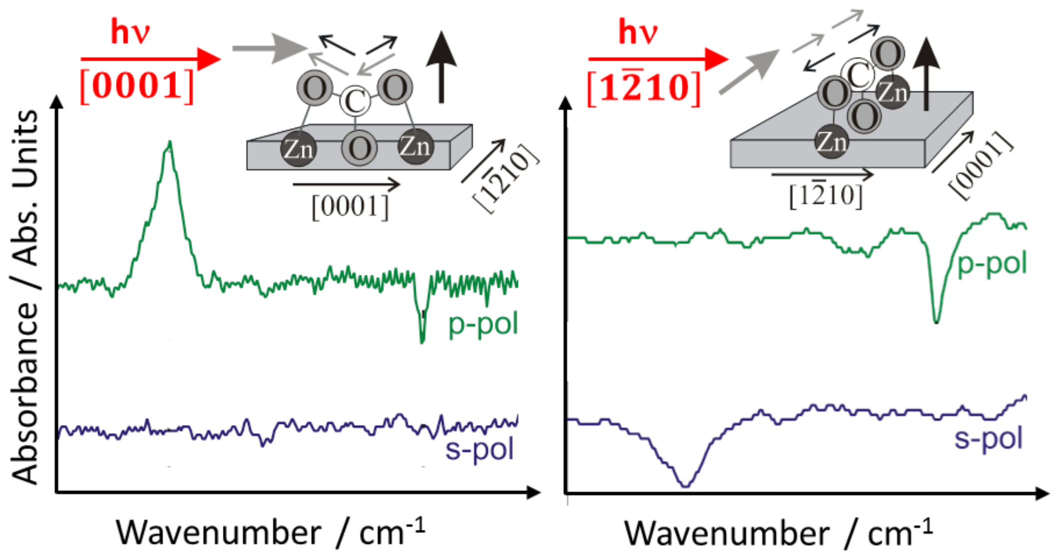
IRRAS on Metal Oxide Single Crystals: CO and CO_2 Adsorption on ZnO(10-10)

<u>Fabian Bebensee</u>, Maria Buchholz, Peter G. Weidler, Alexei Nefedov, and Christof Wöll

Institute of Functional Interfaces, Department Chemistry of Oxydic and Organic Interfaces



MOTIVATION: Catalysis by ZnO

- **Industrial Methanol Synthesis**
  - **Catalyst used: $Cu/ZnO/Al_2O_3$**
  - **Industrially most important process converting CO_2 into larger molecules**
  - **Annual production volume for methanol exceeds 24 billion gallons**

- **CO_2 Activation on ZnO below RT**
  - **Carbon fixation**
  - **Carbamate synthesis**

Chemical Activity of Thin Oxide Layers: Strong Interactions with the Support Yield a New Thin-Film Phase of ZnO

V. Schott et all., *Angew. Chem. Int. Ed.* **2013**, 52, 11925-11929.

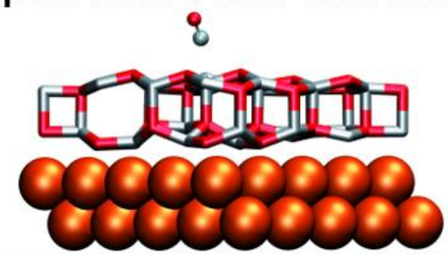


Photo: BASF Pressefoto

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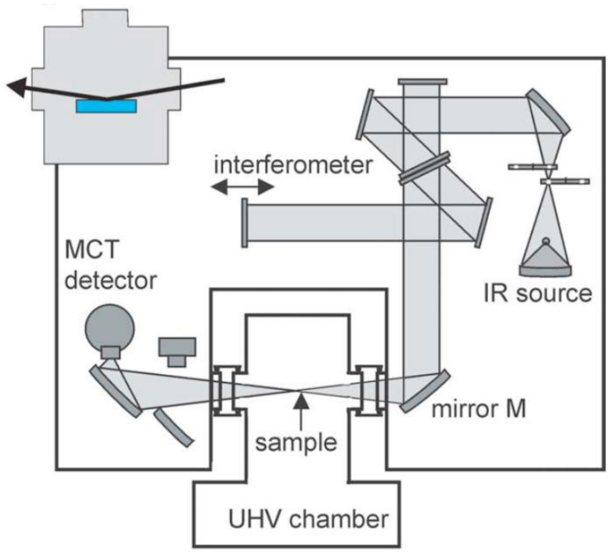
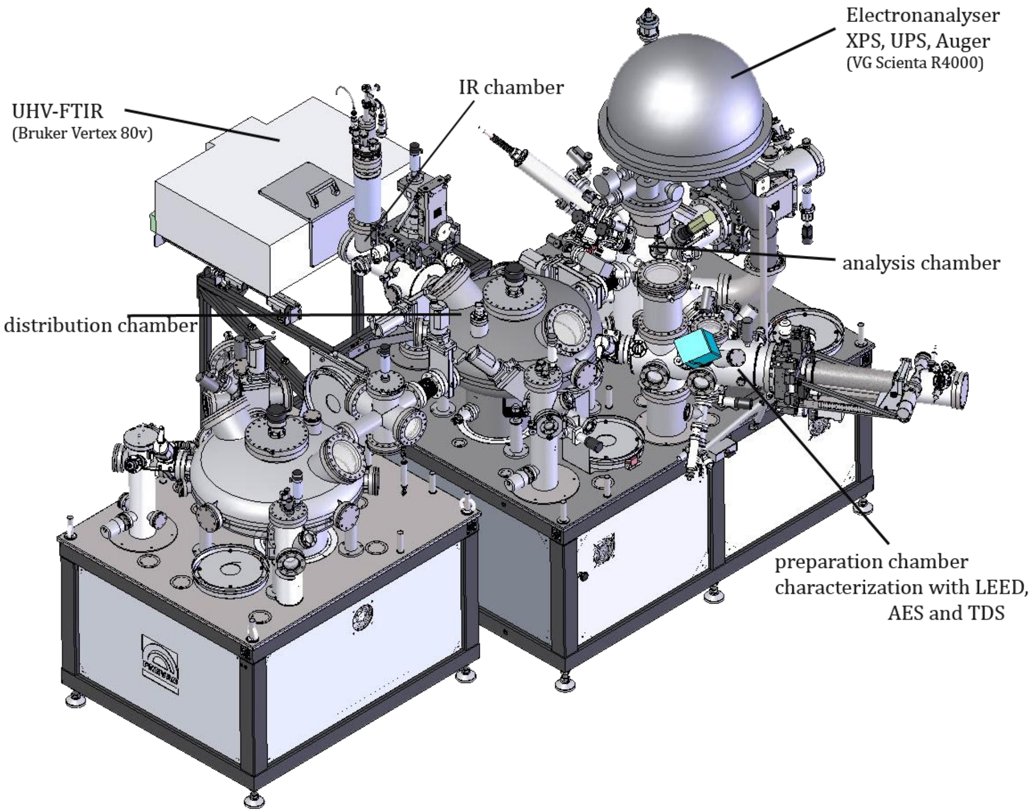
MOTIVATION: Demonstrate IRRAS Capabilities

