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

Infrared reflection absorption spectroscopy on metal oxide single crystals

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Motivation

Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Most of the heterogeneous catalysts are solids and the great majority of reactants are gases or liquids.

- One or more of the reactants are adsorbed on to the surface of the catalyst at active sites. These active sites are mainly on the surface. The investigation of the interaction between the adsorbed species and the substrate is therefore from great interest.
- The surface science approach is using model systems to simplify these complex systems.
- Ultra-high vacuum is used, because there is no contamination by adsorption of gases from the air, and so the pure reaction between the catalyst and the reactant can be studied.

METHANOL SYNTHESIS

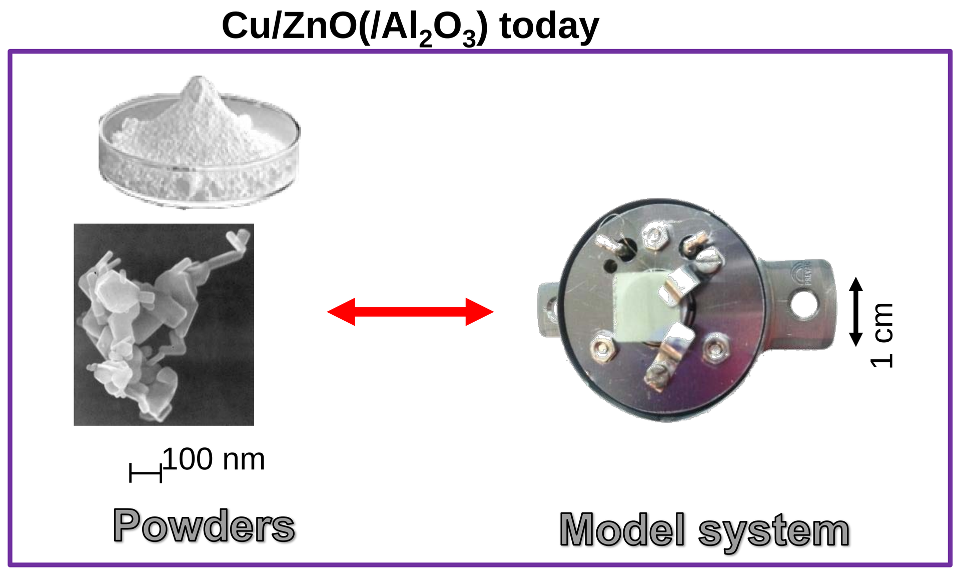
Production: 30 Mio tons per year (2000)

