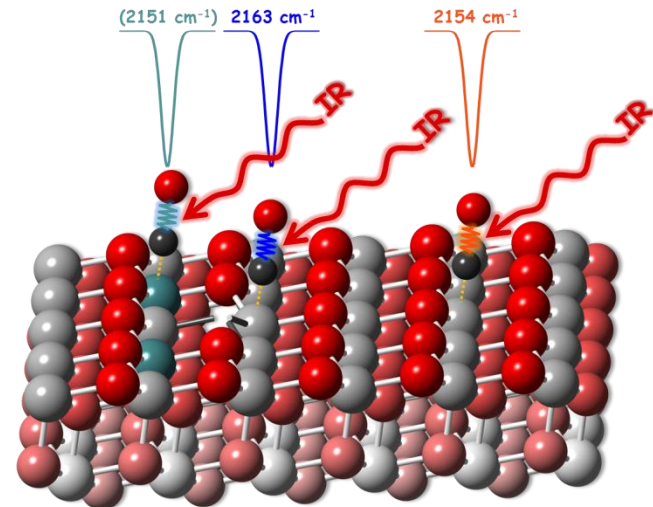
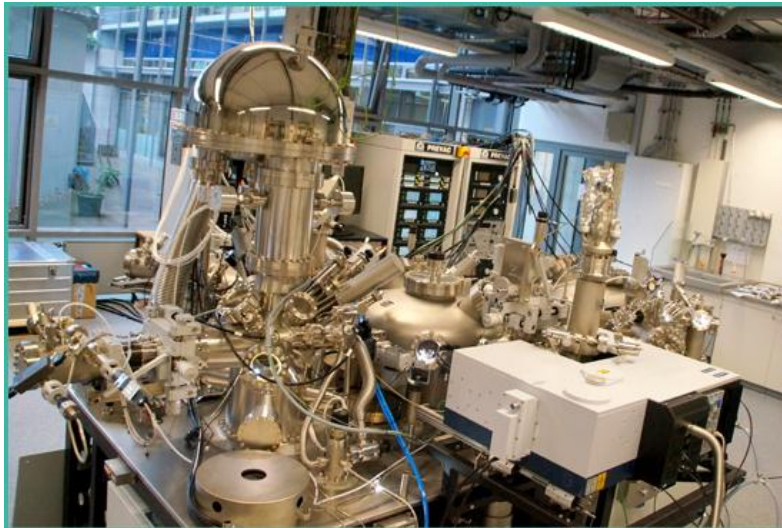


UHV-IR spectroscopy study of carbon monoxide adsorption on ceria single crystal surfaces

Chengwu Yang, Alexei Nefedov, Yuemin Wang, Christof Wöll

Institute of Functional Interfaces (IFG)



■ Introduction

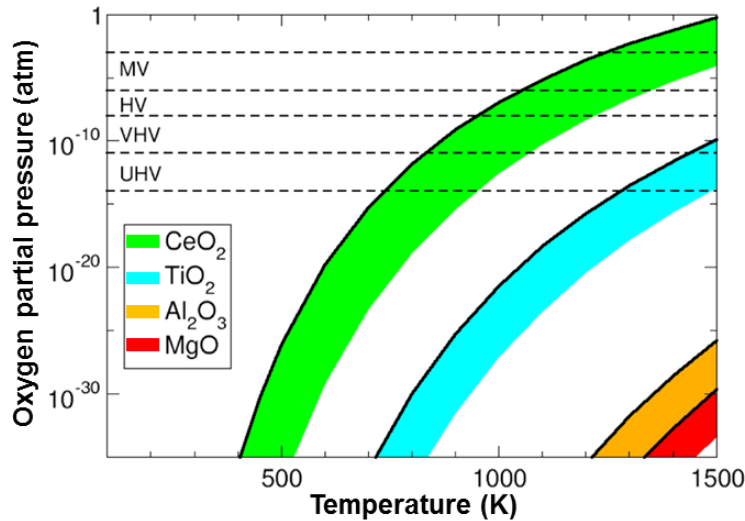
- Reducibility of ceria (CeO_2 , cerium dioxide)
- Controversial assignments of CO IR-bands on ceria powders
- UHV-FTIR apparatus

■ Results and discussions

- CO adsorption on $\text{CeO}_2(111)$
- CO adsorption on $\text{CeO}_2(110)$
- CO adsorption on reduced $\text{CeO}_2(100)$

■ Summary

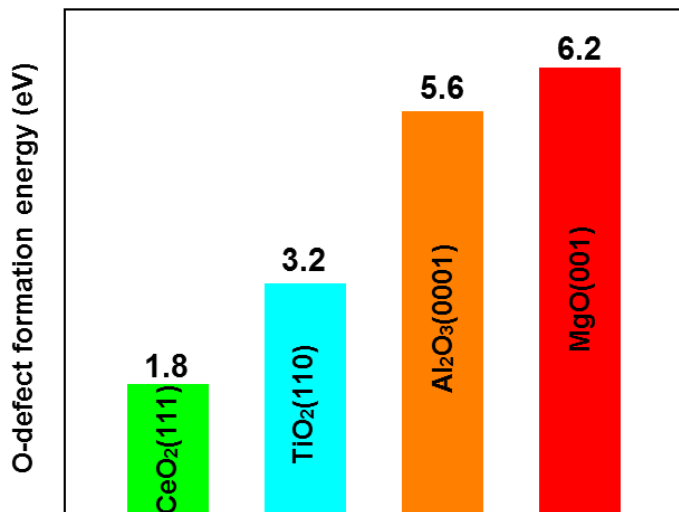
Reducibility of ceria (CeO_2 , cerium dioxide)



$p(\text{O}_2)$ vs T phase diagram.

