

UHV - FTIRS and STM - investigations of oxide surfaces and oxide films

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FTIR- and RAIR - spectroscopy of oxide surfaces

Oxides have found numerous applications, e. g. in catalysis, for producing sensors, solar cells and electronic devices. In the past decades numerous IR investigations of oxide powders have been reported. To understand the complex IR spectra recorded for such powder, it is necessary to obtain data for well-defined model systems with reduced complexity, e. g. single-crystal surfaces. Unfortunately, studies on oxide single crystals are extremely scarce. As a result of severe technical problems, in case of rutile TiO_2 so far only one IR-study^[1] has been reported. Reflection-absorption infrared spectroscopy (RAIRS) on metal surfaces is governed by the so-called surface selection rule: Vibrational modes with a transition dipole moment (TDM) orientated parallel to the surface cannot be seen. For dielectric surfaces the situation is more complicated, both s- and p-polarized light couple to adsorbate vibrations. In addition absorption bands of molecular adsorbates on metals can lead to a reduction in reflectivity (positive bands) as in the case of metals, but also to an enhancement of reflectivity (negative bands). For s-polarized light the bands will always be negative, for p-polarized light the bands can be negative or positive depending on the incidence angle Θ and the refractive index n of the substrate (Fig.1). We have designed a new UHV-IR/XPS-apparatus^[2], with which data for molecular adsorbates on oxide single-crystals can be recorded in a routine fashion (Fig.3).

