Karlsruhe Institute of Technology

Institute of Functional Interfaces

# UHV – FTIR - study of benzoic and terephthalic acids adsorption on Rutile $TiO_2$ (110)

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## FTIR- and IRRA - spectroscopy of oxide surfaces

Oxides have found applications in catalysis, for producing sensors, solar cells and electronic devices. 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. Unfortunately, studies on oxide single crystals are extremely scarce. Infrared reflection absorption spectroscopy (IRRAS) 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. Absorption bands of molecular adsorbates on metals can lead to a reduction in reflectivity (positive bands), 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).

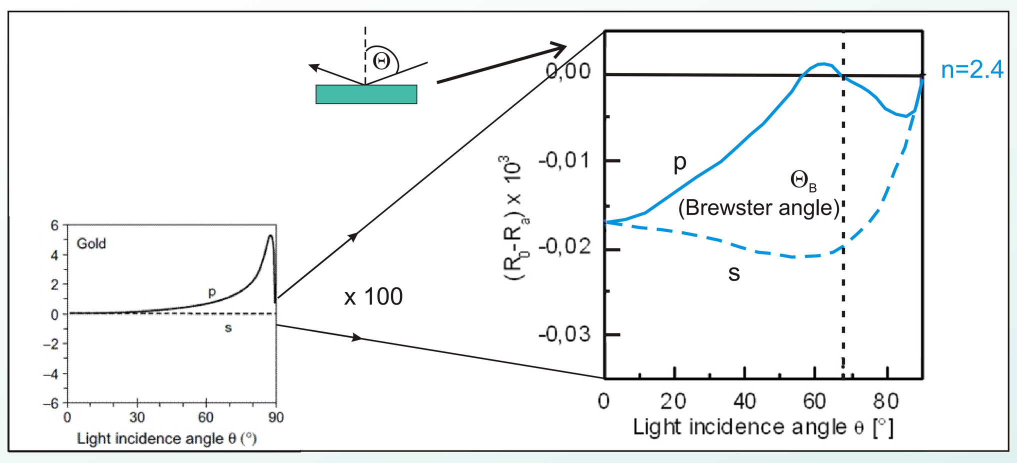


*Fig.1: Calculated reflectivity differences between the clean substrate ($R_0$) and the adsorbate covered substrate ($R_f$) for different substrate materials as a function of the light incidence angle for p-polarized radiation and s-polarized radiation.*

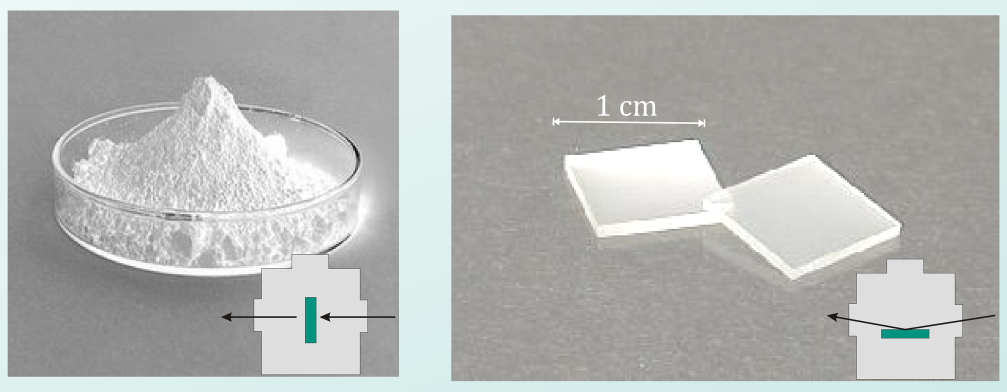


*Fig.2: Powder IR - measurements in transmission mode (left), oxide single crystals IR - measurements in reflection mode (right)*