$CO + 2H_2 \rightleftharpoons CH_3OH$ $\Delta E = -92$ kJ/mol

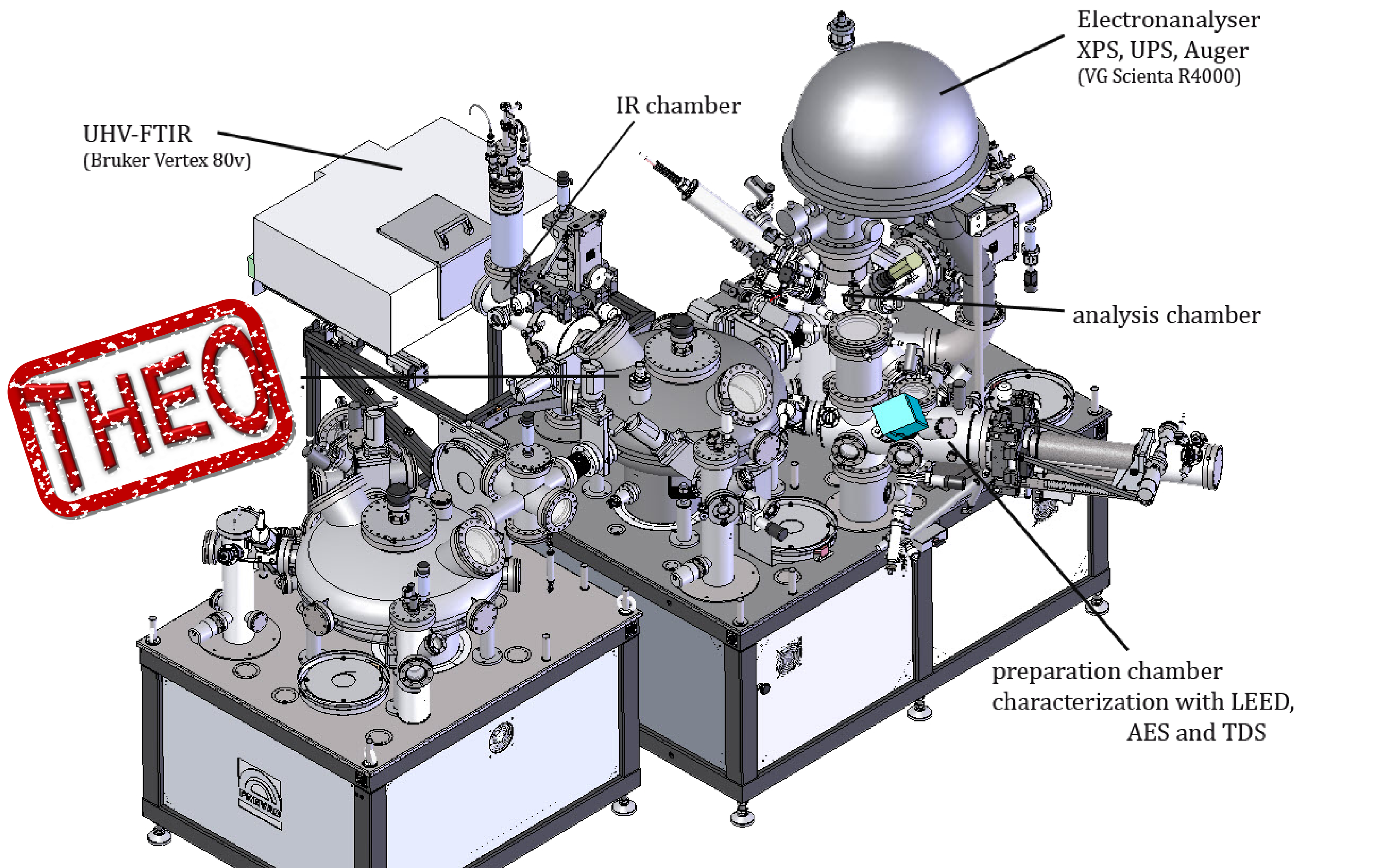
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta E = -50$ kJ/mol

Catalyst: **ZnO (till 1960)**

$Cu/ZnO(/Al_2O_3)$ today



- ZnO (10$\bar{1}$0):Lowest energy facet of ZnO and most dominant on particles

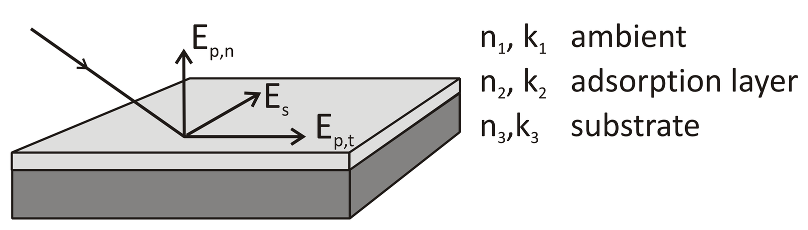


UHV-IR/XPS-chamber at IFG „THEO“.

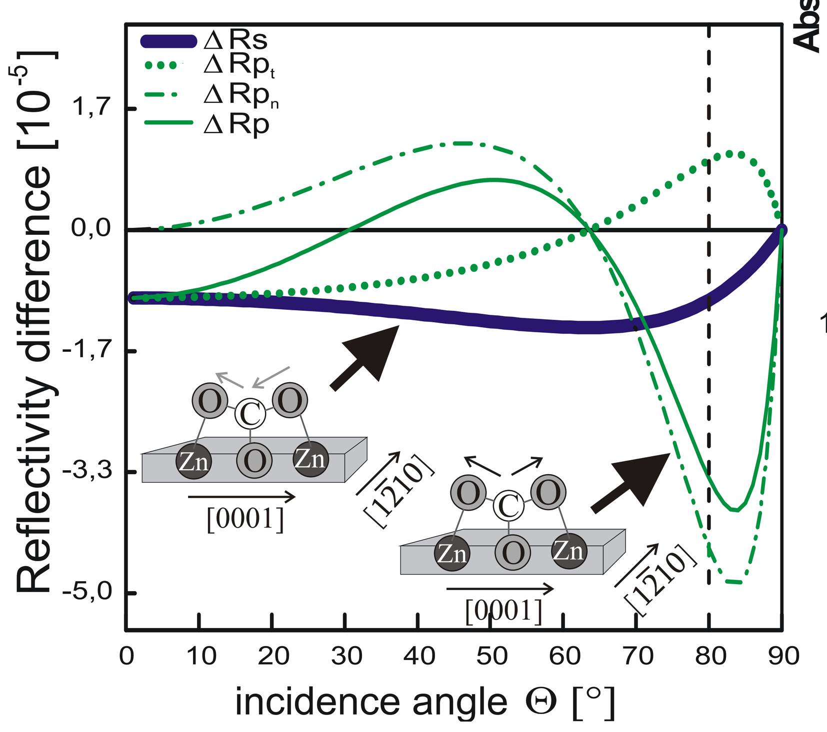
- Transmission measurements on powder samples and reflection measurements on flat samples are possible
- Cooling to 100 K (LN_2), in IR- chamber to 30 K (LHe), heating to 1300 K