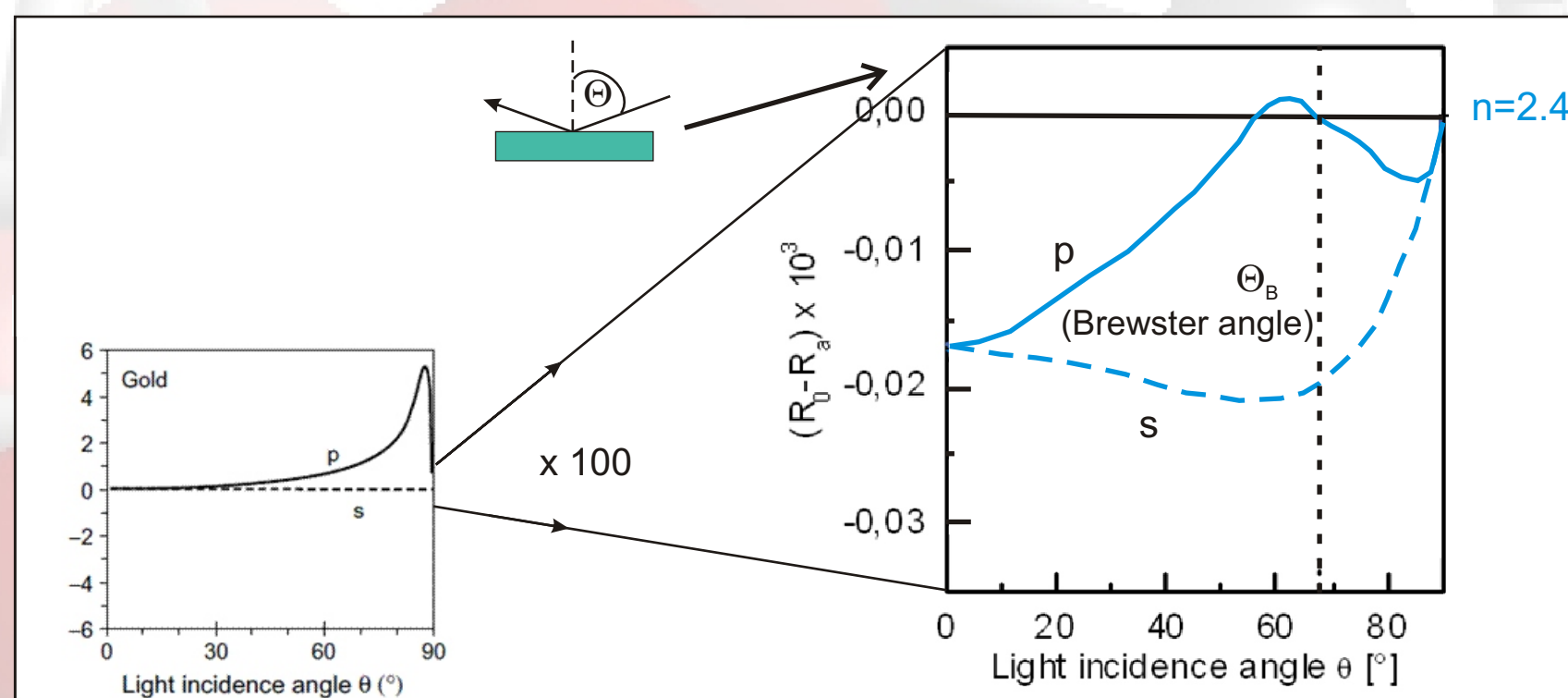


Fig.1: Calculated reflectivity differences between the clean substrate (R_s) and the adsorbate covered substrate (R_a) for different substrate materials as a function of the light incidence angle for p-polarized radiation and s-polarized radiation.

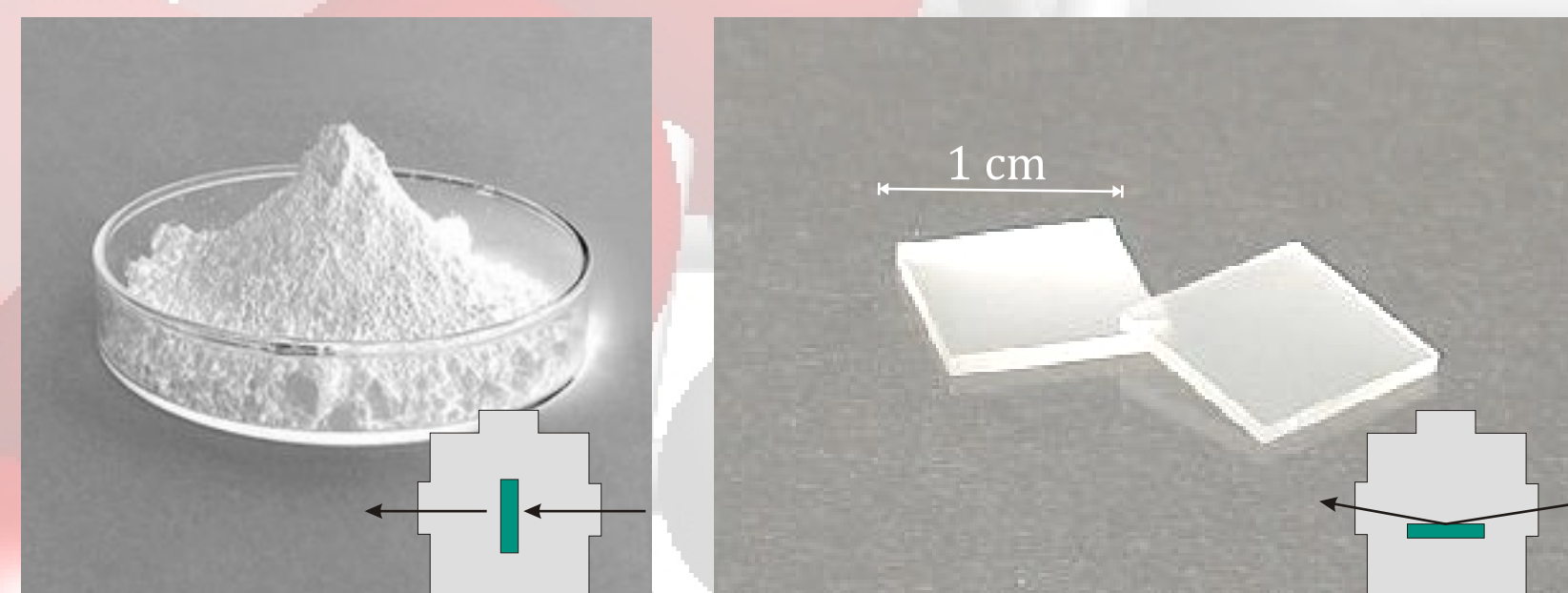


Fig.2: Powder IR - measurements in transmission mode (left), oxide single crystals IR - measurements in reflection mode (right)