- **Challenges for IRRAS on bulk metal oxides:**
- **Typically low reflectivity in the IR-regime**





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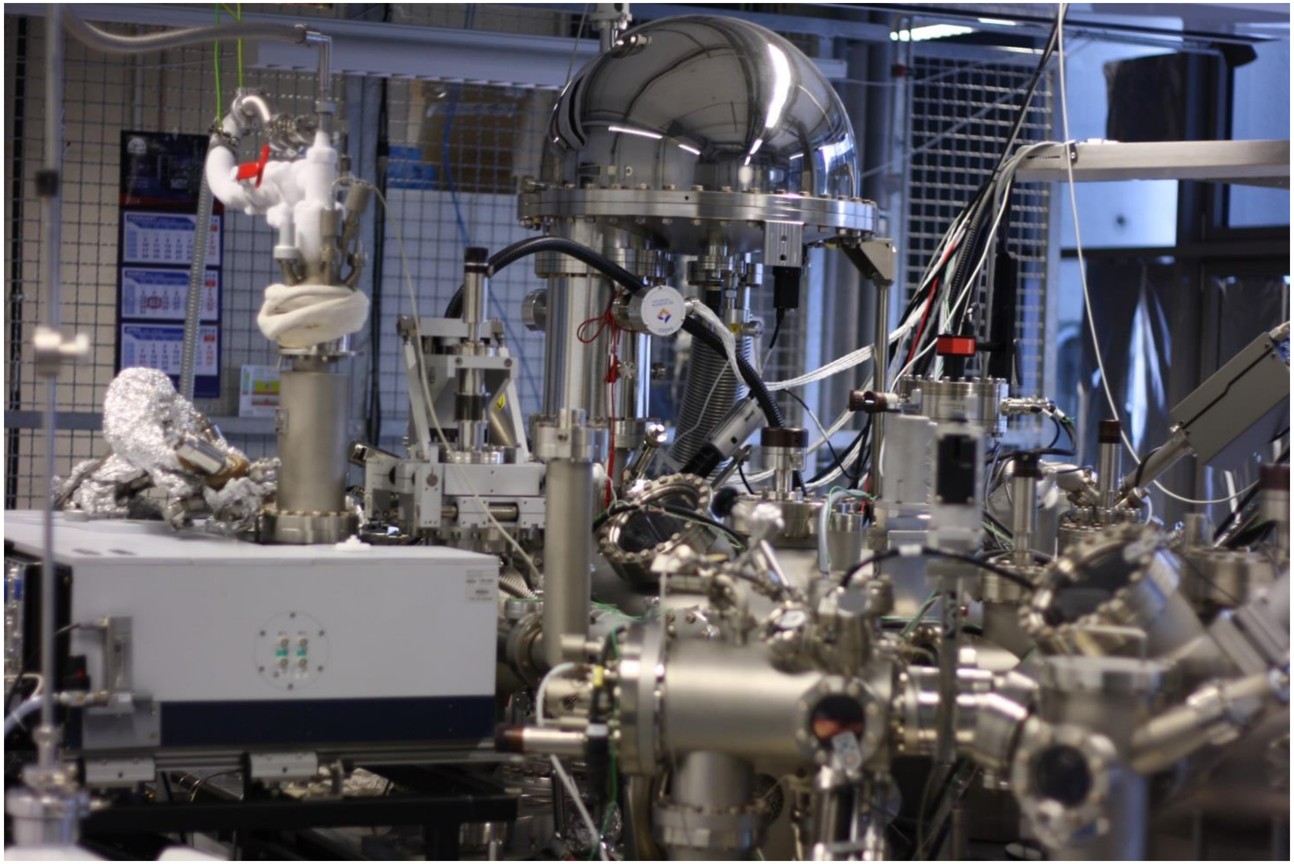

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J. Evans et al., *Surf. Sci.*, **360**, 61-73 (1996)
B. E. Hayden et al., , Surf. Sci. **397**, 306-313 (1998)
B. E. Hayden et al., *J. Phys. Chem. B*, **103**, 203-208 (1999)
Z. Chang et al., *Surf. Sci.*, **467**, L841-844 (2000)
M. Schiek et al., *Phys. Chem. Chem. Phys.*, **8**, 1505-1512 (2006)
H. Noei et al., *Phys. Status Solidi B,* **250**, 1204-1221 (2013)

- **Classic „surface selection rule" does not apply**

Spectra interpretation more complex

Polarisation becomes important

→ **Direct determination of adsorption geometry!!**

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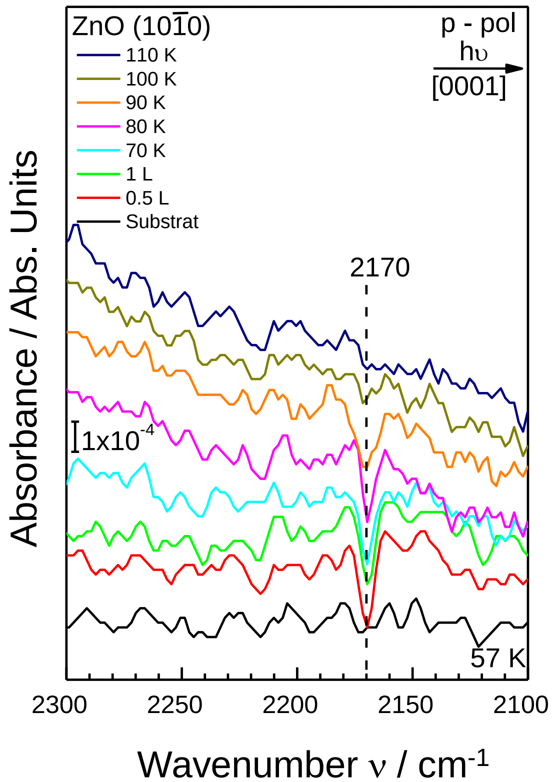
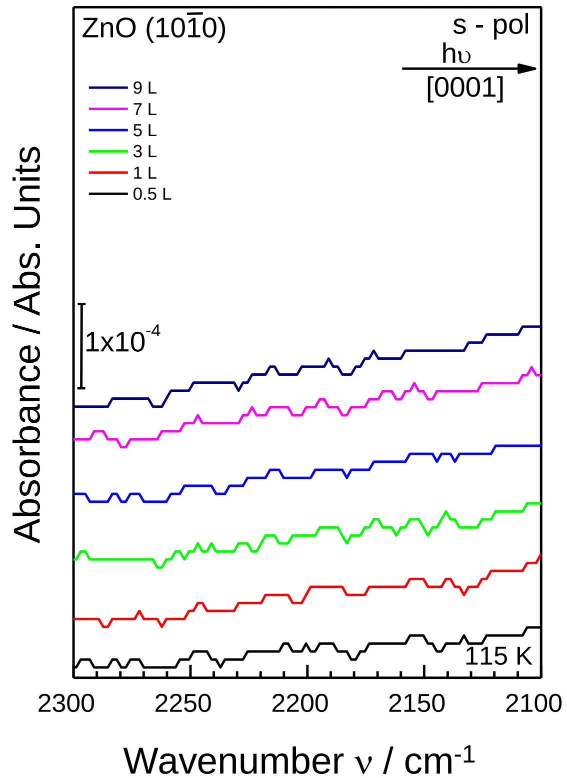
CO Adsorption on ZnO(10-10): First Spectra

