substrate materials as a function of the light incidence angle for p-polarized radiation and s-polarized radiation.

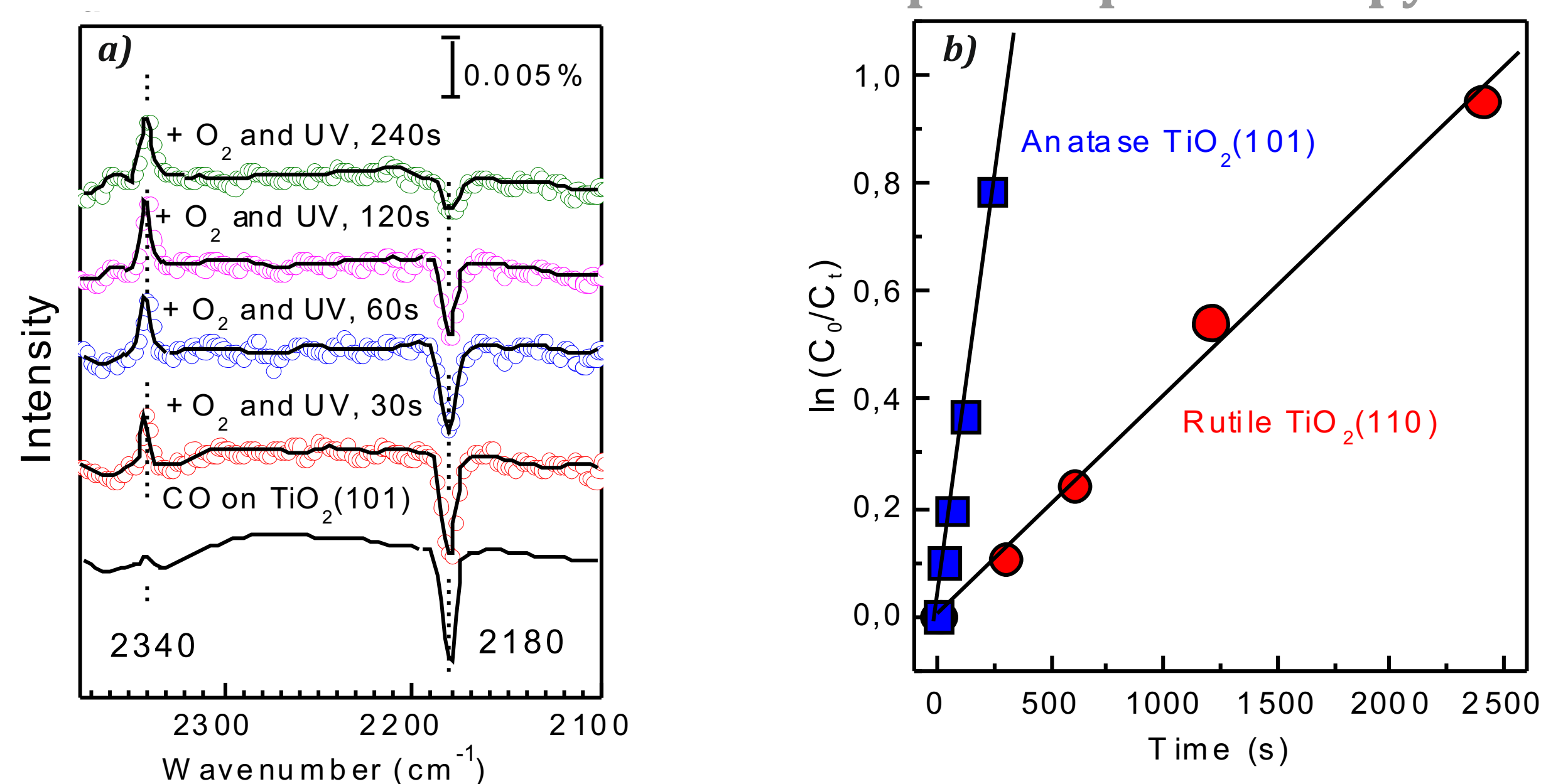
Photocatalytic differences between TiO₂ Anatase and Rutile

- Both crystal forms exhibit significant photocatalytic activity
- Mechanism responsible for this behaviour is a controversial subject
- Hypothesis proposed:**
 - Powder particle size, surface area, defect density, porosity may influence rate of recombination of electrons and holes
 - Higher Fermi levels in anatase than in rutile ($\Delta 0.2$ eV)
 - Different oxygen affinity for oxygen, higher density of hydroxyl groups on anatase surface, which in turn influences photocatalytic activity
 - e-h lifetimes will be longer in anatase with indirect band-gap than in rutile
 - Higher charge carrier mobility (in particular electrons) in anatase smaller electron effective mass and hence higher mobility.



Ball- and stick models of different titania surfaces. A) Anatase TiO₂ (101). B) Rutile TiO₂ (110). CO bind via the C-atom to a surface Ti ion.

Infrared Reflection Absorption Spectroscopy



a) RAIRES data of CO and CO₂ during photo-induced CO oxidation reaction on the anatase TiO₂ (101) single crystal surface at 100 K. b) Comparison of the reaction cross section Q of CO photooxidation on rutile TiO₂ (110) and anatase TiO₂ (101). C₀ is the initial CO coverage before UV irradiation and C_t is the CO coverage after irradiation time at time t.