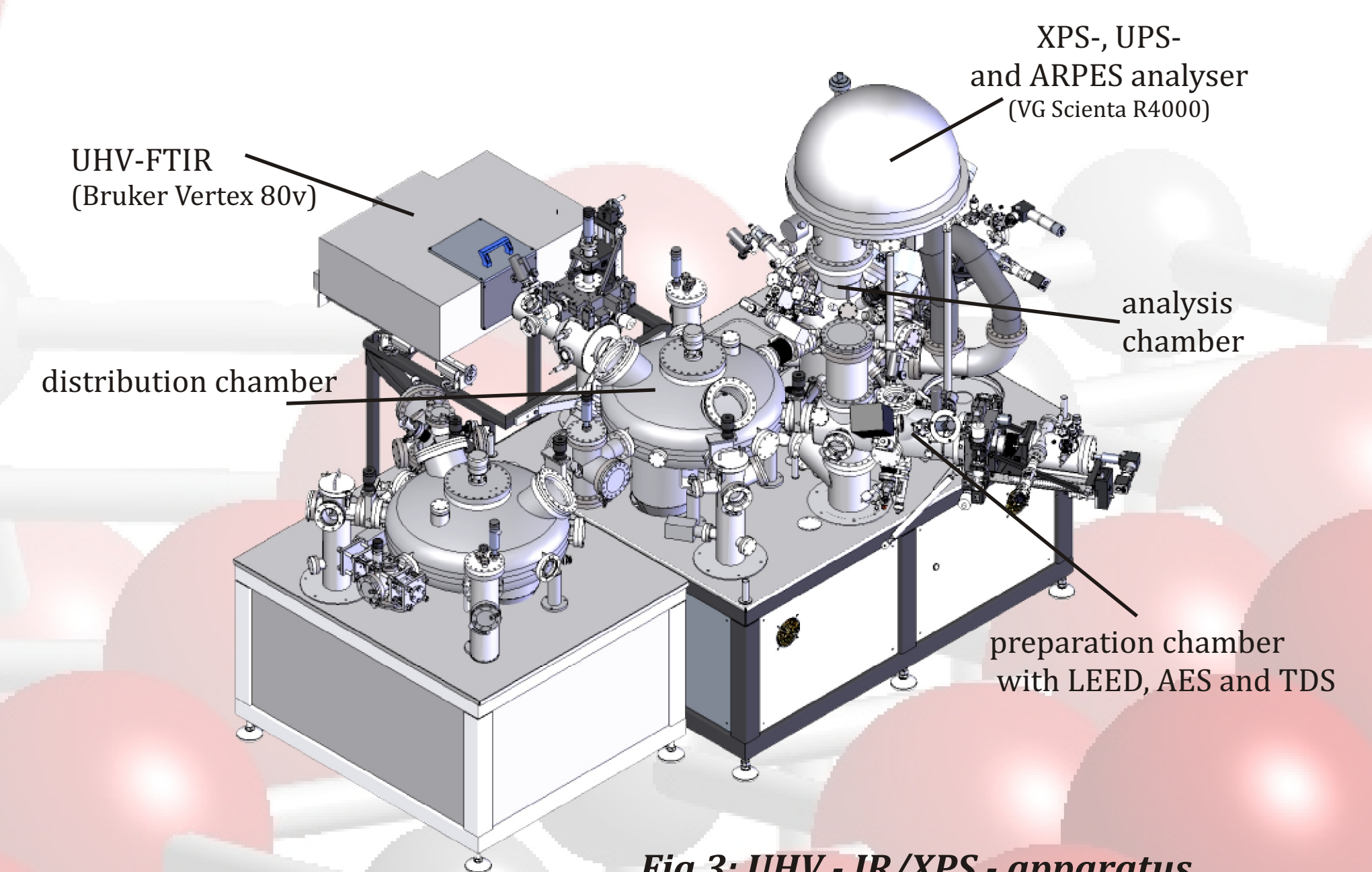


Fig.3: UHV - IR/XPS - apparatus

Photocatalytic reactions on TiO_2