Karlsruhe Institute of Technology

Spectra recorded by M. Buchholz





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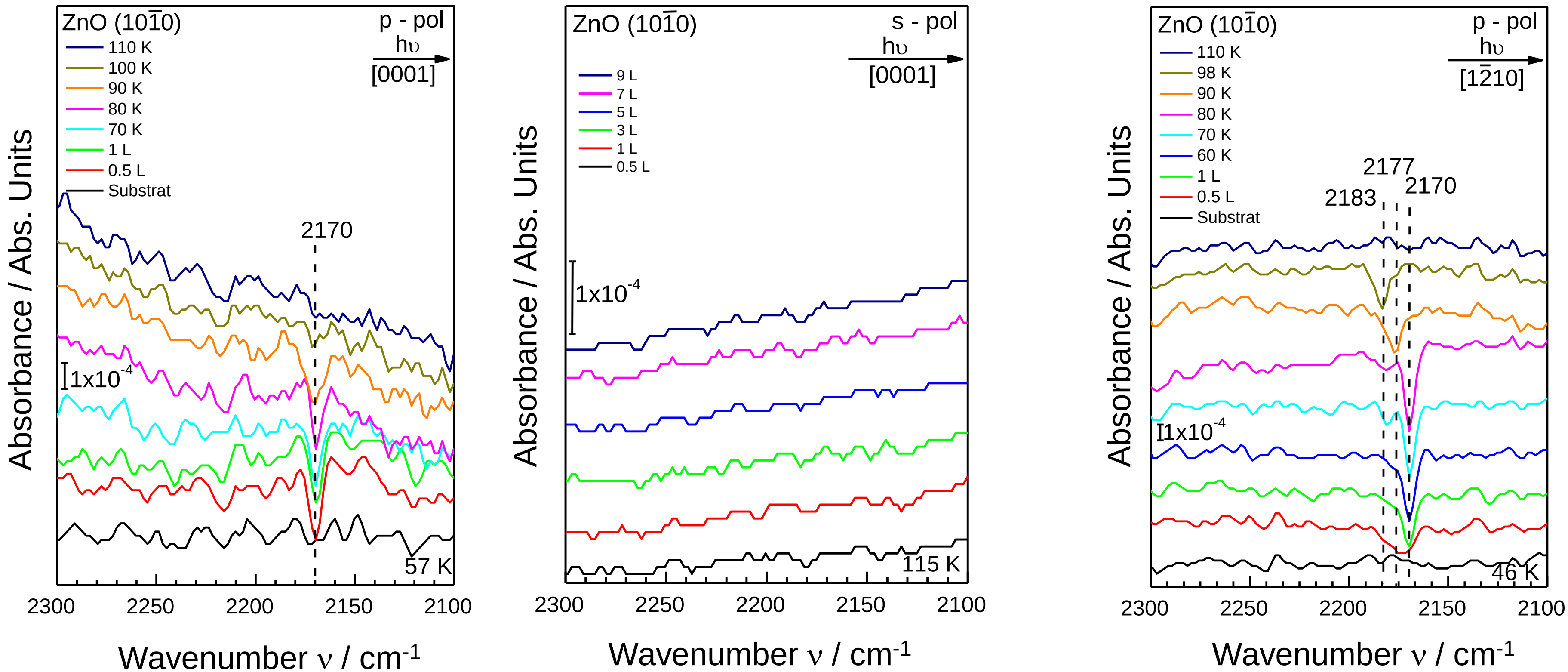

- One adsorption band indicating a single adsorption site
- Signal is blue shifted with respect to gas phase CO (2143 cm^{-1})
- Signal vanishes upon heating to 100 K or beyond

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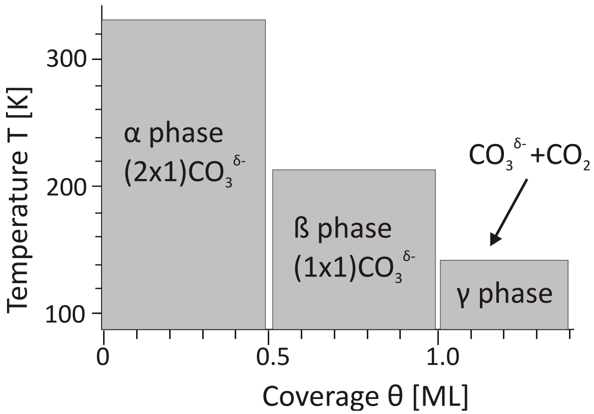
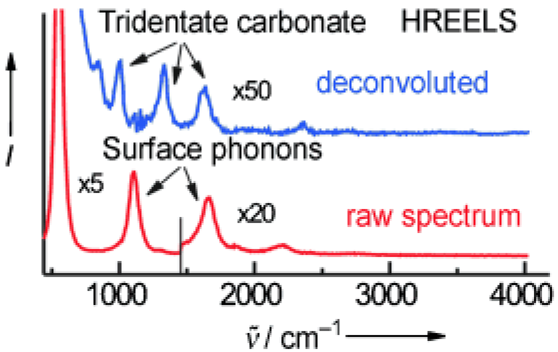
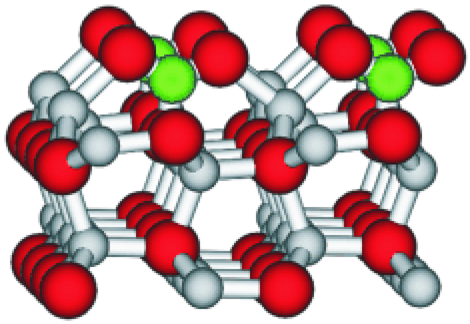
Introduction: CO_2 Adsorption on ZnO(10-10)







