

# IR-absorption studies on ZnO(10 $\bar{1}0$ ) and rutile TiO<sub>2</sub>(110) single crystals: from molecular vibrations to electronic excitations of polarons

F. Bebensee<sup>a</sup>, M. Buchholz<sup>a</sup>, H. Sezen<sup>a</sup>, P. G. Weidler<sup>a</sup>, C. Natzeck<sup>a</sup>, S. Heissler<sup>a</sup>, C. Di Valentin<sup>b</sup>, A. Nefedov<sup>a</sup>, C. Wöll<sup>a</sup>

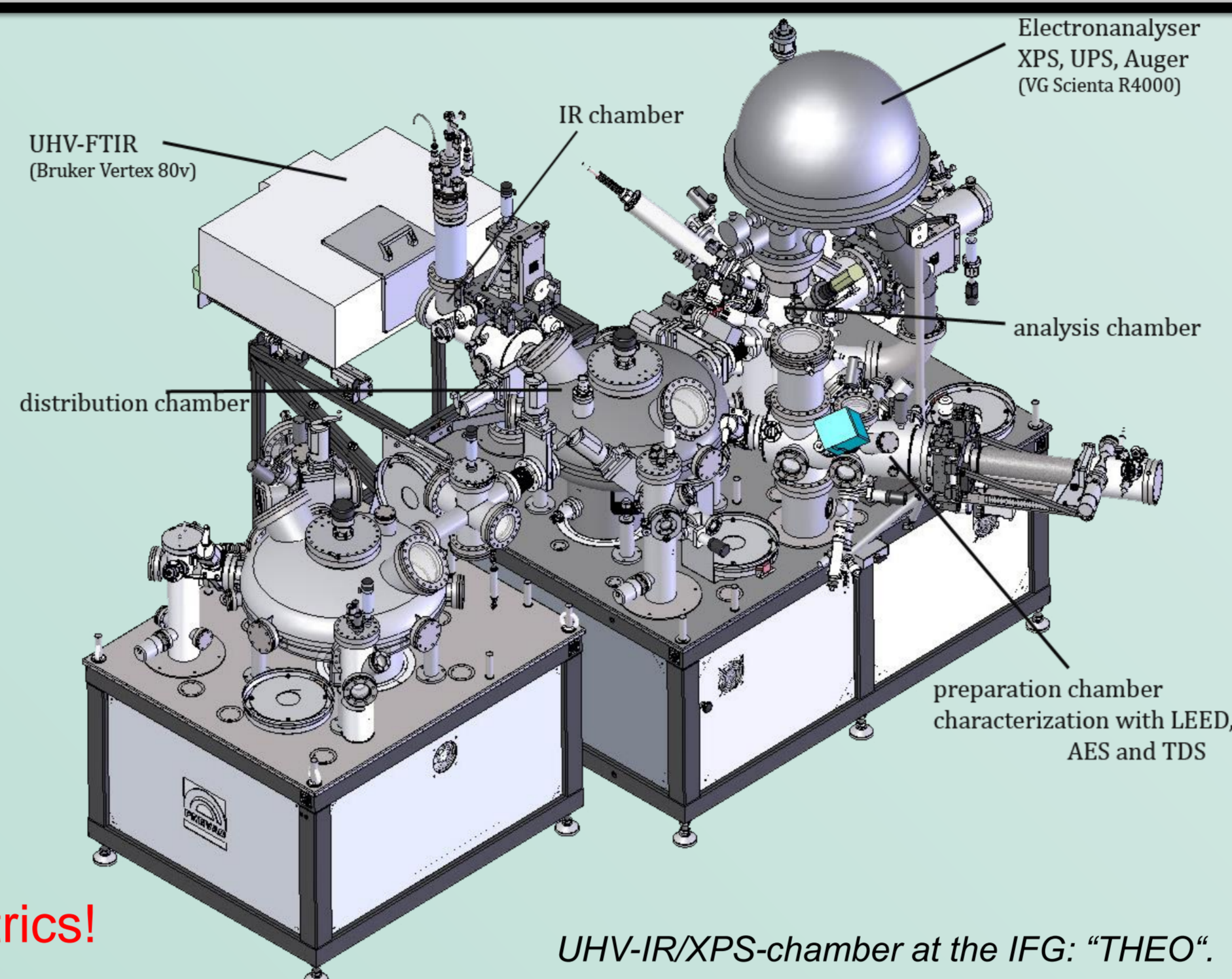
## Infrared Reflection Absorption Spectroscopy (IRRAS) on Oxides