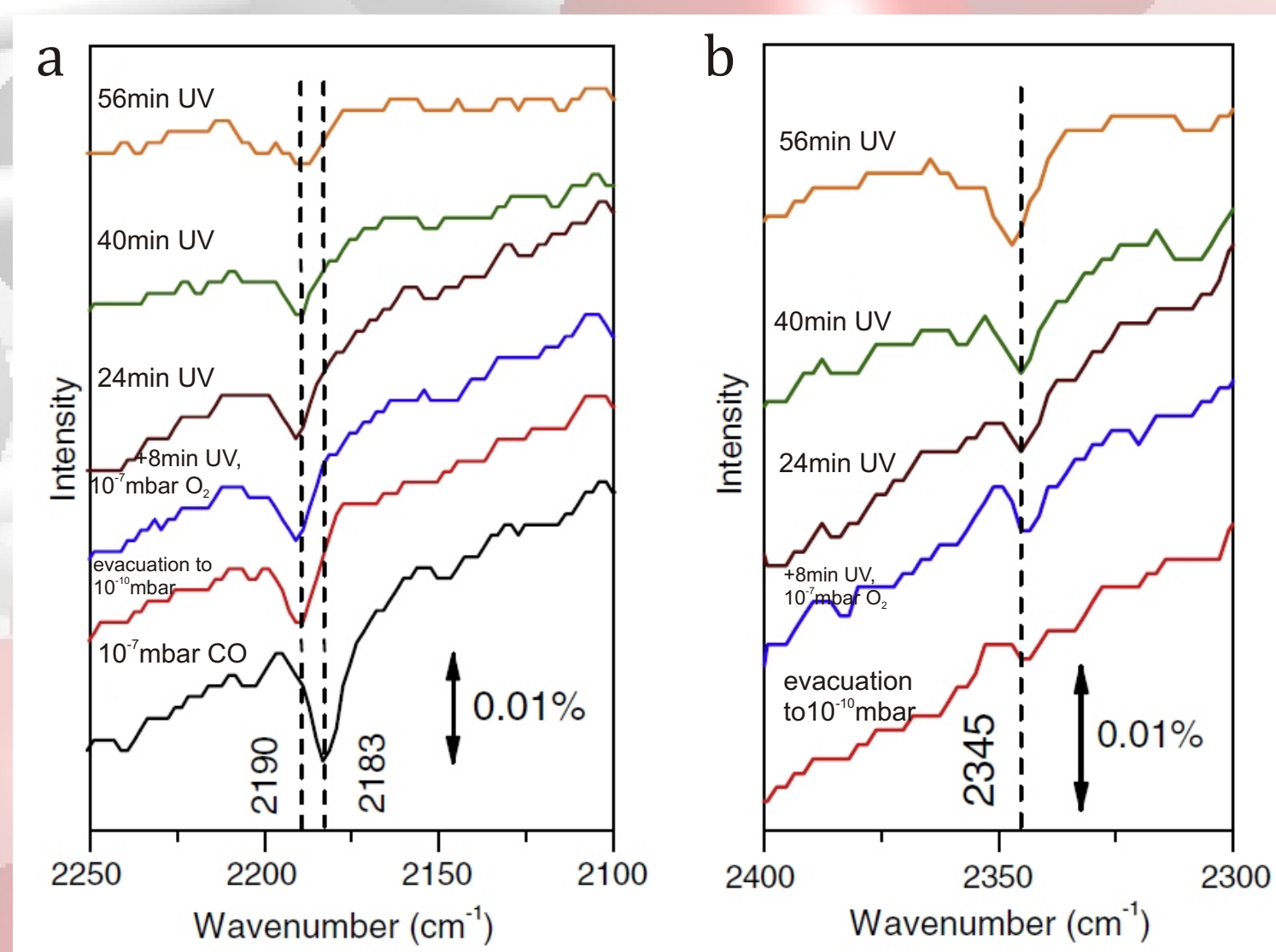


Fig.5: a) RAIRS data of CO on $\text{TiO}_2(110)$ single-crystal surface at 110K, b) CO_2 region of a)