Y. Wang et al., *Angew. Chem. Int. Ed.*, **46**, 5624-5627 (2007)

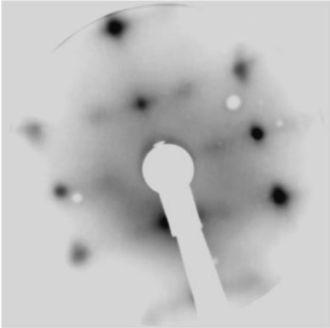
- **CO_2 can be activated on ZnO(10-10) even at low temperature (95 K)**
- **Formation of a rather unusual tridentate carbonate species**
- **DFT suggests an upright carbonate species along the [0001]-direction**
- **BUT: experimental findings suggest a significant tilt angle**

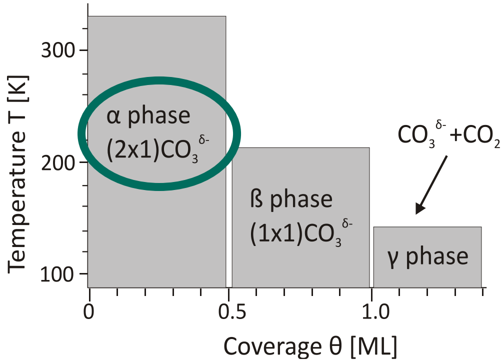
K. Kotsis et al., *Z. Phys. Chem.*, **222**, 891-915 (2008)

Experimental

Sample Preparation

- Ar-Sputtering (1.5 keV, 6 mA, 3×10^{-6} mbar) and annealing (800 K) cycles
- LEED: structural quality
- XPS: sample cleanliness





IRRAS-Measurements

- Pressure: ≤ 2×10^{-10} mbar
- 2048 scans at a resolution of 4 cm^{-1} per spectrum; Reflection mode
- Incidence angle: 80°

CO_2 Exposure

- Air Liquide; 99.995 vol%
- Dose: 1.5 L, via backfilling
- Sample temperature: ≤100 K

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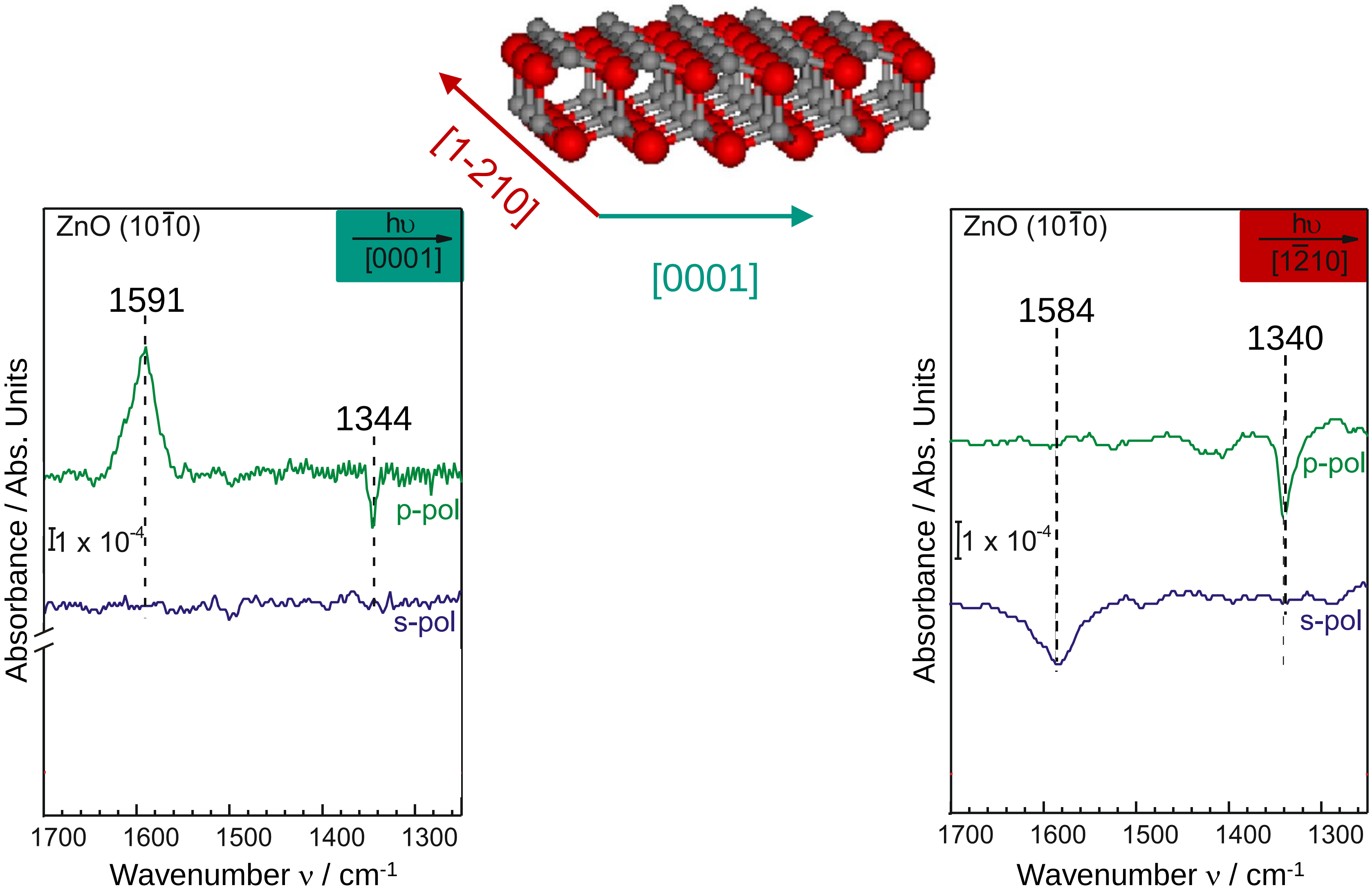
Results: IR-Spectra of CO_2 / ZnO(10-10)



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Results: Predicting Sign & Intensity of IR-Bands

Change in Reflectivity

$$\Delta R_i(\Theta) = R_i^0(\Theta) - R_i(\Theta) = R_i^0(\Theta)/10^{\Delta A_i(\Theta)}$$

Reflectivity of Substrate

$$R_s^0(\Theta) = (|\xi_3(\Theta) - \xi_1(\Theta)/\xi_3(\Theta) + \xi_1(\Theta)|)^2$$

$$R_{pt}^0(\Theta) = R_{pn}^0(\Theta) = \left(\left|\left(\frac{\xi_3(\Theta)}{(n_3)^2} - \frac{\xi_1(\Theta)}{(n_1)^2}\right) / \left(\frac{\xi_3(\Theta)}{(n_3)^2} + \frac{\xi_1(\Theta)}{(n_1)^2}\right)\right|\right)^2$$

$$\xi_j(\Theta) = \sqrt{\left[\left(\hat{n}_j\right)^2 \cdot n_1 \cdot (\sin\Theta)^2\right]}$$

