Karlsruhe Institute of Technology

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Helmholtz Research School „Energy-related catalysis“

IR-probes for Ceria Surfaces: A Comparison of CO and CH_3OH adsorbed on $CeO_2(111)$, $CeO_2(110)$ and Ceria Powders

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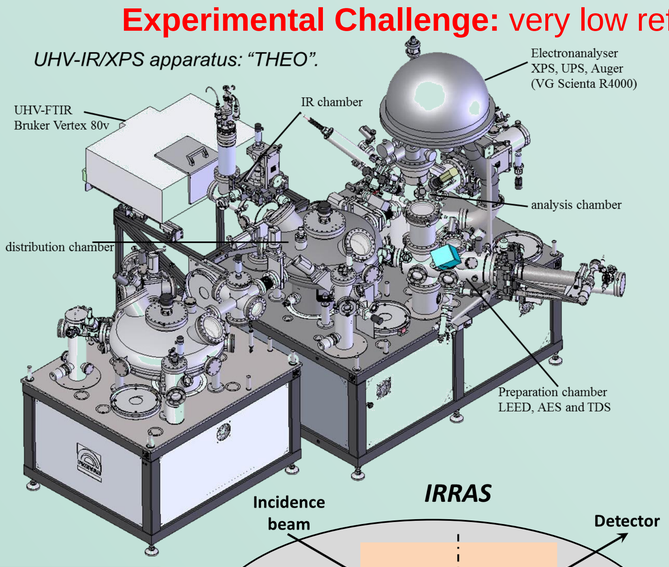
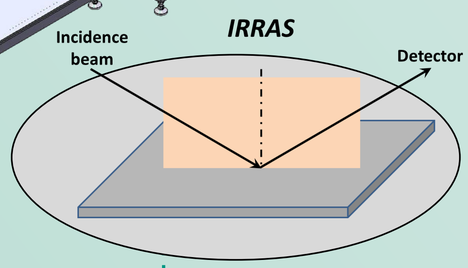
Introduction

Ceria (CeO_2), one of the most easily reducible metal oxides, exhibits extraordinary activities in diverse catalytic processes. The importance of this material has triggered numerous experimental and theoretical studies. The studies on bulk single crystal surfaces, however, are still scarce. Here we used a novel UHV-IR/XPS apparatus to investigate the behaviors of two sensitive probe molecules, carbon monoxide (CO) and methanol (CH_3OH), adsorption at stoichiometric and reduced bulk $CeO_2(111)$ and $CeO_2(110)$ single crystal surfaces.[1, 2] Our results indicate that CO and CH_3OH are capable of probing surface oxygen vacancies and distinguishing facet orientations, which also firmly clarify the ambiguous assignments derived from previous powder and thin film data.

Infrared Reflection Absorption Spectroscopy on Oxides

Experimental Challenge: very low reflectivity of dielectrics and consequently small signals!





Strategy to overcome challenge of low reflectivity[3]:

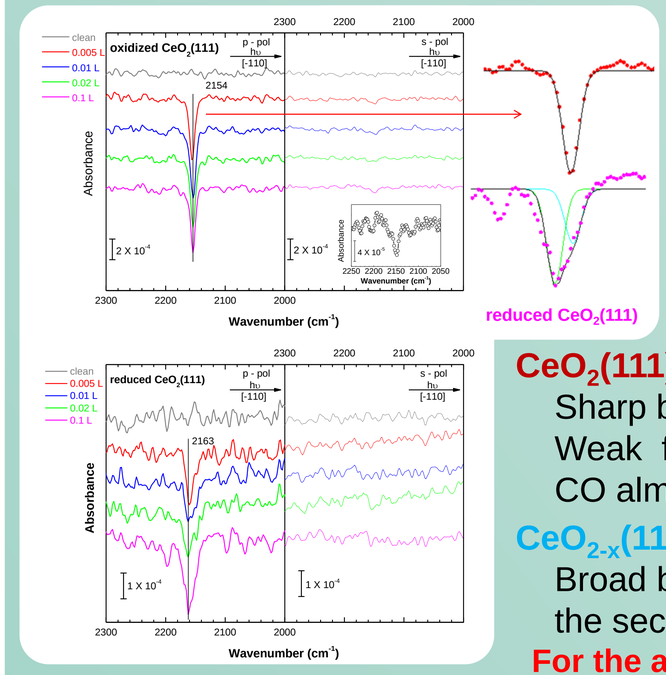
- Attach spectrometer directly to UHV chamber.
- Do not introduce any additional optical element, i.e. use the standard optical path within the IR-spectrometer.
- Minimize mechanical vibrations, e.g. damp mechanical vibrations of (turbo) pumps – crucial for time-resolved experiments.