Titania (TiO_2) presently attracts a lot of interest because of its photovoltaic and photochemical properties. The first RAIRS results^[3] of CO photooxidation to CO_2 on $\text{TiO}_2(110)$ single-crystal surfaces are displayed in Fig.5. In the presence of 10^{-7} mbar CO on $\text{TiO}_2(110)$ at 110K, the internal stretching mode of CO adsorbed on Ti_{1c} sites is seen at 2183cm^{-1} . At higher coverages this band shifts slightly to 2190cm^{-1} . After exposure to UV-light (3.2eV) no photo-induced desorption of CO was detected, only in the presence of O_2 a decrease of the band-intensity reveals photooxidation. In the RAIRS data no intermediates which can be attributed to reaction intermediates like formate or carbonate species were present. We conclude that the activated O_2 molecules react directly with the adsorbed CO to yield CO_2 . Some of the product CO_2 remain adsorbed in the surface, as indicated by the new band at 2345cm^{-1} (Fig.5b).

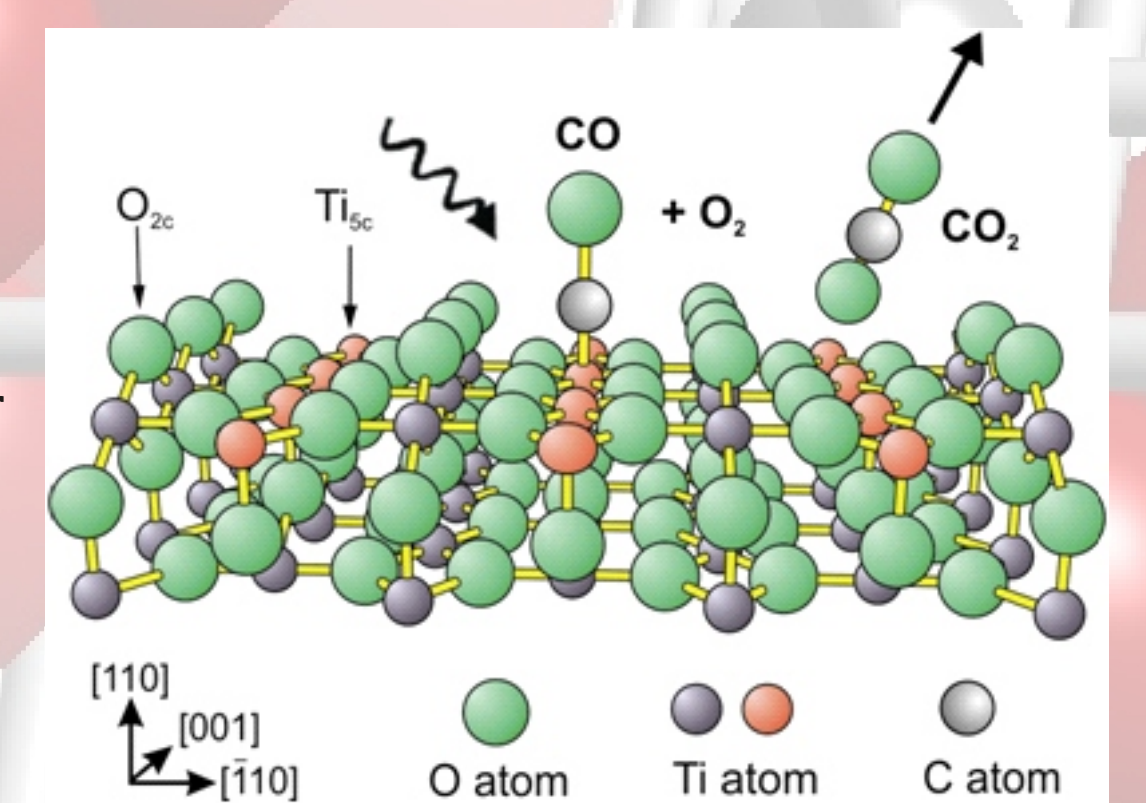


Fig.4: Side view of the $\text{TiO}_2(110)$ surface and adsorbed CO molecules on top of Ti atoms (red), which are five fold coordinated to oxygen atoms (green); formation of CO_2 via photooxidation of CO.