Absorbance

$$\Delta A_x(\Theta) = \frac{-16\pi}{ln(10)} \cdot \left(\frac{cos(\Theta)}{\left(\frac{(\xi_3(\Theta))^2}{(n_3)^4}\right) - (cos(\Theta))^2}\right) \cdot \left[\frac{-(\xi_3(\Theta))^2}{(n_3)^4}\right]$$

$$\Delta A_y(\Theta) = \frac{-16\pi}{ln(10)} \cdot \left(\frac{cos(\Theta)}{(n_3)^2 - 1}\right) \cdot \frac{n_2 \cdot k_2 \cdot d_2}{\lambda}$$

$$\Delta A_z(\Theta) = \frac{-16\pi}{ln(10)} \cdot \left(\frac{cos(\Theta)}{\left(\frac{(\xi_3(\Theta))^2}{(n_3)^4}\right) - (cos(\Theta))^2}\right) \cdot \left[\frac{-(sin(\Theta))^2}{((n_2)^2 + (k_2)^2)^2}\right]$$

J. A. Mielczarski and R. H. Yoon, *The Journal of Physical Chemistry*, 1989, **93**, 2034-2038
W. N. Hansen, *J. Opt. Soc. Am.*, 1968, **58**, 380 / W. N. Hansen, *Symposia of the Faraday Society*, 1970, **4**, 27

Results: Predicting Sign & Intensity of IR-Bands

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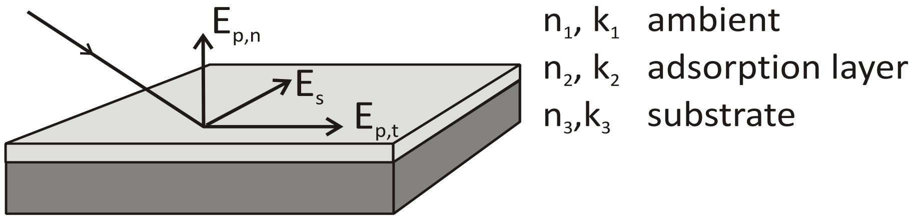

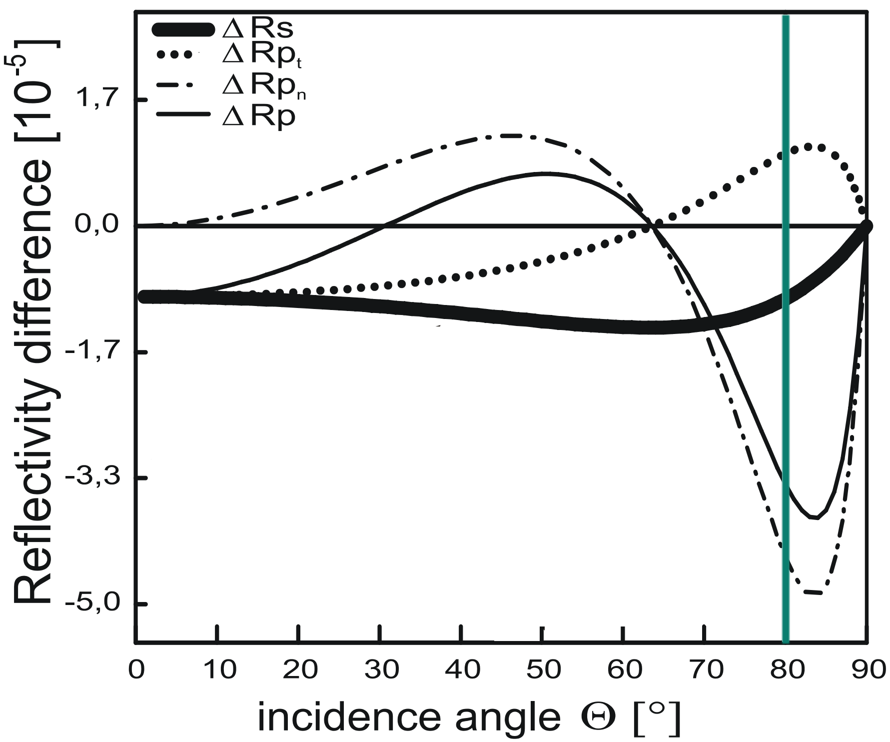

Observations for oxide substrates:

- **In s-polarization, bands are always negative**
- **In p-polarization, bands may be either positive or negative**
- **Different components in p-polarization always yield bands of opposite sign**

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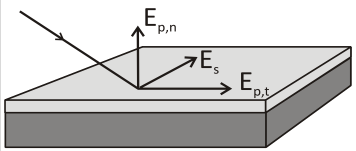
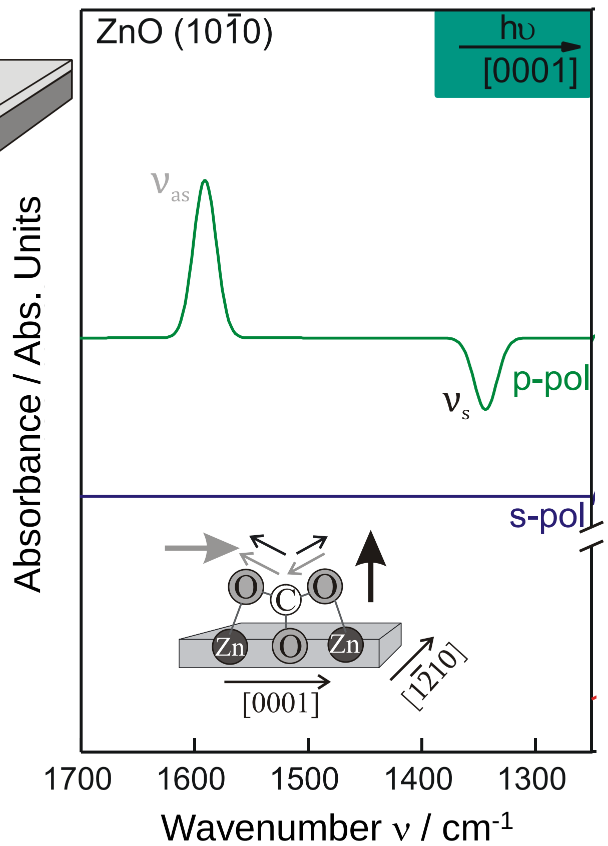
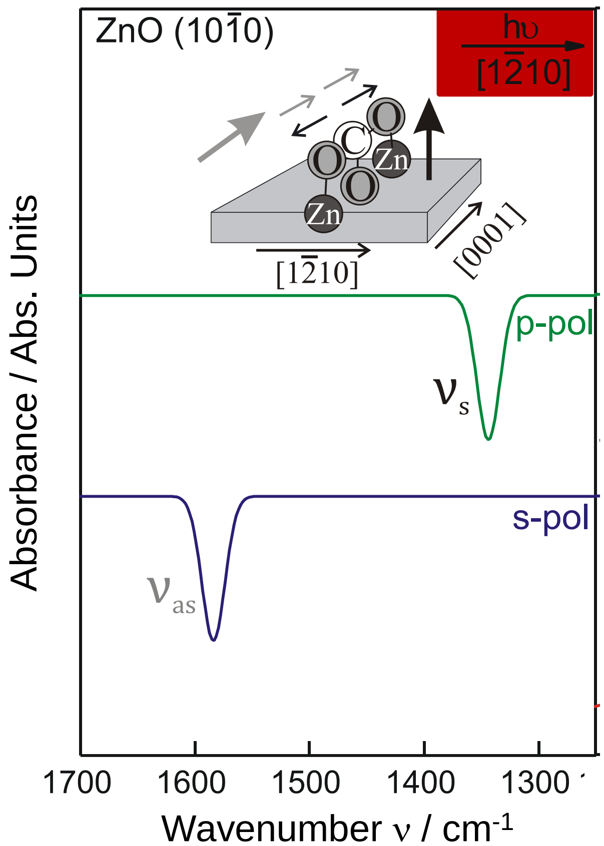
Results: Predicting Sign & Intensity of IR-Bands