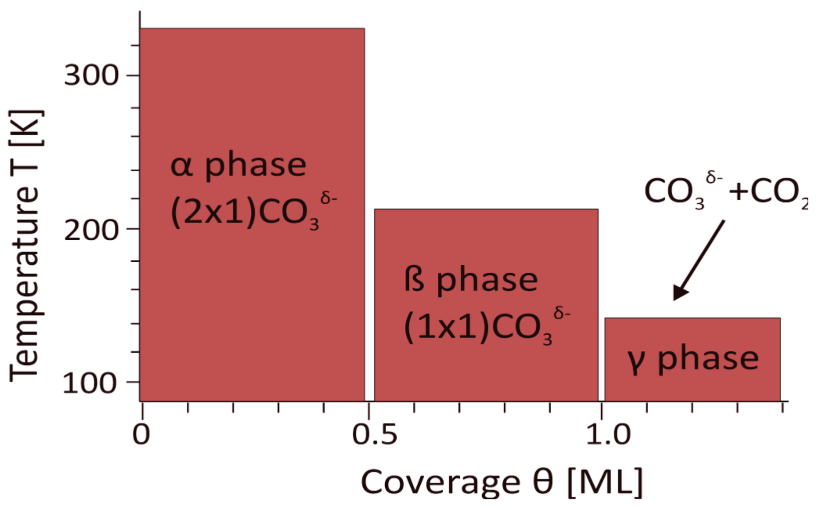
Carbon dioxide on ZnO (10$\bar{1}$0)

Reflectivity calculation



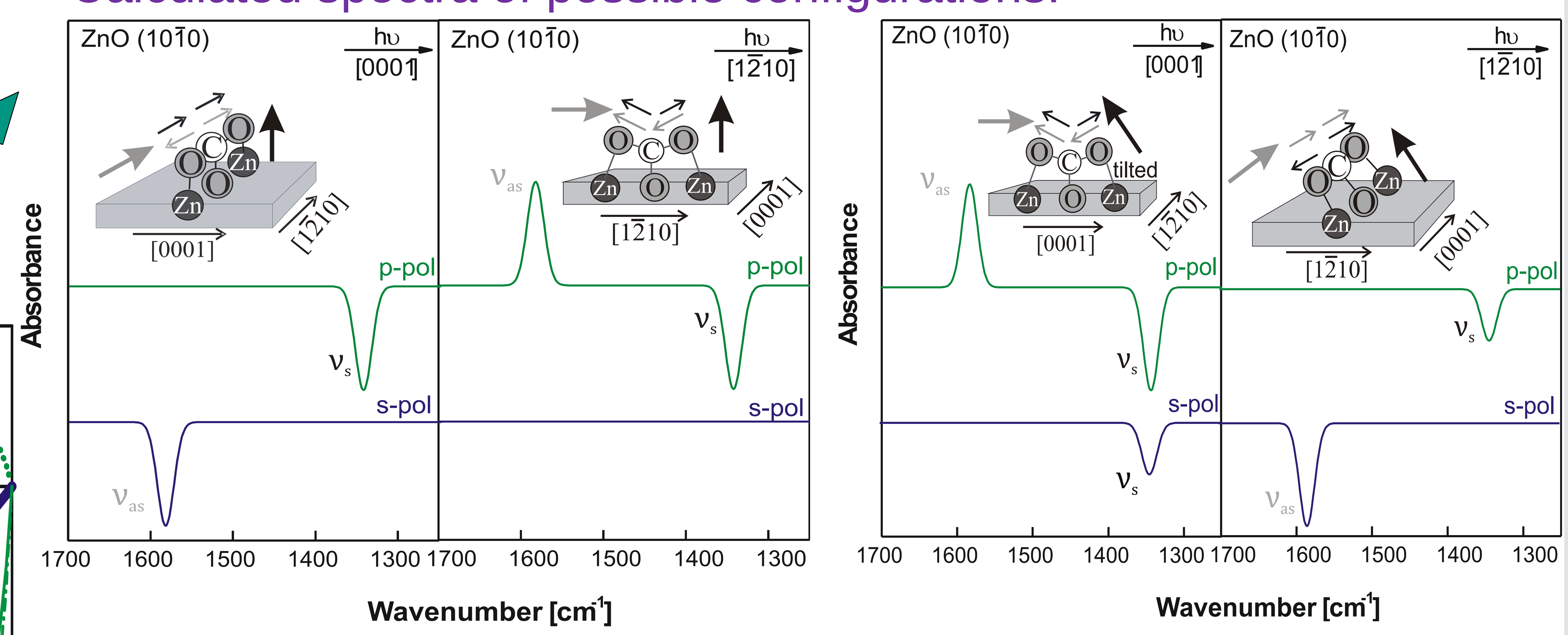
- *dielectric surfaces*: both s- and p-polarized light couple to adsorbate vibrations.
- Reduction in reflectivity (positive bands), but also to an enhancement of reflectivity (negative bands).
- s-polarized light: bands will always be negative
- p-polarized light: bands can be negative or positive depending on the incidence angle θ and the refractive index n of the substrate.