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  $\theta$  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<sup>[1]</sup>:

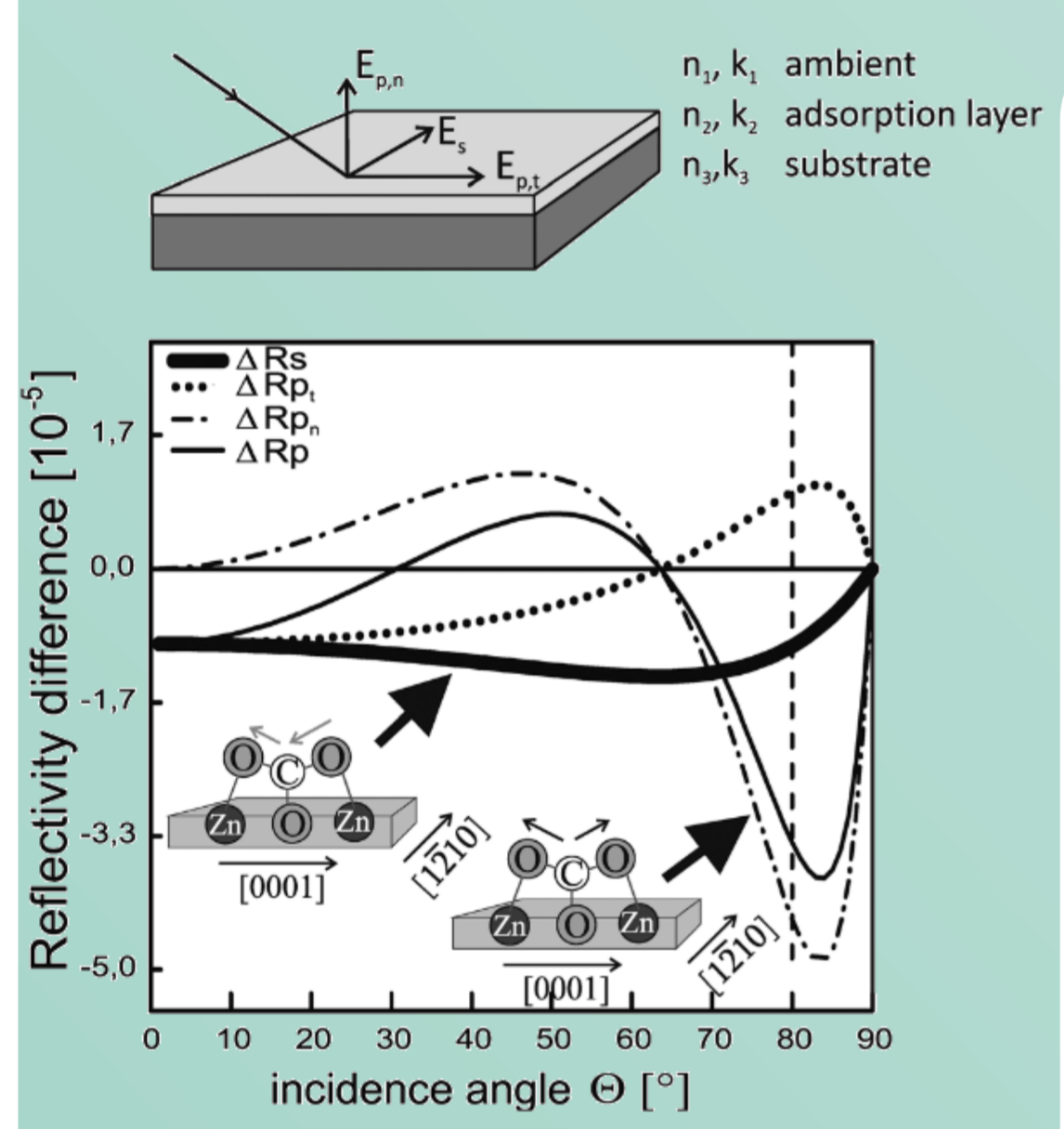
- Attach spectrometer directly to UHV chamber
- Do not introduce any additional optical element, i.e. use the standard optical path within the IR-spectrometer
- Minimize mechanical vibrations