Tridentate carbonate along [0001]







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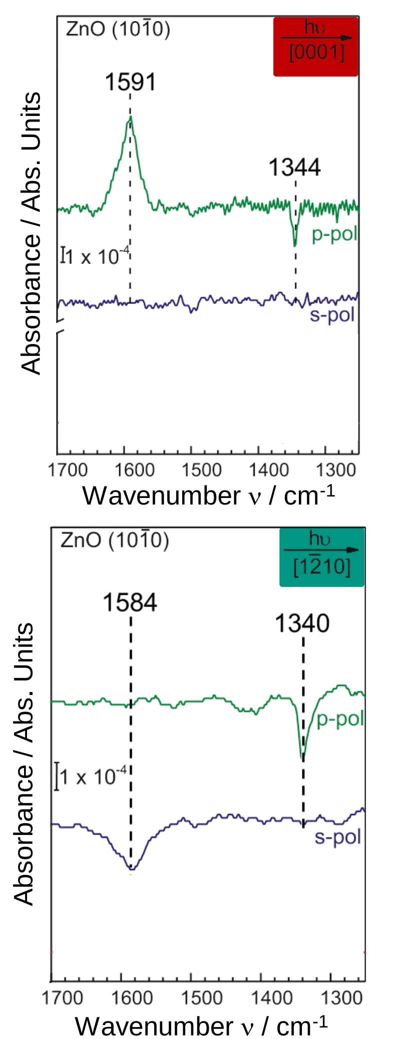
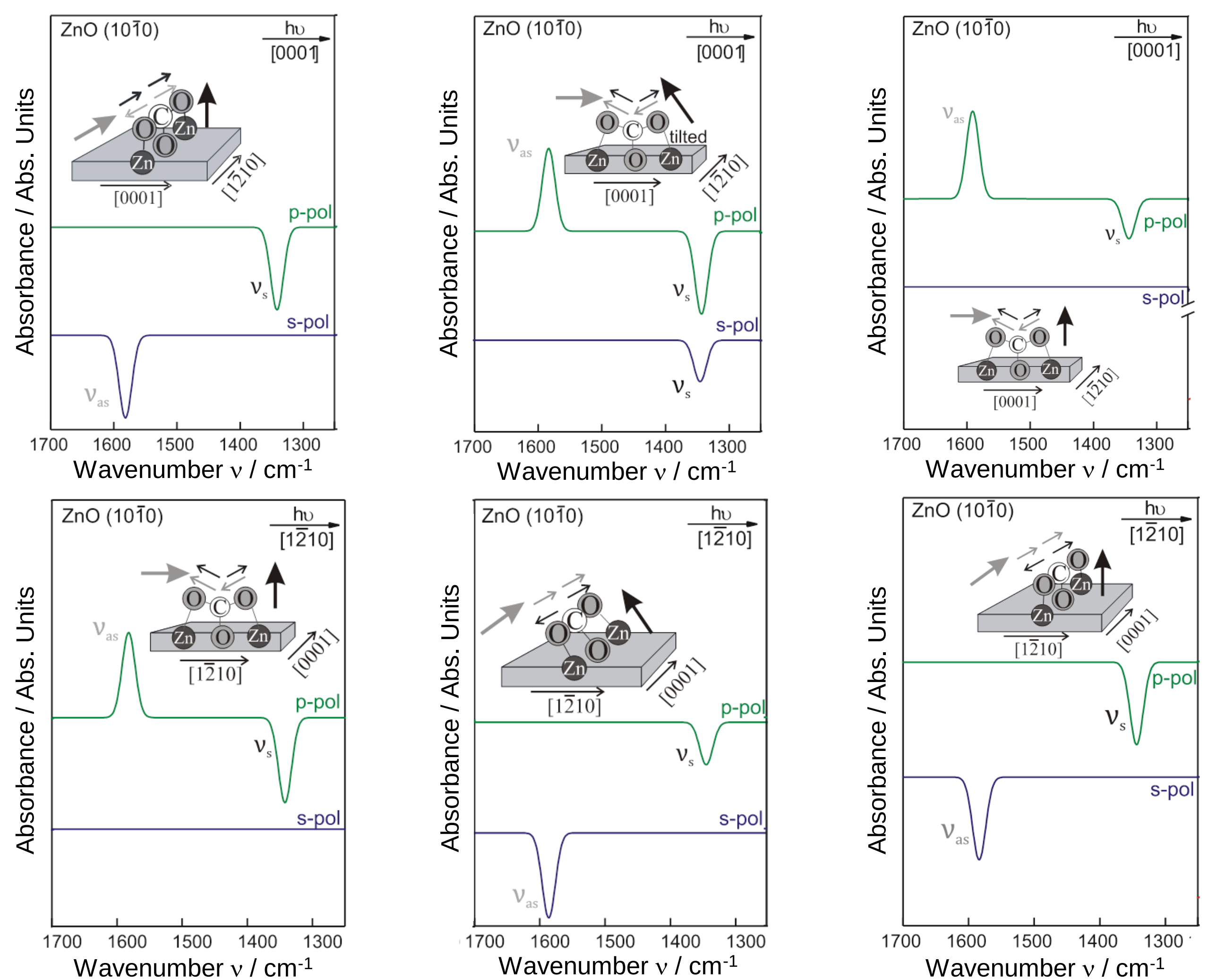
Results: Experiment Meets Theory

