Institute of Functional Interfaces
Helmholtz Research School „Energy-related catalysis“

IR-absorption studies on ZnO(10$\bar{1}$0) and rutile TiO_2(110) single crystals: from molecular vibrations to electronic excitations of polarons

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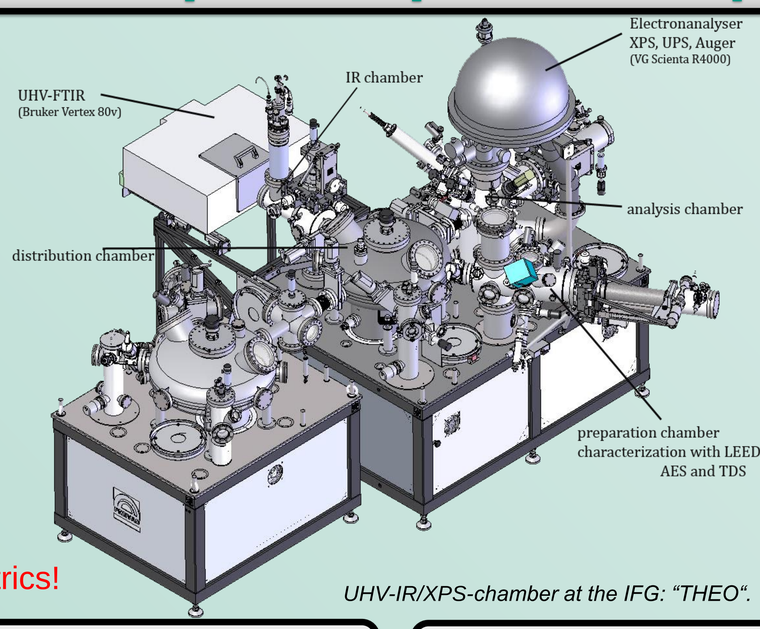
Infrared Reflection Absorption Spectroscopy (IRRAS) on Oxides

On dielectric surfaces, the classic surface selection rule does not apply!

***Consequences*:**

- both s- and p-polarized light can couple to adsorbate vibrations:
  - s-polarized light: bands will always be negative
  - p-polarized light: bands can be negative or positive depending on the incidence angle θ and the refractive index n of the substrate
- From considering all three components ($E_{p,n}$, $E_{p,t}$, and s) of the incident polarized light separately, the adsorption structure can be obtained directly

Experimental Challenge: very low reflectivity of dielectrics!



UHV-IR/XPS-chamber at the IFG: “THEO“.

Strategy to overcome challenge of low reflectivity[1]:

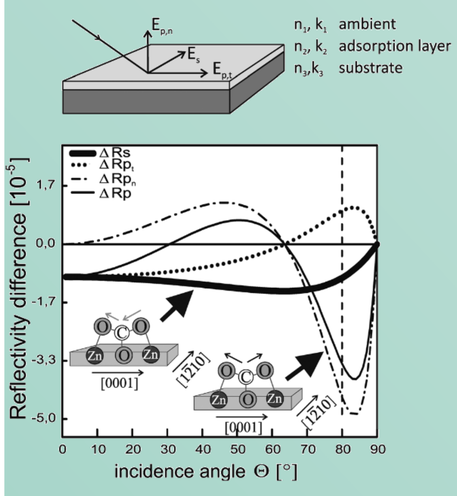
- Attach spectrometer directly to UHV chamber
- Do not introduce any additional optical element, i.e. use the standard optical path within the IR-spectrometer
- Minimize mechanical vibrations

Additional features of “THEO”:

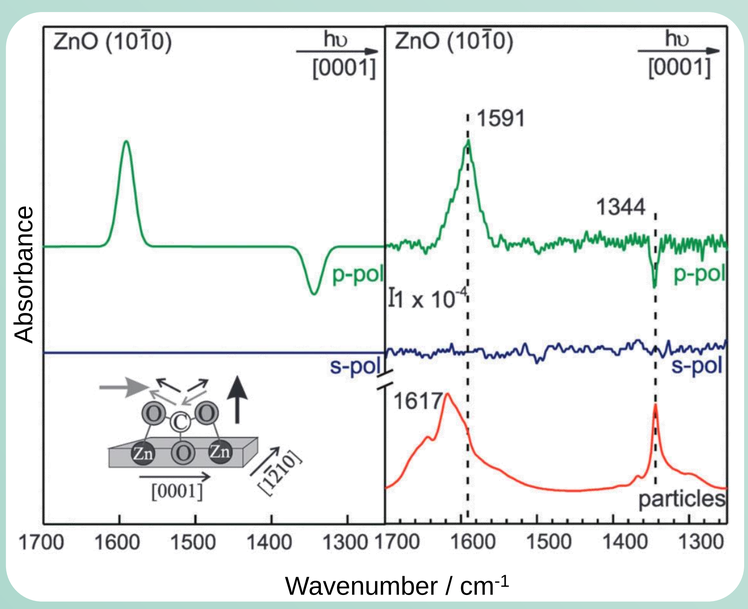
- Allows transmission measurements on powder samples for straight forward comparison of single crystal and powder samples
- Cooling to 100 K (LN_2) or 30 K (LHe); heating up to 1300 K
- Equipped for XPS, UPS, AES, LEIS, and LEED

Carbon Dioxide on ZnO(10$\bar{1}$0)[2]

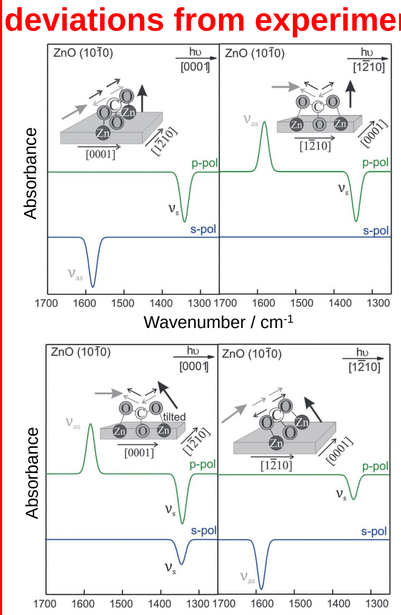
Reflectivity difference used to predict sign of IR-bands

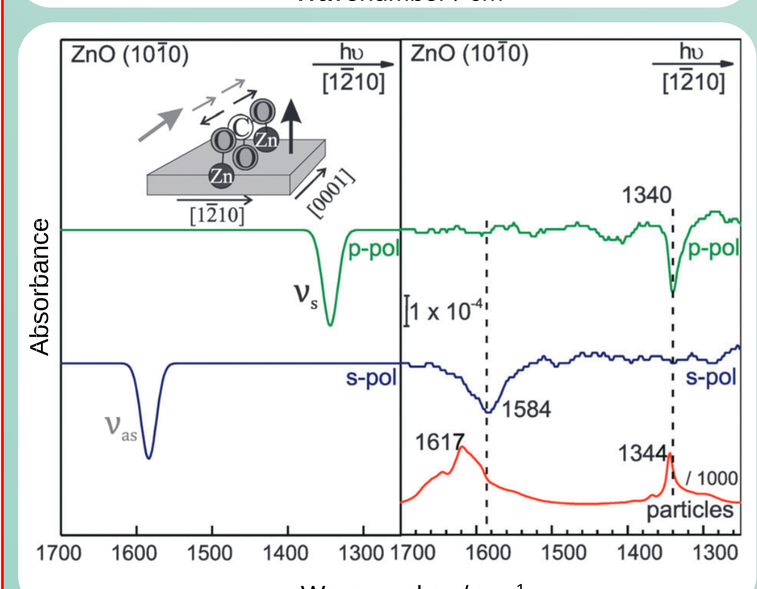


Predicted bands (left) and experimental (right) IR-spectra of CO_2 on ZnO(10$\bar{1}$0)



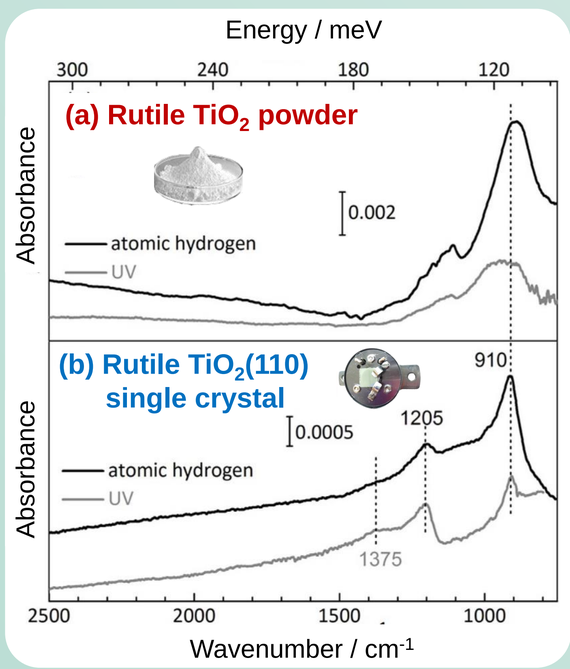
Structures excluded due to deviations from experiment