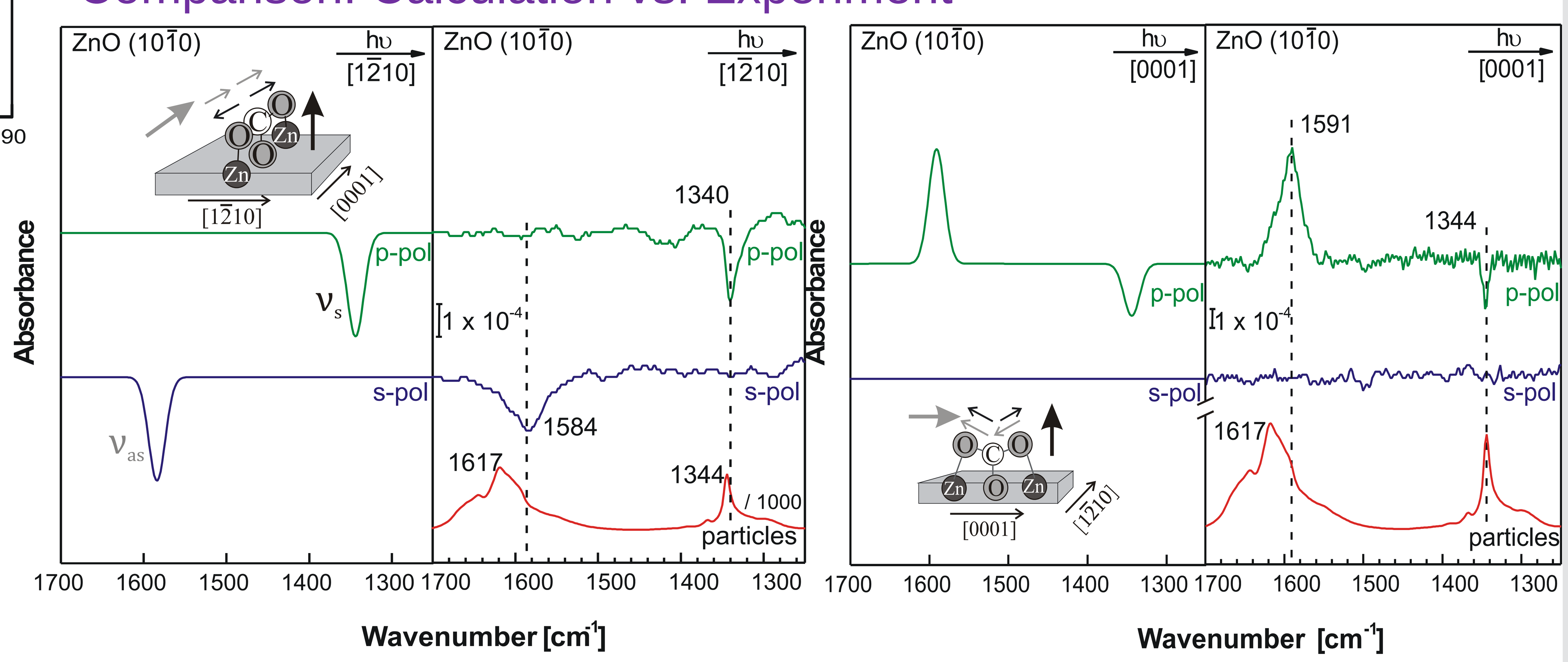


Phase diagram of CO_2 on ZnO (10$\bar{1}$0)[1]