### Additional features of "THEO":

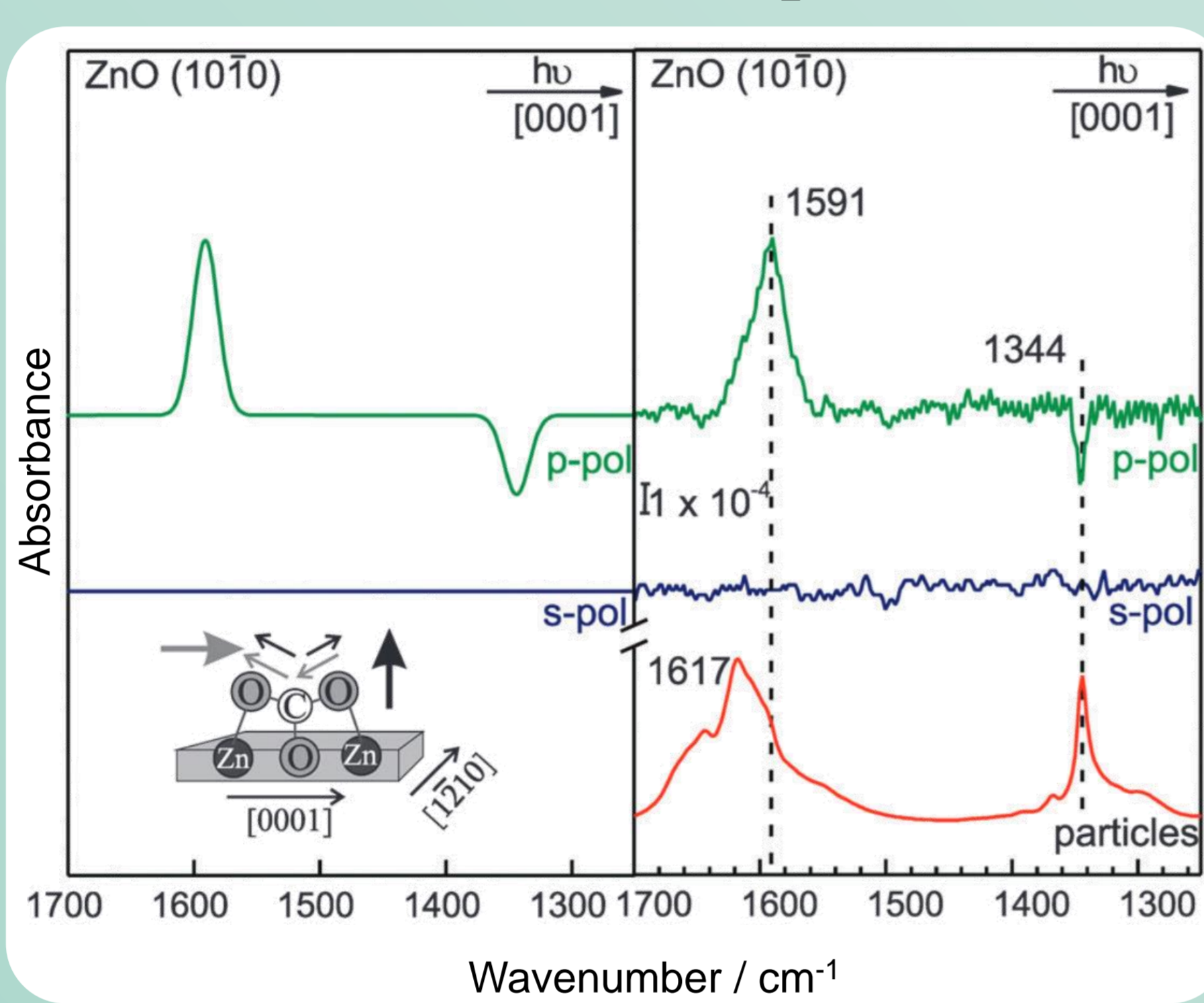
- Allows transmission measurements on powder samples for straight forward comparison of single crystal and powder samples
- Cooling to 100 K (LN<sub>2</sub>) or 30 K (LHe); heating up to 1300 K
- Equipped for XPS, UPS, AES, LEIS, and LEED