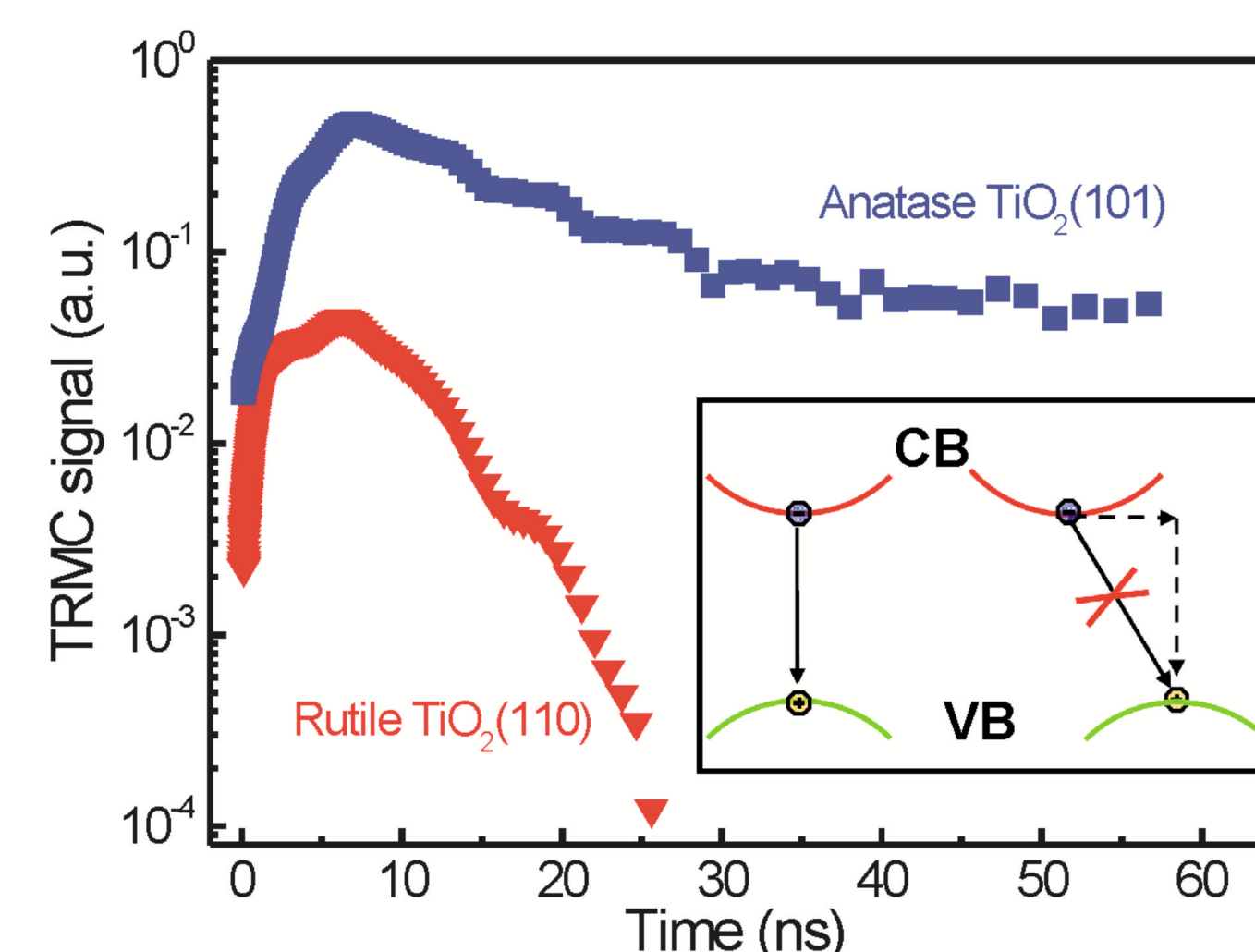
- 2180 cm⁻¹ → CO adsorbed on Ti_{5c} ions (2183 cm⁻¹ for rutile)
- CO+O₂+UV-light (3.4 eV)
 - decrease of the CO band intensity
 - band at 2340 cm⁻¹ (physisorbed CO₂)
- no reaction with only one, UV or O₂
- photoreaction cross section Q for anatase 2.0x10⁻¹⁷ cm² and for rutile 2.0x10⁻¹⁸ cm²

- ⇒ photo-induced oxidation of CO
- ⇒ correlation with different lifetimes of the photogenerated e-h pairs in the two titania pseudomorphs

Conclusion and Outlook

- ⇒ the longer lifetime of e-h pairs in anatase facilitates the translocation of the photon-excited electrons and holes from the bulk to the surface
- ⇒ Disturbing the band structure of anatase, e.g., through dopants, will reduce the lifetimes by making e-h recombinations at localized defects possible. The latter effect will at some point overcompensate for the dopant-induced gain in the photochemical cross section that results from a reduction of the band gap.

Photoconducance measurements



Transient photoconducance measurements at 30GHz induced by 355 nm laser pulses (10ns FWHM) in a rutile and in an anatase TiO₂ single crystal. The inset shows the schematic model of the band gap of rutile (left) and anatase (right).

Rutile

- decay is very fast (< 1 ns)
- already active during excitation Phase
- much smaller signal amplitude in rutile

When electrons relax to the bottom of the conduction band (CB) after they have been photoexcited (vertically) into unoccupied states, they will not be able to recombine directly with holes, thus increasing the e-h lifetime relative to a situation with a direct band-gap.

- ⇒ rutile band-gap might be a direct one, allowing for a much faster recombination of photoexcited e-h pairs in rutile than in anatase.

Anatase

- decay is much slower
- reveals a lifetime of photo-excited carriers of larger than 10 ns

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Reference

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