Calculated spectra of possible configurations:

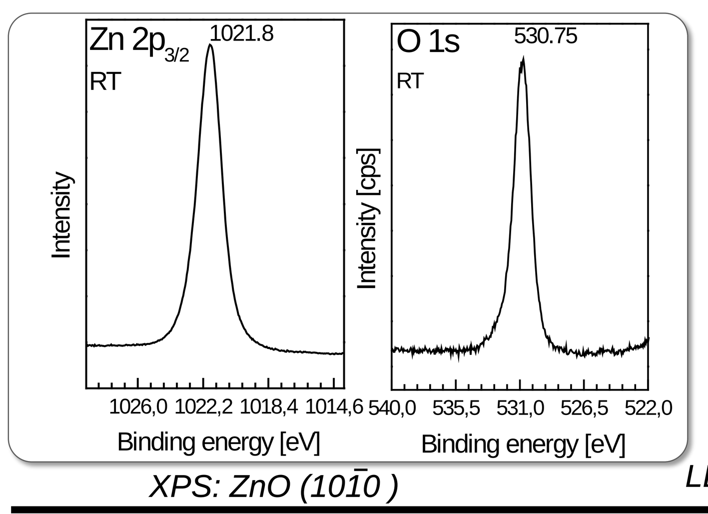


Comparison: Calculation vs. Experiment



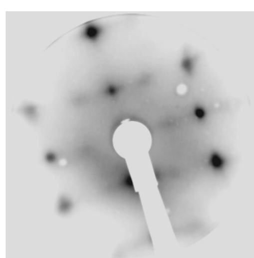
Preparation

Sputtering: Ar $1 \cdot 10^{-6}$ mbar, 1 kV, 6 mA
Annealing: 800 K
Check quality with LEED and/or XPS
CO_2-dosing directly in IR-chamber @ 110 K



XPS: ZnO (10$\bar{1}$0)

ZnO (10$\bar{1}$0)single crystal on sample holder.

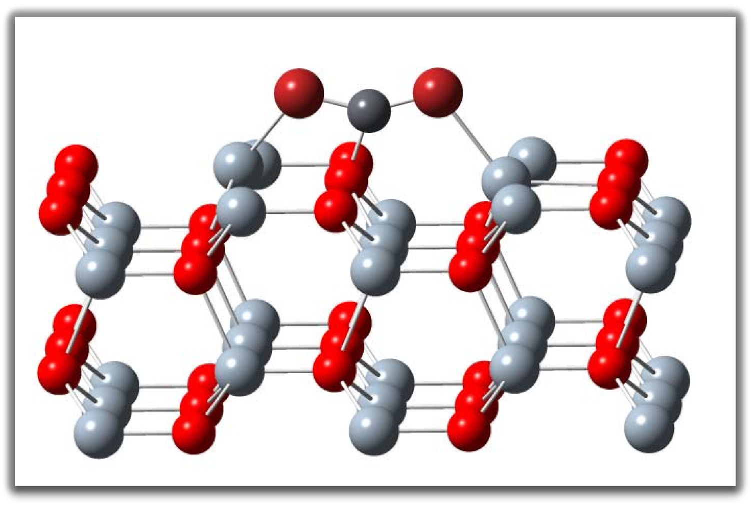


LEED: (2x1) – Phase of CO_2 on ZnO (10$\bar{1}$0)

Conclusion

The analysis of azimuth- and polarisation dependences allow us to get the information about the adsorption geometry of adsorbates on the oxide surface.

Such knowledge will allow to improve the real catalyst, e.g the structure and the particle size.



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References
[1] Y. Wang, R. Kováčik, B. Meyer, K. Kotsis, D. Stodt, V. Staemmler, H. Qiu, F. Traeger, D. Langenberg, M. Muhler, C. Wöll, *Angew. Chem.Int. Ed.* **2007**, 5624-5627.
[2] H. Noei, H. Qiu, Y. Wang, M. Muhler, C. Wöll, *ChemPhysChem* **2010**, 3604-3607.
[3] M. Buchholz, P. G. Weidler, F. Bebensee, A. Nefedov, C. Wöll, „Carbon dioxide on ZnO (10-10): Tridentate carbonate orientation proved by infrared reflection absorption spectroscopy“, *Phys. Chem. Chem. Phys.* **2013**, DOI: 10.1039/C3CP54643H.