## Carbon Dioxide on ZnO(10 $\bar{1}0$ )<sup>[2]</sup>

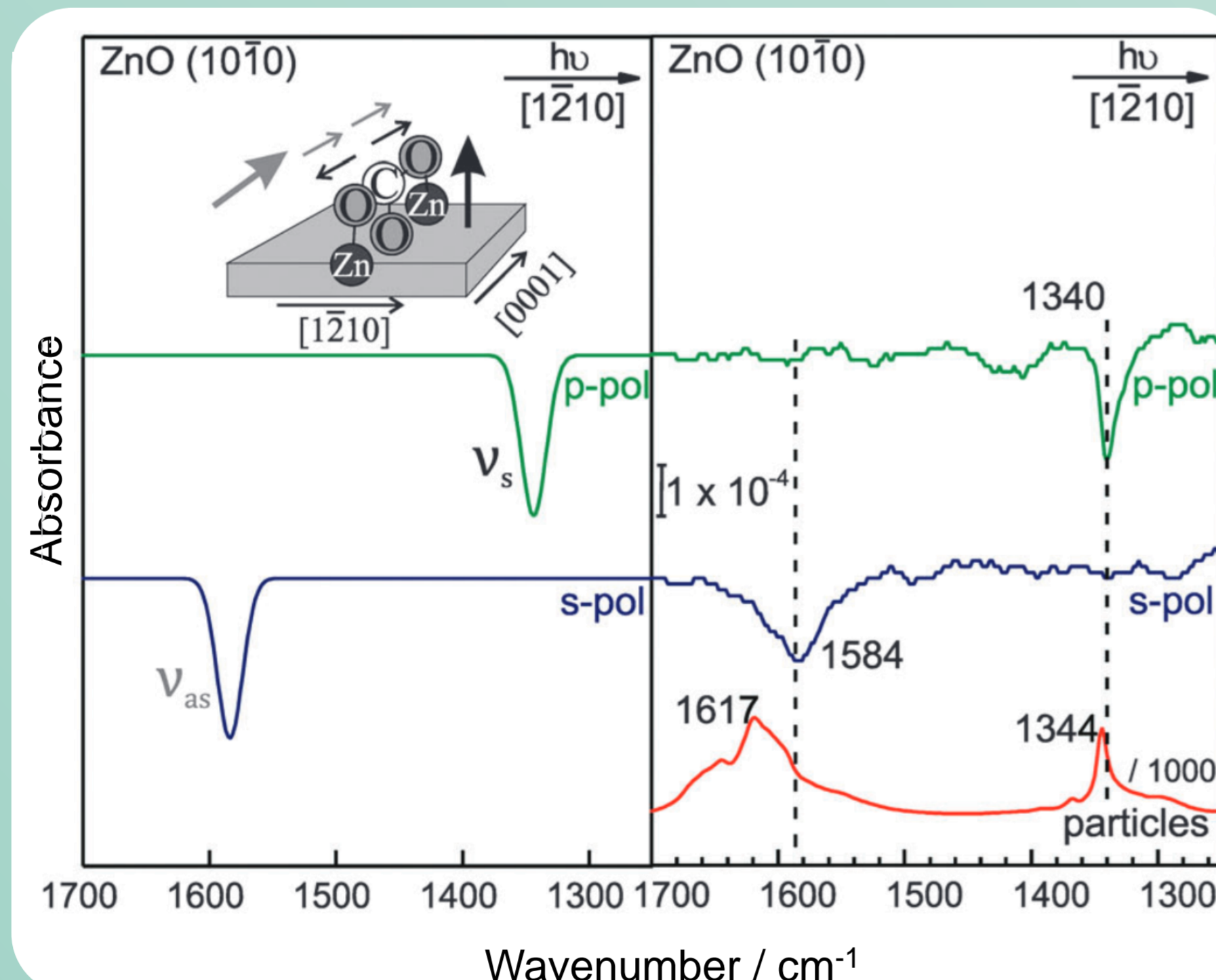