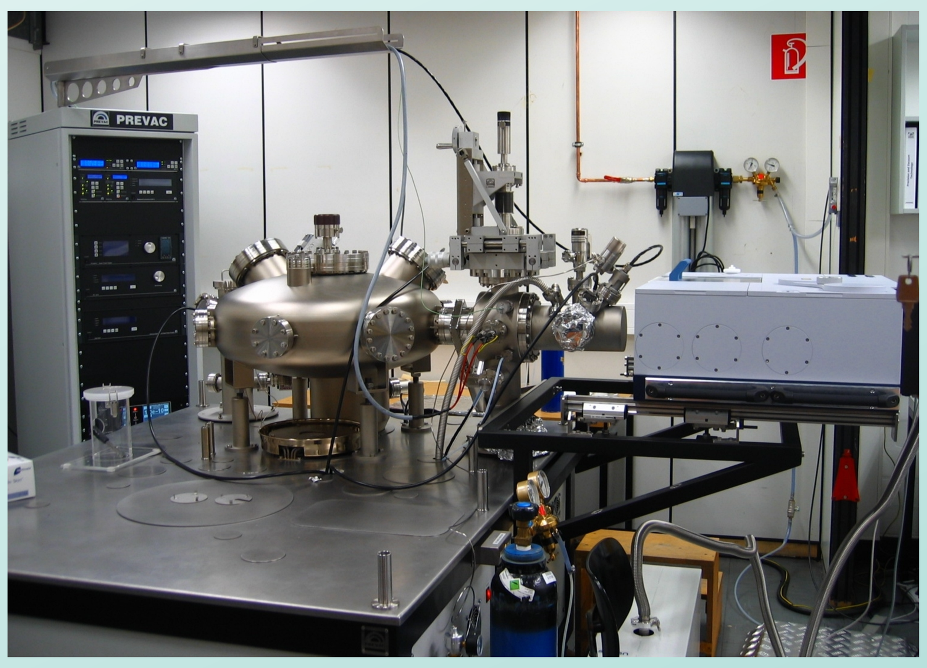

*Fig.3: UHV - IR - apparatus*

## Benzoic acid (BA) and terephthalic acid (TPA) on Rutile $TiO_2$ (110)

*Preparation:*

In the case of the monolayer BA, monolayer TPA and the multilayer TPA, the Rutile $TiO_2$ surface is kept at RT. For obtaining a multilayer BA, the $TiO_2$ surface is kept at -153°C. The pressure is $p_{prep} = 5\text{-}8\cdot10^{-9}$ mbar in the preparation chamber and $p_{anal} = 2\cdot10^{-10}$ mbar inthe analysis chamber. The molecules are evaporated at RT with a knudsen cell evaporator in the preparation chamber. The spectra are measured in a grazing incidence of 80° with 2048 scans and a resolution of 4 $cm^{-1}$. The spectra are taken before and after the deposition of the molecules.