STM-measurements of ultrathin TiO_x - Films on $\text{Pt}_3\text{Ti}(111)$ Research Group of Prof. Dr. K. Wandelt, university of Bonn.

Scanning tunneling microscopy (STM) is a powerful technique for imaging surfaces at the atomic level. The STM probes the local density of states (LDOS) of the sample surface and its electronic properties. This method is limited to conductive samples, making experiments on thin and electron-transparent oxide films particularly attractive.

Four different phases of ordered, ultrathin titanium oxide films (Fig.6) can be prepared in UHV by oxidation of a $\text{Pt}_3\text{Ti}(111)$ single-crystal^[4]. These different phases have been investigated by low-energy electron diffraction (LEED) and a home-built STM. Two commensurate phases with zig-zag stripes (z' - TiO_x) and with a wagonwheel-like structure (w' - TiO_x) are obtained at low oxygen pressures. In both cases the resulting homogeneous oxide films wets the complete surface and consist of Ti-O bilayers. At high oxygen partial pressures two incommensurate structures can be prepared: a fully oxidized rect- TiO_2 film, that forms a film which contains holes to release stress, that arises from the lattice mismatch between film and substrate. The second (z - TiO_x) shows a very disordered surface morphology.

z' - TiO_x	w' - TiO_x	z - TiO_x	rect- TiO_2
rect-($6 \times 3 \sqrt{3}$) commensurate	hex-(7×7) $R21.8^\circ$ commensurate	incommensurate	incommensurate
10 L - 200 L O_2	220 L - 1500 L O_2	900 L - 2700 L O_2	6000 L O_2
1000 K	1000 K	900 K	800 K
$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-7}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar

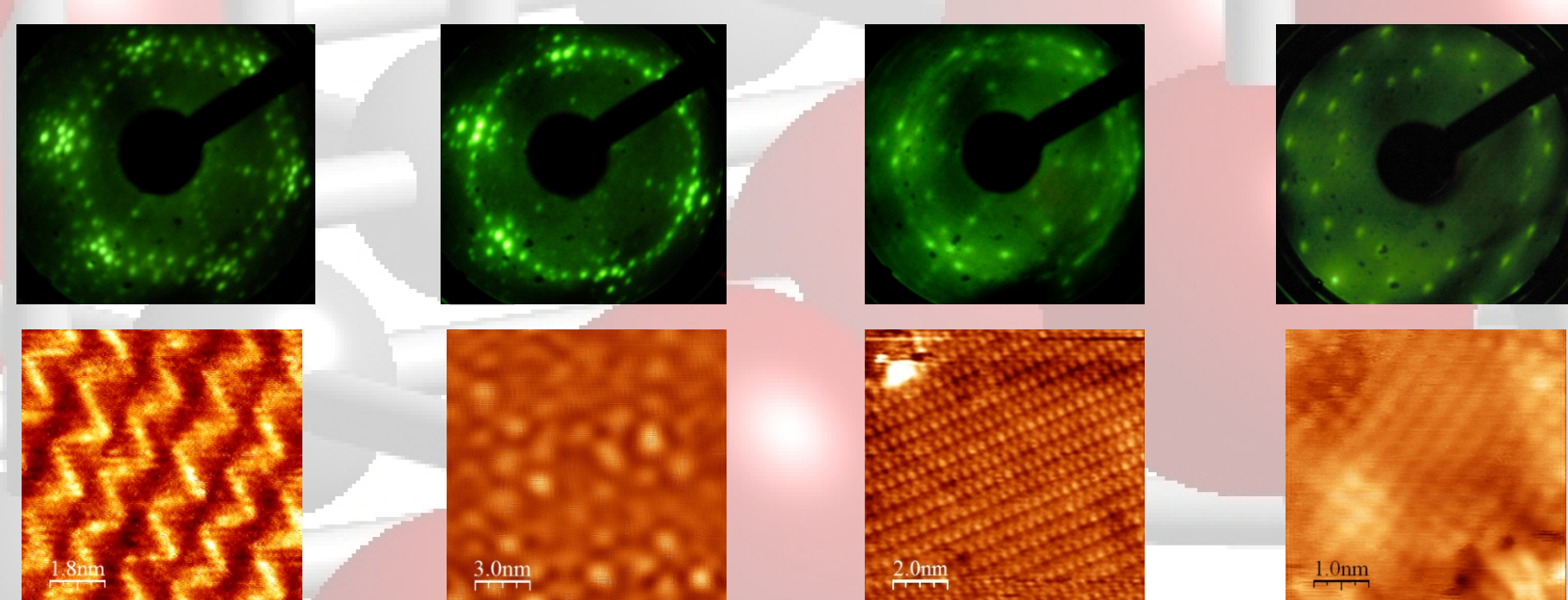


Fig.6: Overview of different titania phases on $\text{Pt}_3\text{Ti}(111)$, observed with LEED and STM. The structures of the different phases are very similar to them of $\text{TiO}_2/\text{Pt}(111)$ ^[6], $\text{VO}/\text{Rh}(111)$ ^[7] and $\text{VO}/\text{Pd}(111)$ ^[8] systems.

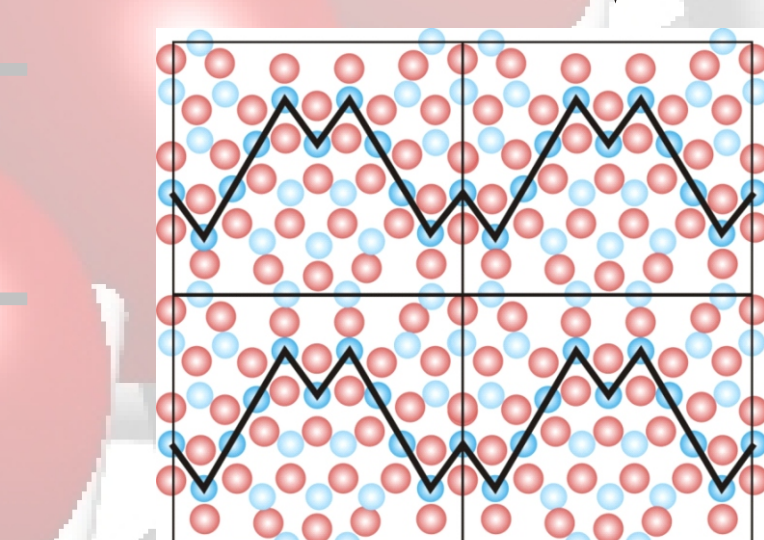


Fig.7: Model of z' - TiO_x - phase on $\text{Pt}_3\text{Ti}(111)$ getting from the STM-results. Four fold coordinated Ti atoms (dark blue) form the zig-zag structure, three fold Ti (light blue) and oxygen (red) are in between.