Electrons in Polaronic Trap States[3]

IR-spectra of rutile TiO_2 exposed to UV-light or atomic hydrogen



Irradiation with UV-light (at 365 nm) and atomic hydrogen treatment yield very similar IR-spectra.

Powder:

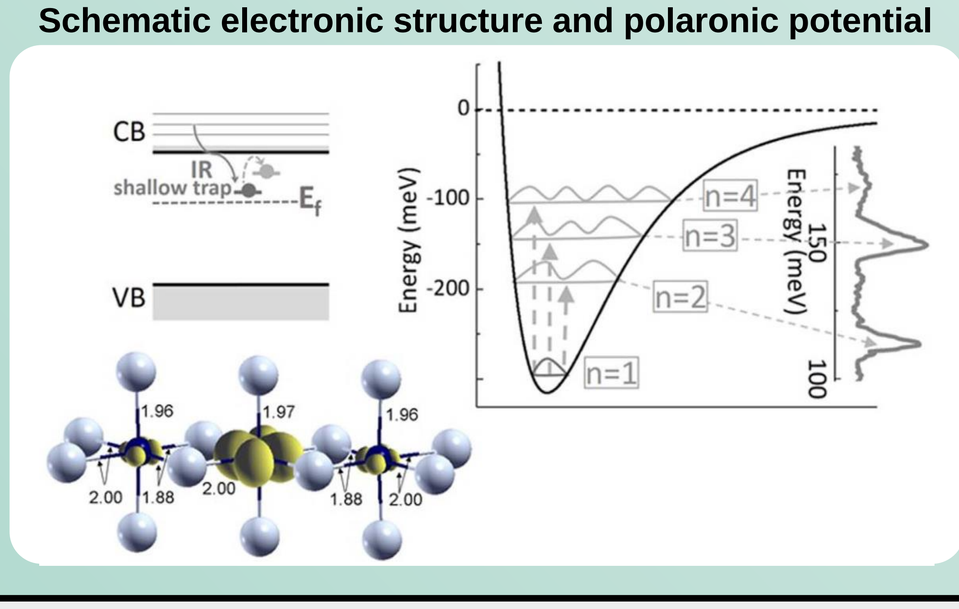
- Prominent absorption at 900-940 cm^{-1}
- Broad absorption at 1100-1400 cm^{-1}

Single crystal:

- Features are significantly sharper
- Most intense feature at 910 cm^{-1}
- Two additional features at 1205 cm^{-1} and at 1375 cm^{-1}

Features are attributed to shallow trap states in accordance with literature.

Schematic electronic structure and polaronic potential



Conclusions

- CO_2 forms a tridentate surface-carbonate on ZnO(10$\bar{1}$0)
- The carbonate is upright standing with the backbone oriented along the [0001]-direction
- The favored adsorption site on ZnO-powder is not the (10$\bar{1}$0) facet
- Data for single crystal show unprecedented sharp features
- We propose excitation into “hydrogenic“ states within the polaron trap potential as the origin of the observed absorption features, as a high-energy tail of transitions into the conduction band is missing

In addition to providing vibration frequencies of adsorbed species, which are lacking for many single-crystal oxide systems, we have demonstrated that Infrared Reflection Absorption Spectroscopy is a valuable tool to directly determine adsorbate structures or even probe electronic excitations, e.g. from shallow trap states!

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References
[1] M. Xu, Y. Gao, E. Martinez Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss and C. Wöll, *PRL* **2011**, 106, 138302.
[2] M. Buchholz, P. G. Weidler, F. Bebensee and C. Wöll, *PCCP* **2014**, 16, 1672-1678.
[3] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin and C. Wöll, *Scientific Reports* **2014**, 4, 3808.