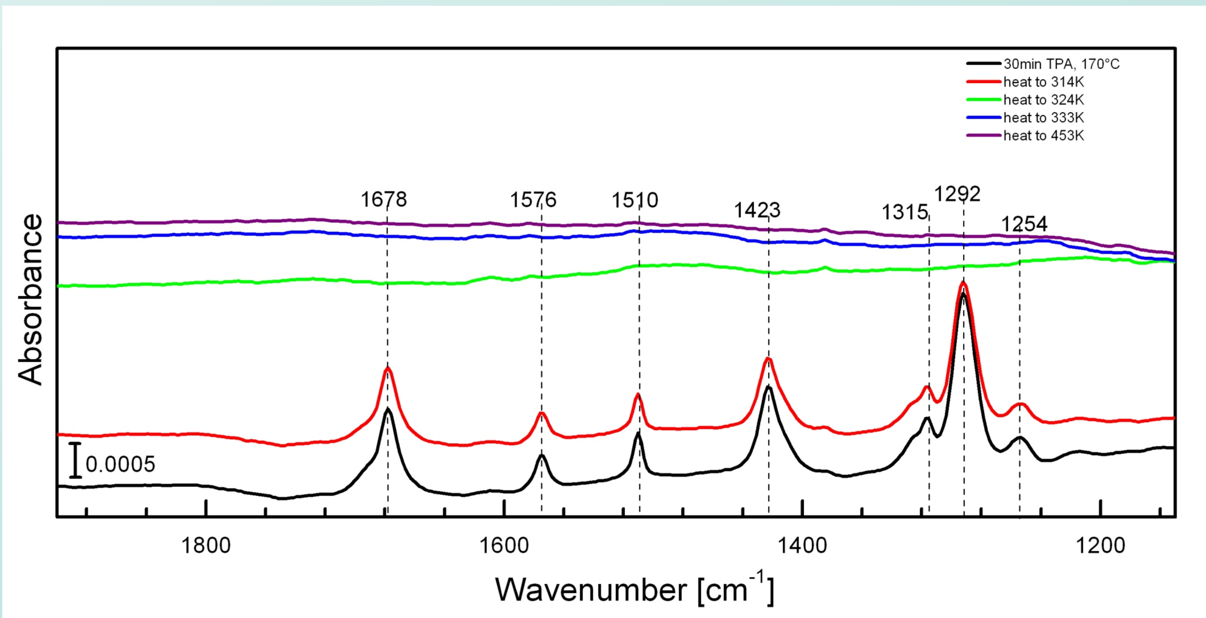


*Fig.6: IRRAS data of a multilayer of TPA on $TiO_2$ (110) surface*

| Multilayer [$cm^{-1}$] | Assignments |
|---|---|
| 1680 | ν (C=O), δ(COH) |
| 1576 | ß (CCH), ν (C=C) |
| 1510 | ß (CCH), ν (C=C) |
| 1421 | $ν_s$ ($CO_2^-$) |
| 1288 | δ(COH), ν(C-O) |

*Tab.1: Assignments of the IRRAS data of a multilayer of TPA on $TiO_2$ (110) surface*