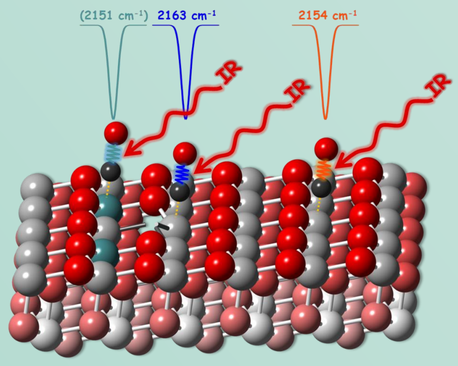
Additional features of “THEO”:

- 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 monoxide adsorption

CO on $CeO_2(111)$





$CeO_2(111)$:

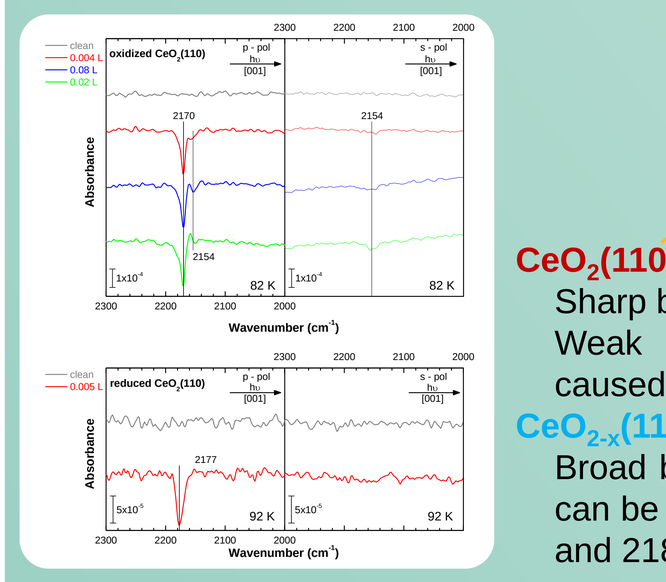
Sharp band at 2154 cm^{-1} in *p*-polarization.
Weak feature in *s*-polarization indicating CO almost perpendicular to the surface.

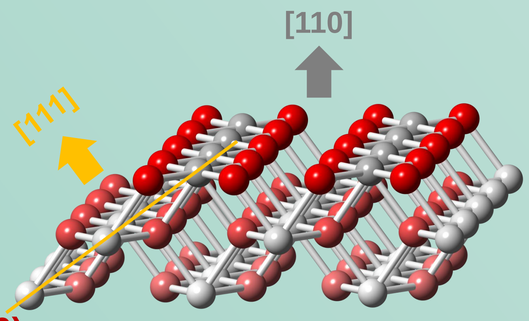
$CeO_{2-x}(111)$:

Broad band at 2163 cm^{-1} can be fitted with the second component of 2154 cm^{-1}.

For the assignments see the graph above.

CO on $CeO_2(110)$





$CeO_2(110)$:

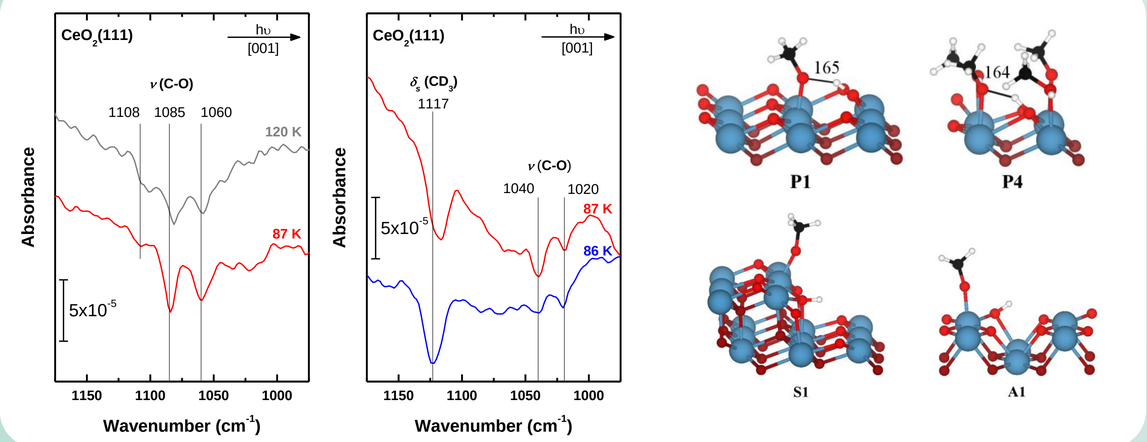
Sharp band at 2170 cm^{-1} in *p*-polarization
Weak features in *p* and *s*-polarization caused by CO on (111) step edges.

$CeO_{2-x}(110)$:

Broad band at 2177 cm^{-1} in *p*-polarization can be fitted with two components at 2170 and 2182 cm^{-1}.