Benzoic acid on TiO_2

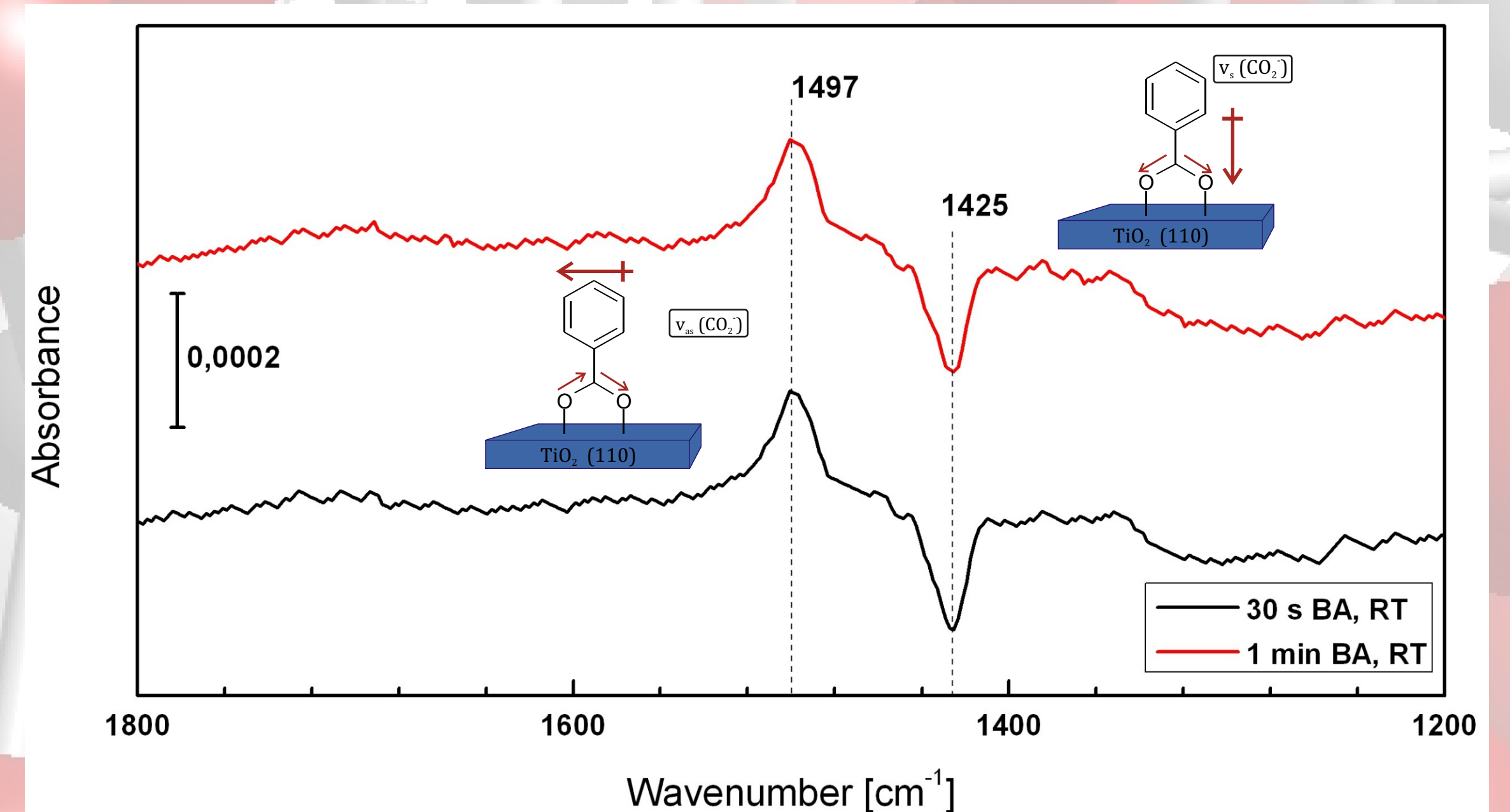


Fig.8: RAIRS data of a monolayer of BA on $\text{TiO}_2(110)$ surface

The benzoic acid (BA) molecules are evaporated in the preparation chamber at room temperature. A monolayer has been achieved within an evaporation time from 30 seconds to 16 minutes. The RAIR spectra are taken after deposition of the molecules on the rutile $\text{TiO}_2(110)$ surface. The background spectrum is taken before the deposition at the same temperature and all spectra are measured at grazing incidence of 80° with 2048 scans and a resolution of 4cm^{-1} . Fig. 8 shows the RAIR spectra of BA on $\text{TiO}_2(110)$ surface. Only two bands are visible in the spectra. The negative signal at 1425cm^{-1} is obviously the adsorption of the symmetrical carboxylate vibration, whose TDM is perpendicular to the surface. The asymmetrical carboxylate vibration with TDM parallel to the surface is at 1497cm^{-1} .

References

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