Experiment



Theory for different configurations



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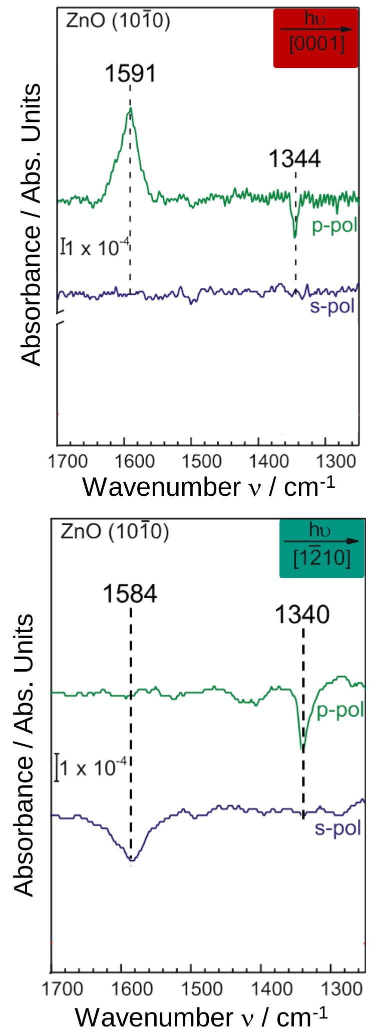

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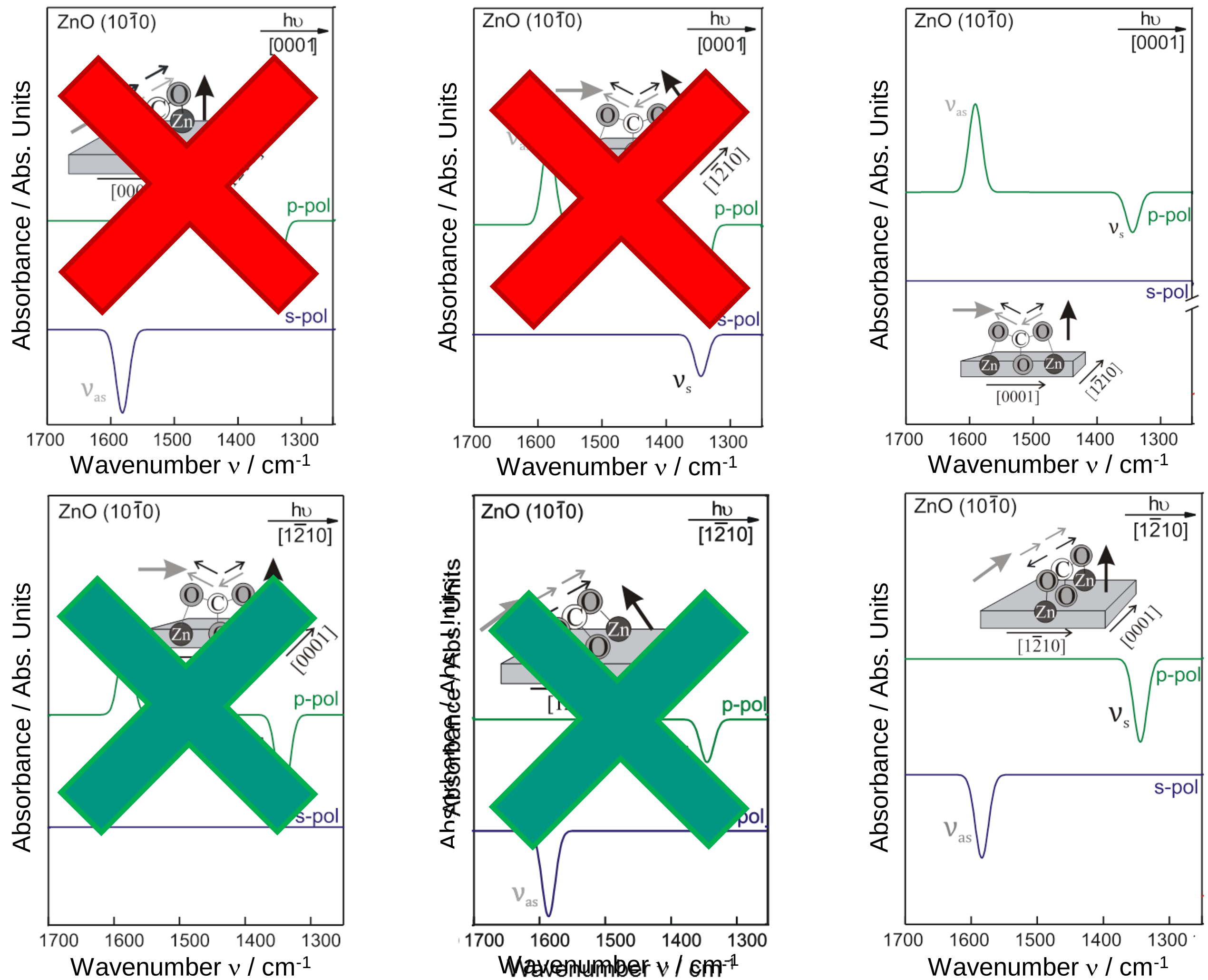
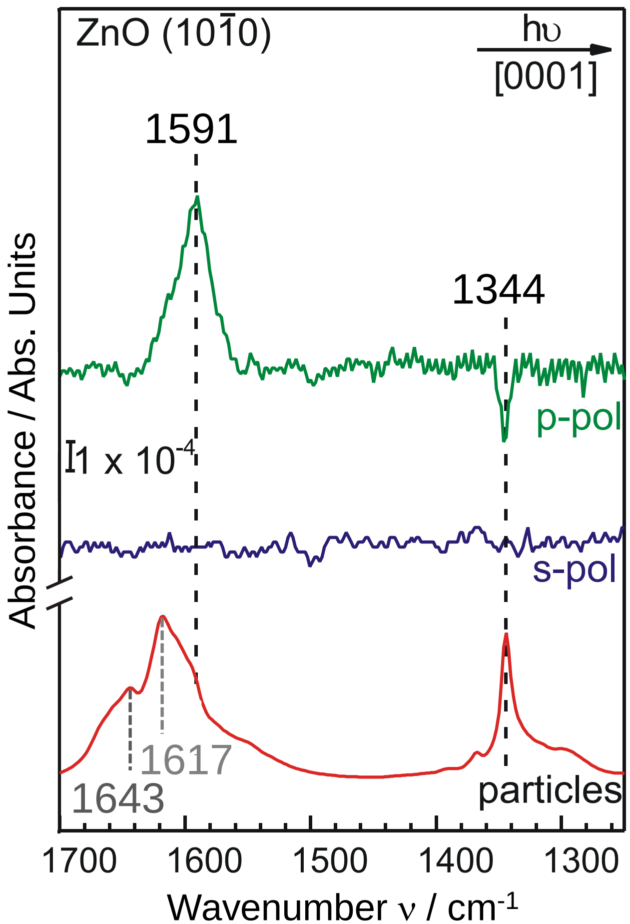
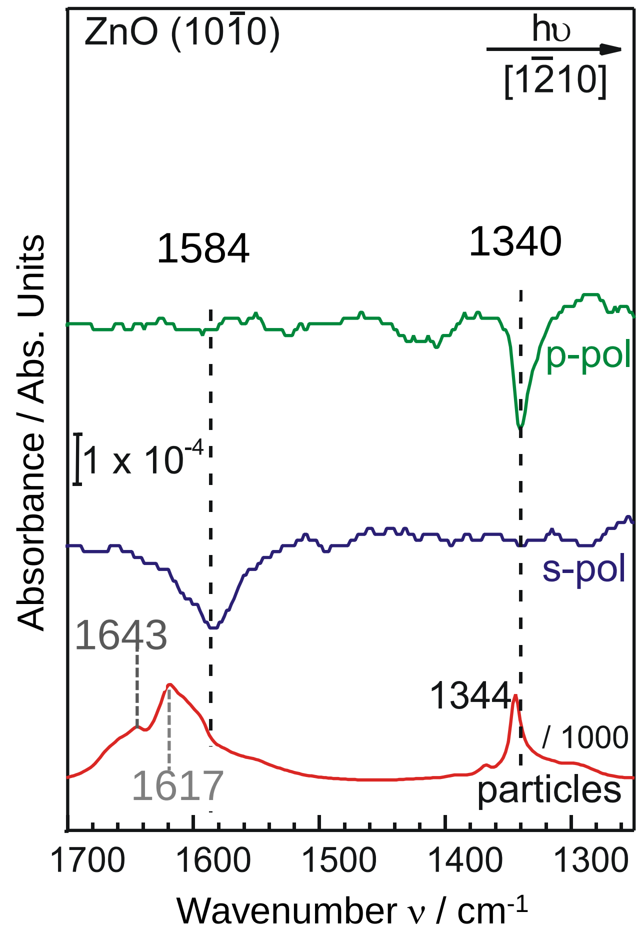