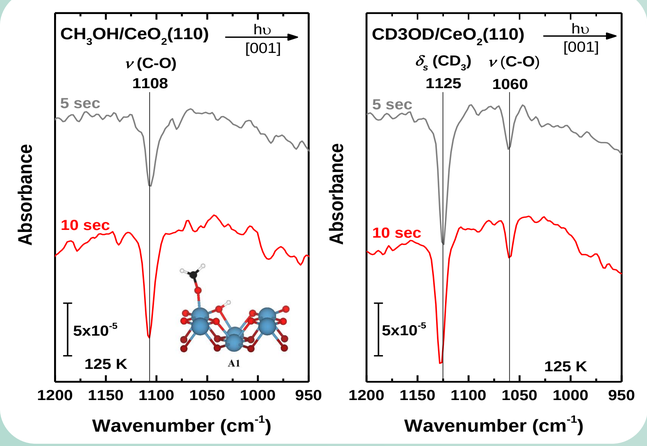
Methanol adsorption

CH_3OH/CD_3OD on $CeO_2(111)$

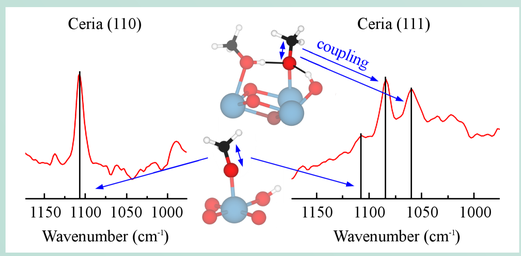


Strong bands at 1085 and 1060 cm^{-1} are assigned to a methanol monolayer at the pristine (111) surface that consists of H-bonded methoxide and molecularly adsorbed methanol species. The isotope induced bands are shifted to 1040 and 1020 cm^{-1}.
The assignment of weak feature at 1108 cm^{-1} is as below.

CH_3OH/CD_3OD on $CeO_2(110)$

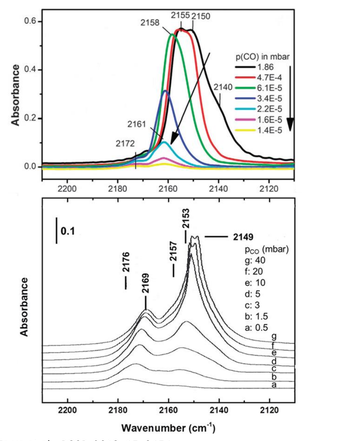


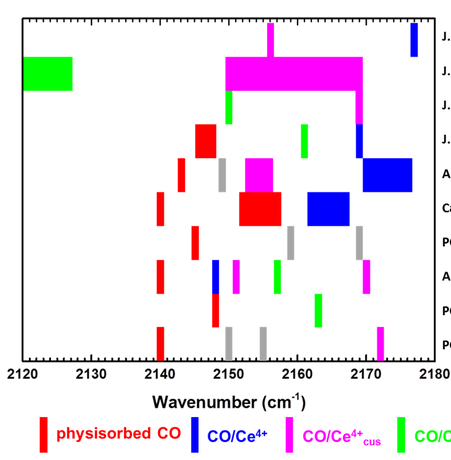
One intense band at 1108 cm^{-1} causes by methoxy monomers bound to the surface, which is isotopically shifted to 1060 cm^{-1}.
The band at 1125 cm^{-1} is assigned to CD bending mode.



Reassignments of IR bands of methanol adsorption

Reassignments of CO bands of ceria powders





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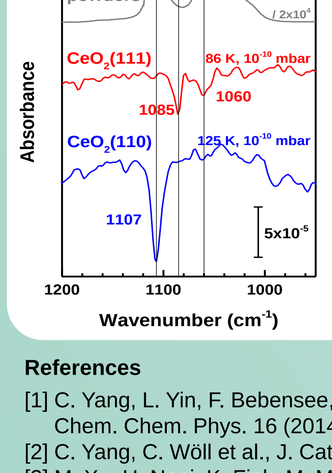
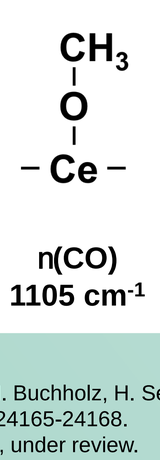
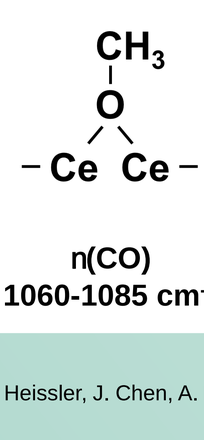
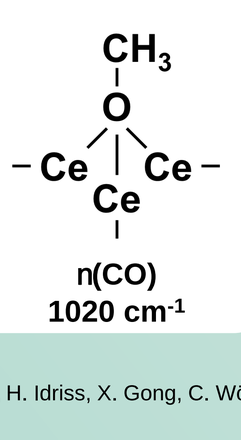


Previous assignments

monodentate	bidentate	tridentate
		
n(CO) 1105 cm^{-1}	n(CO) 1060-1085 cm^{-1}	n(CO) 1020 cm^{-1}

References

[1] C. Yang, L. Yin, F. Bebensee, M. Buchholz, H. Sezen, S. Heissler, J. Chen, A. Nefedov, H. Idriss, X. Gong, C. Wöll, Phys. Chem. Chem. Phys. 16 (2014) 24165-24168.
[2] C. Yang, C. Wöll et al., J. Catal., under review.
[3] M. Xu, H. Noei, K. Fink, M. Muhler, Y. Wang, C. Wöll, Angew. Chem. Int. Edit. 51 (2012) 4731-4734.