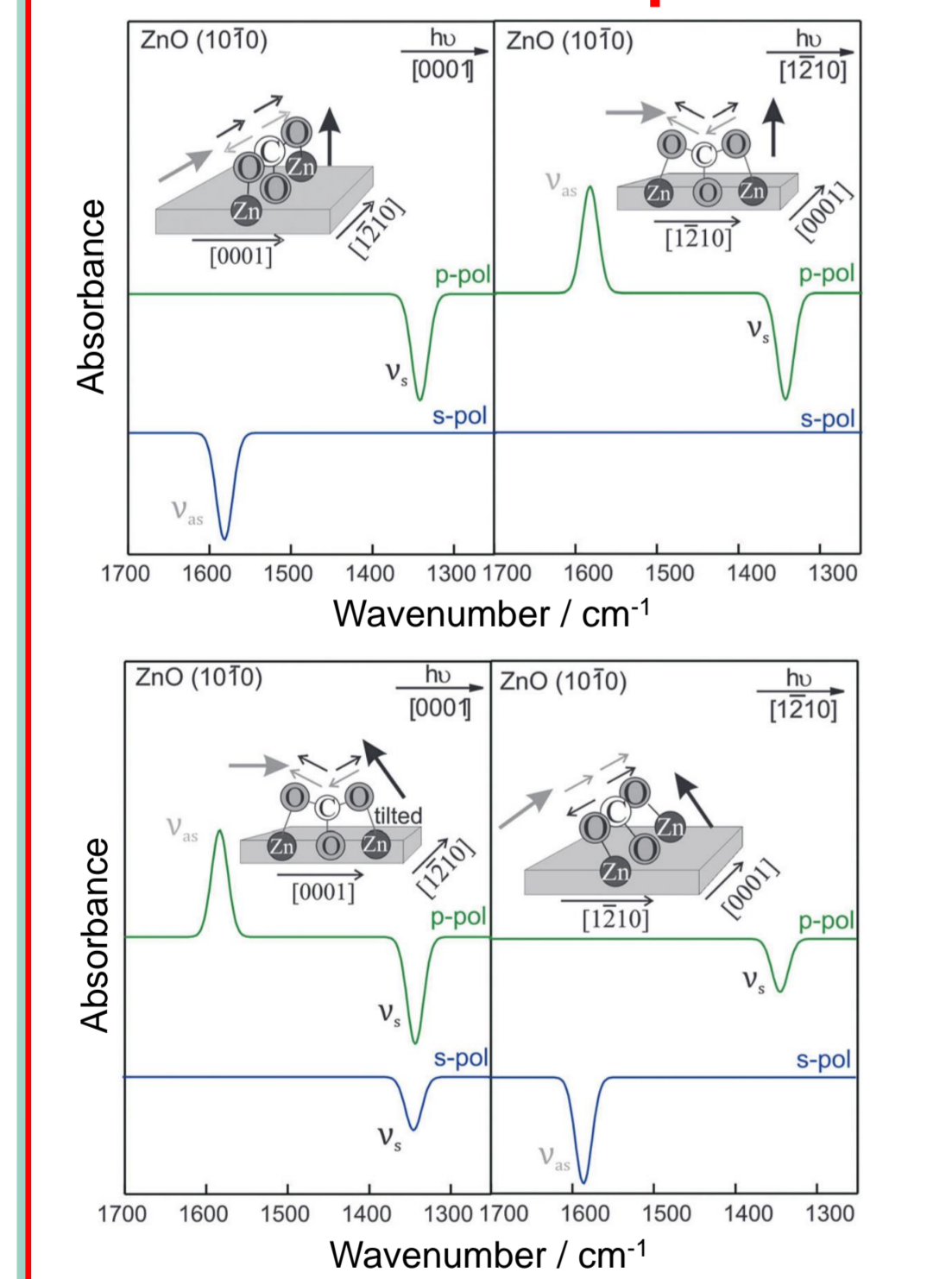
### Reflectivity difference used to predict sign of IR-bands