Results: Single Crystal versus Powder Particles





IR-Spectra of ZnO Powder

Symmetric stretch ν_s:

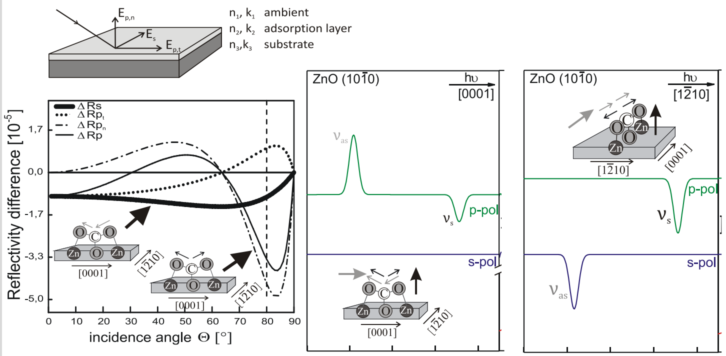
- at same position
- small extra feature

Asymmetric stretch ν_{as}:

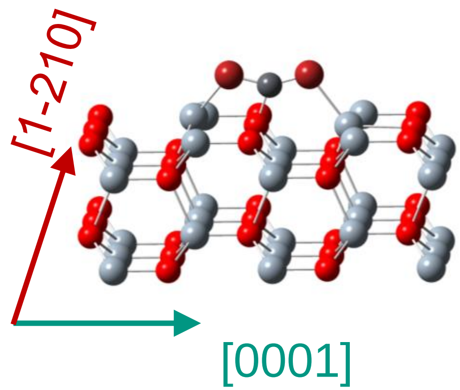
- two main features at higher wavenumbers
- only small shoulder at same position

Powder Data: H. Noei et al., *Journal of Physical Chemistry C*, **115**, 908-914 (2011)

Conclusions



- With the aide of simple calculations, IRRAS can be successfully used to determine the adsorbate geometry on oxide substrates



- CO_2 forms an upright standing tridentate carbonate with its backbone oriented along the [0001]-direction on the ZnO(10-10) single crystal surface

vs.

http://www.meliorum.com

- Surprisingly, the mixed-terminated ZnO(10-10) surface seems not to present the dominating binding site on ZnO nanoparticles

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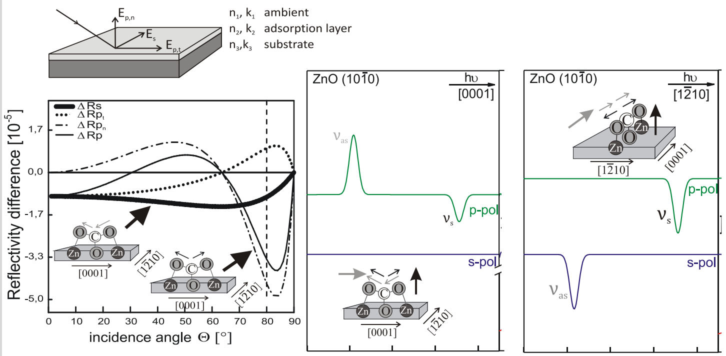
Conclusions



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Carbon dioxide adsorption on a ZnO(10-10) substrate studied by infrared reflection absorption spectroscopy
M. Buchholz, P. Weidler, F. Bebensee, A. Nefedov, and C. Wöll, Phys. *Chem. Chem. Phys.* **2014**, 16, 1672-1678.

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Acknowledgements

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Prof. Christof Wöll

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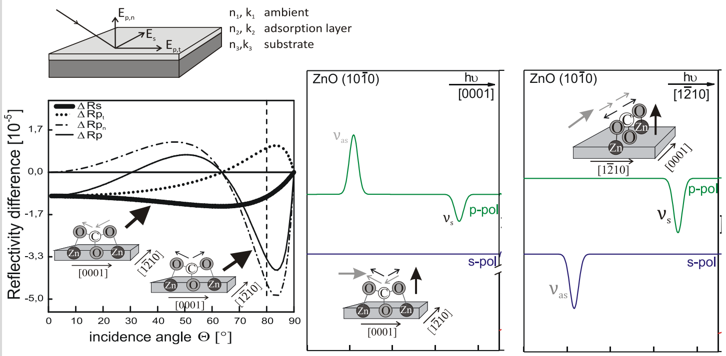
Stiftung/Foundation

"THEO Group"

Science and Technology of Nanosystems (STN)	Helmholtz Research School Energy-related catalysis

Conclusions



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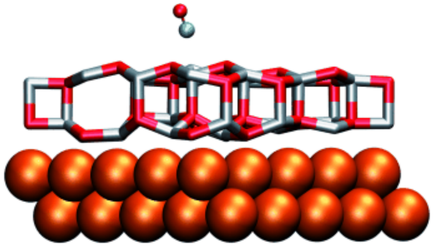

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