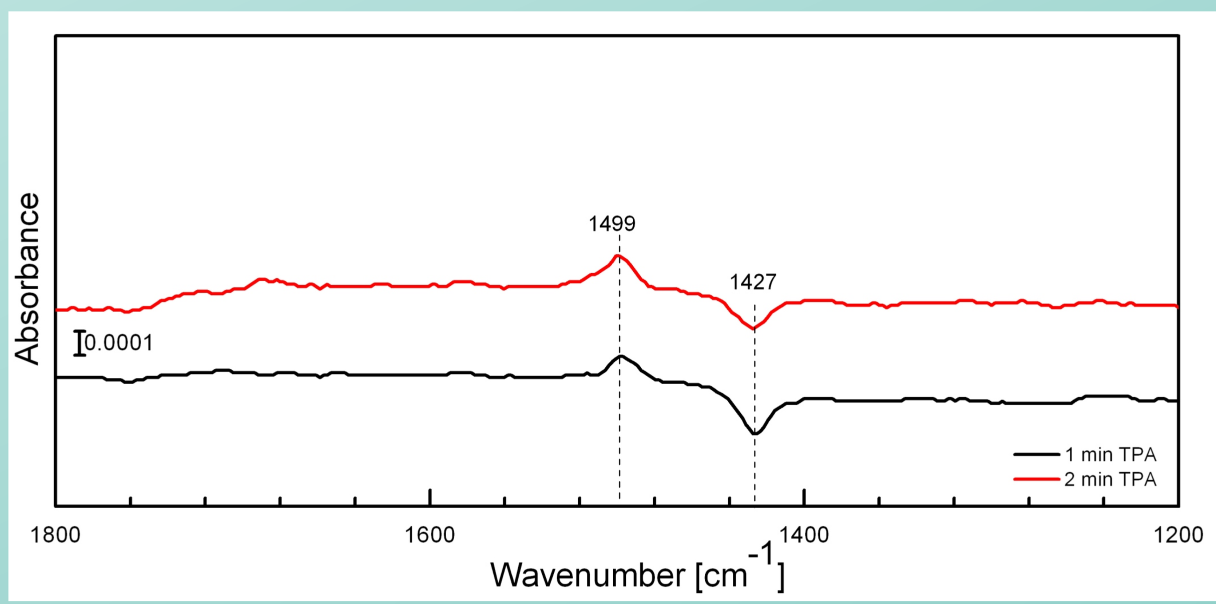


*Fig.4: IRRAS data of a monolayer of TPA on $TiO_2$ (110) surface*

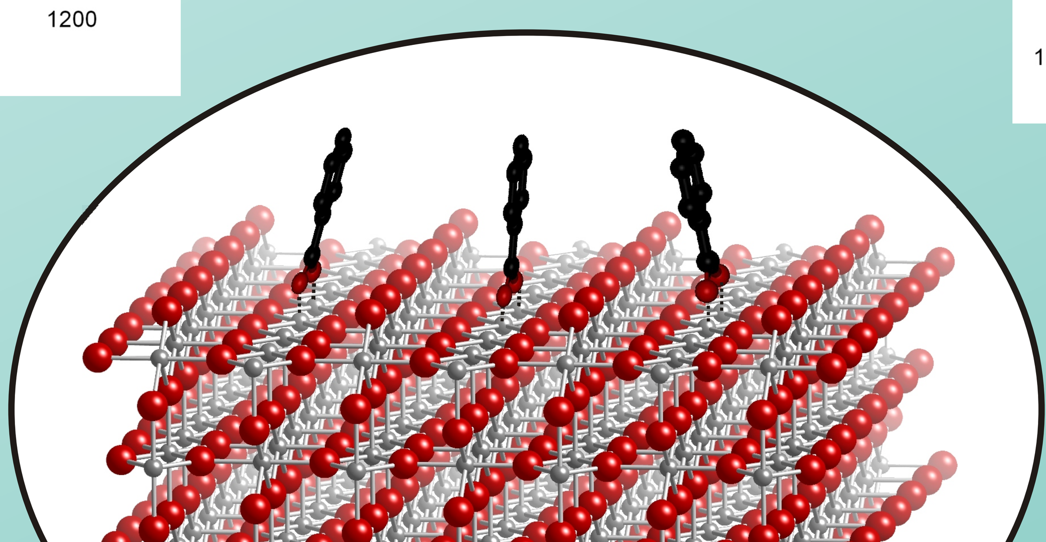

*Fig.8: Modell for adsorption of a monolayer BA on $TiO_2$ (110) surface*

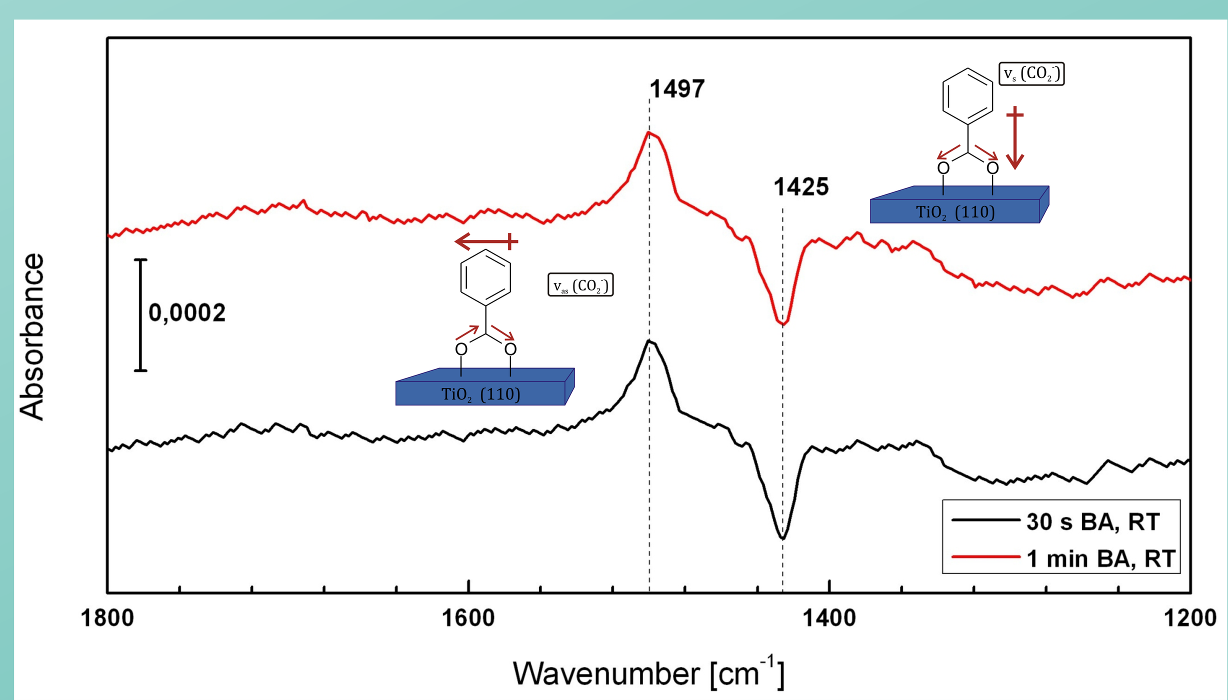


*Fig.5: IRRAS data of a monolayer of BA on $TiO_2$ (110) surface*

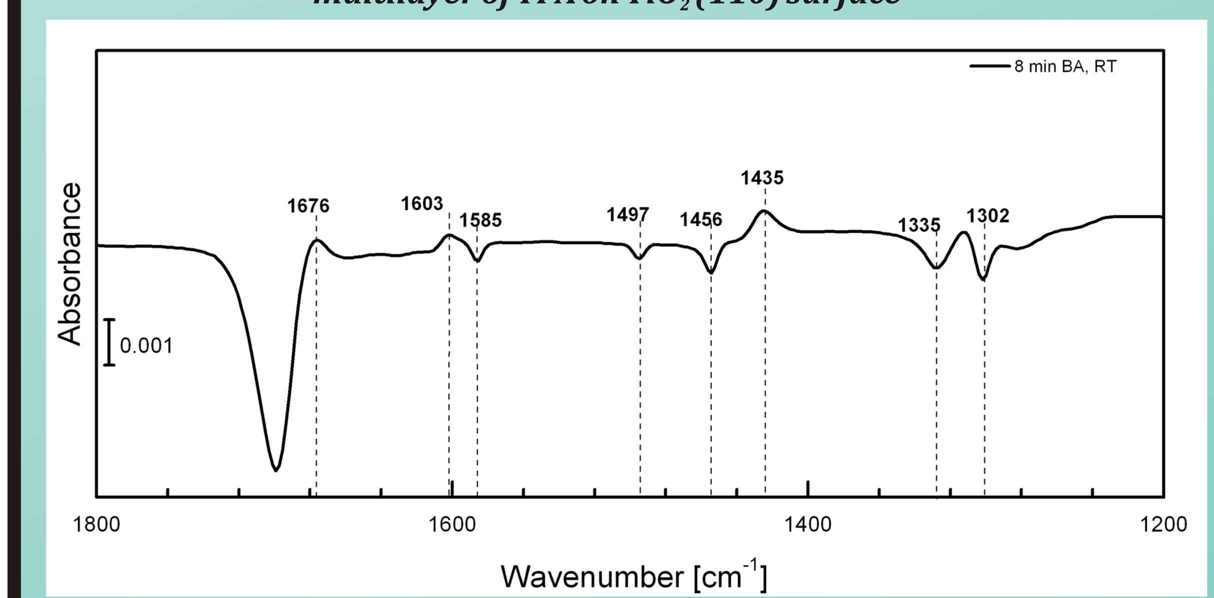


*Fig.7: IRRAS data of a multilayer of BA on $TiO_2$ (110) surface*

| Multilayer [$cm^{-1}$] | 1701 | 1603 | 1585 | 1497 | 1456 | 1435 | 1335 | 1302 |
|---|---|---|---|---|---|---|---|---|
| Assignments | ν(C=O), ν(C=C) | ν(C=C) | ν (C=C) | $ν_{as}$ ($CO_2^-$), ν(C=C) | ν(C=C), ß(COH) | $ν_s$ ($CO_2^-$) | ß (CCH), ß(COH) | $ν_S$ ($CO_2^-$), ν(C=C) |

*Tab.2: Assignments of the IRRAS data of a multilayer of BA on $TiO_2$ (110)*

## References

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