### Predicted bands (left) and experimental (right) IR-spectra of CO<sub>2</sub> on ZnO(10 $\bar{1}0$ )

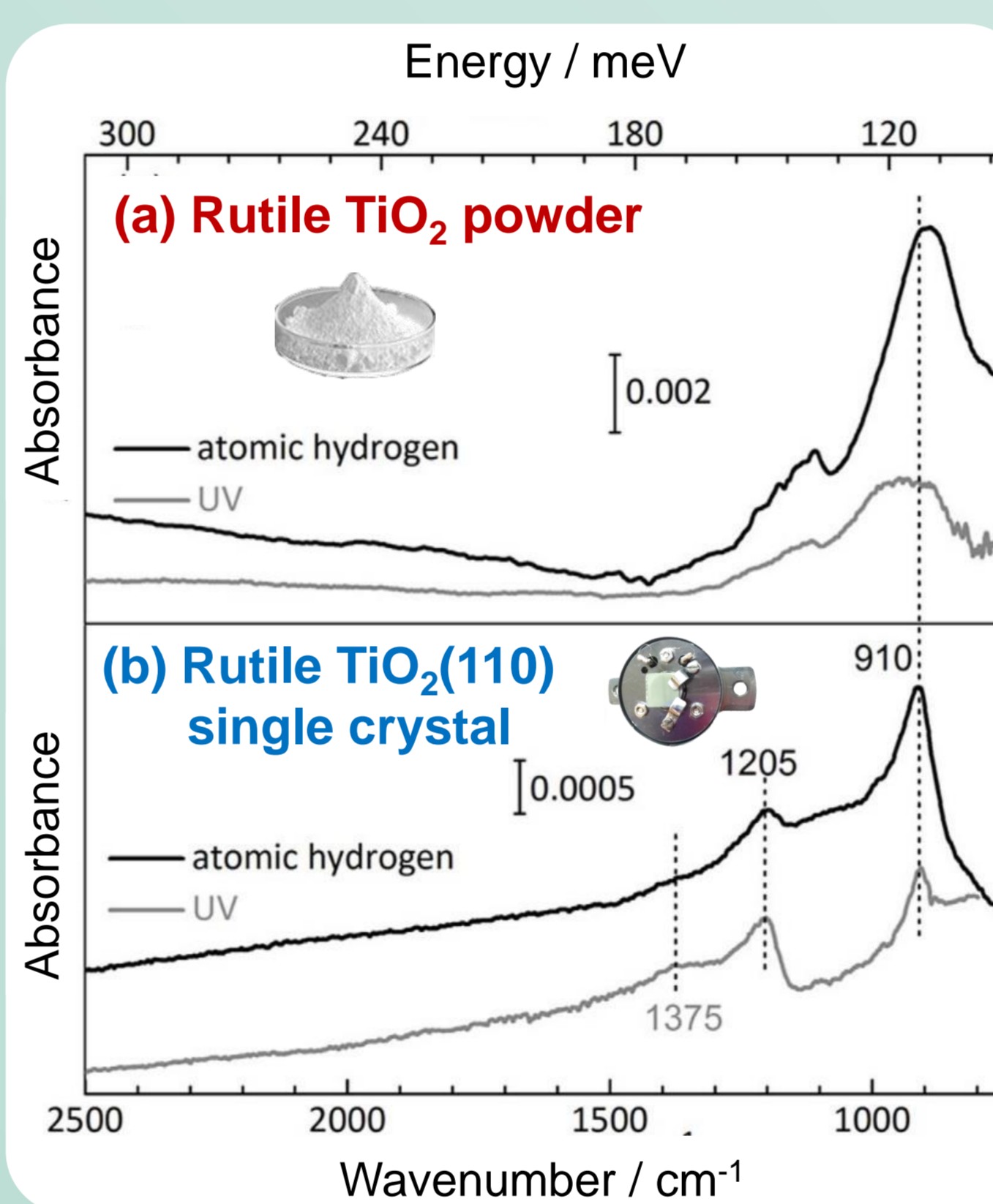


### Structures excluded due to deviations from experiment



## Electrons in Polaronic Trap States<sup>[3]</sup>

### IR-spectra of rutile TiO<sub>2</sub> exposed to UV-light or atomic hydrogen



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

### Powder:

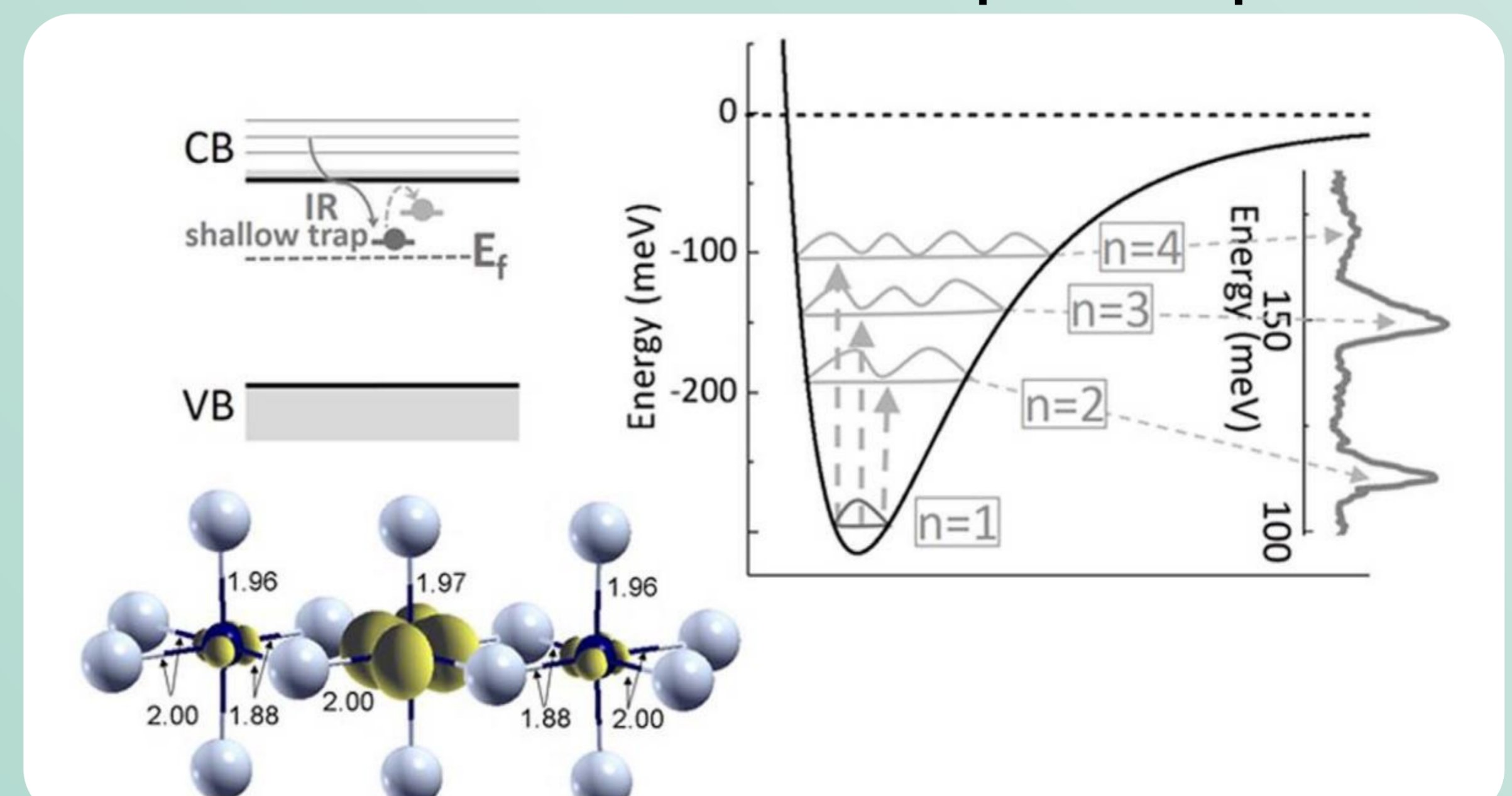
- Prominent absorption at 900-940 cm<sup>-1</sup>
- Broad absorption at 1100-1400 cm<sup>-1</sup>

### Single crystal:

- Features are significantly sharper
- Most intense feature at 910 cm<sup>-1</sup>
- Two additional features at 1205 cm<sup>-1</sup> and at 1375 cm<sup>-1</sup>

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

### Schematic electronic structure and polaronic potential



## Conclusions

- CO<sub>2</sub> 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!

<sup>a</sup>KIT, Institute of Functional Interfaces, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

<sup>b</sup>Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via R. Cozzi 55, 20125 Milano, Italy

### 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.