The left graphs are based on PBE+U(4.5) calculations for $\text{CeO}_2(111)$ and PBE calculations for $\text{TiO}_2(110)$, $\text{Al}_2\text{O}_3(0001)$, and $\text{MgO}(001)$ surfaces.

J. Paier, C. Penschke, J. Sauer, *Chem. Rev.*, 2013, 113, 3949.



Calculated oxygen defect formation energy.

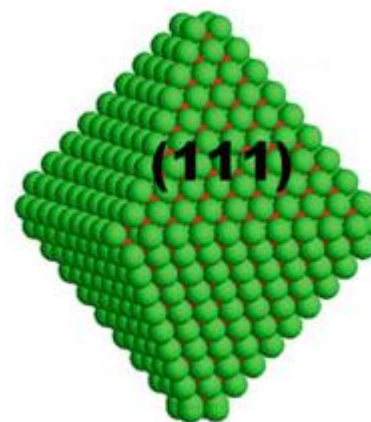
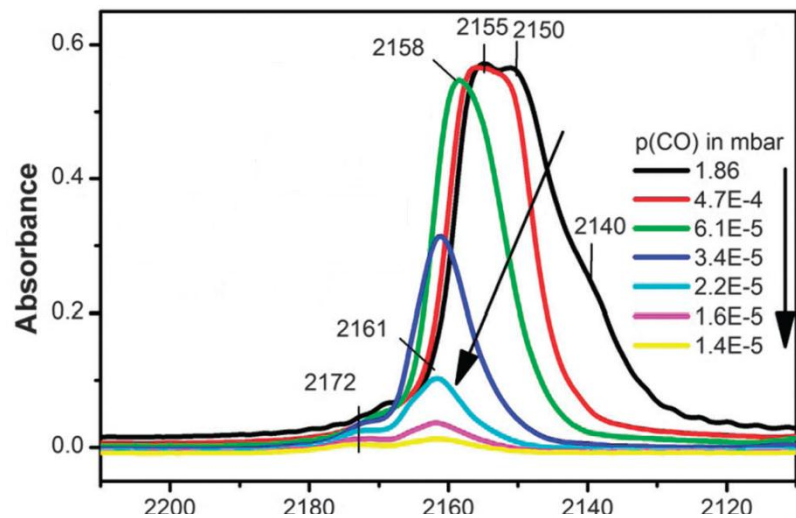
Stability and reducibility of ceria surfaces

| Surface | Surface energy ($\text{J}\cdot\text{m}^{-2}$) | O-vacancy formation energy (eV) |
|---------|---|---------------------------------|
| (111) | 0.68 | 2.60 |
| (110) | 1.01 | 1.99 |
| (100) | 1.41 | 2.27 |

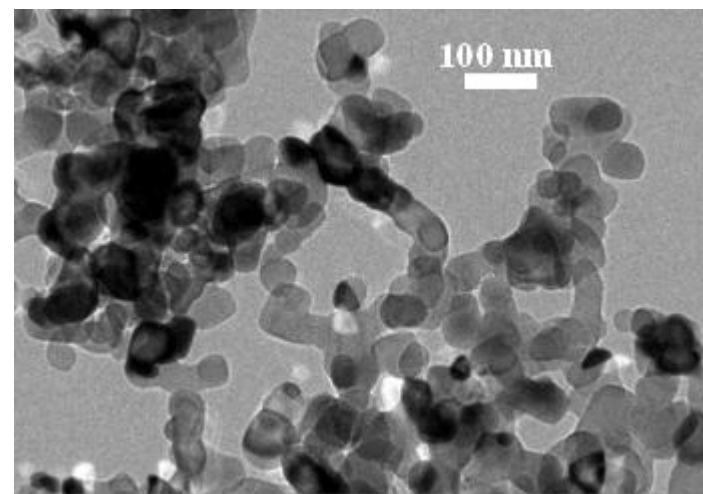
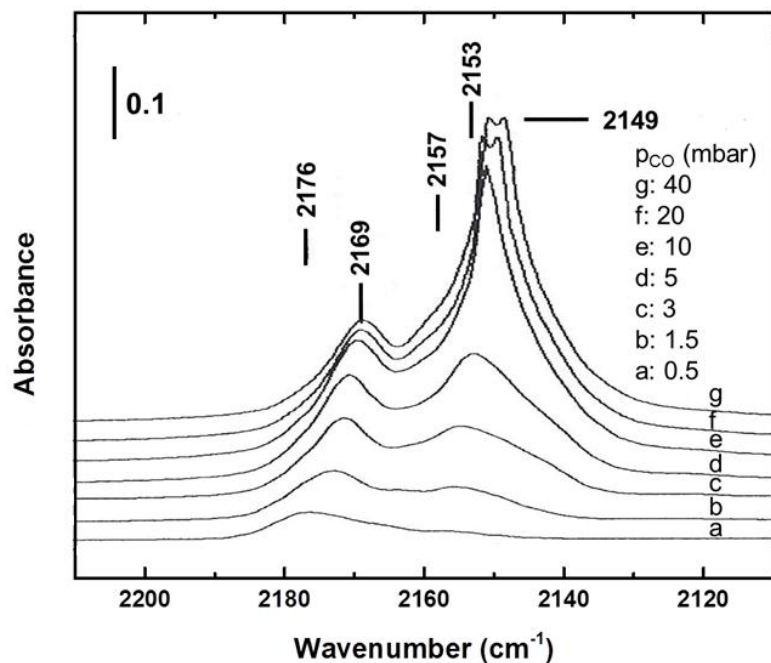
M. Nolan et al., *Surf. Sci.*, 2005, 576, 217.

M. Nolan et al., *Surf. Sci.*, 2005, 595, 223.

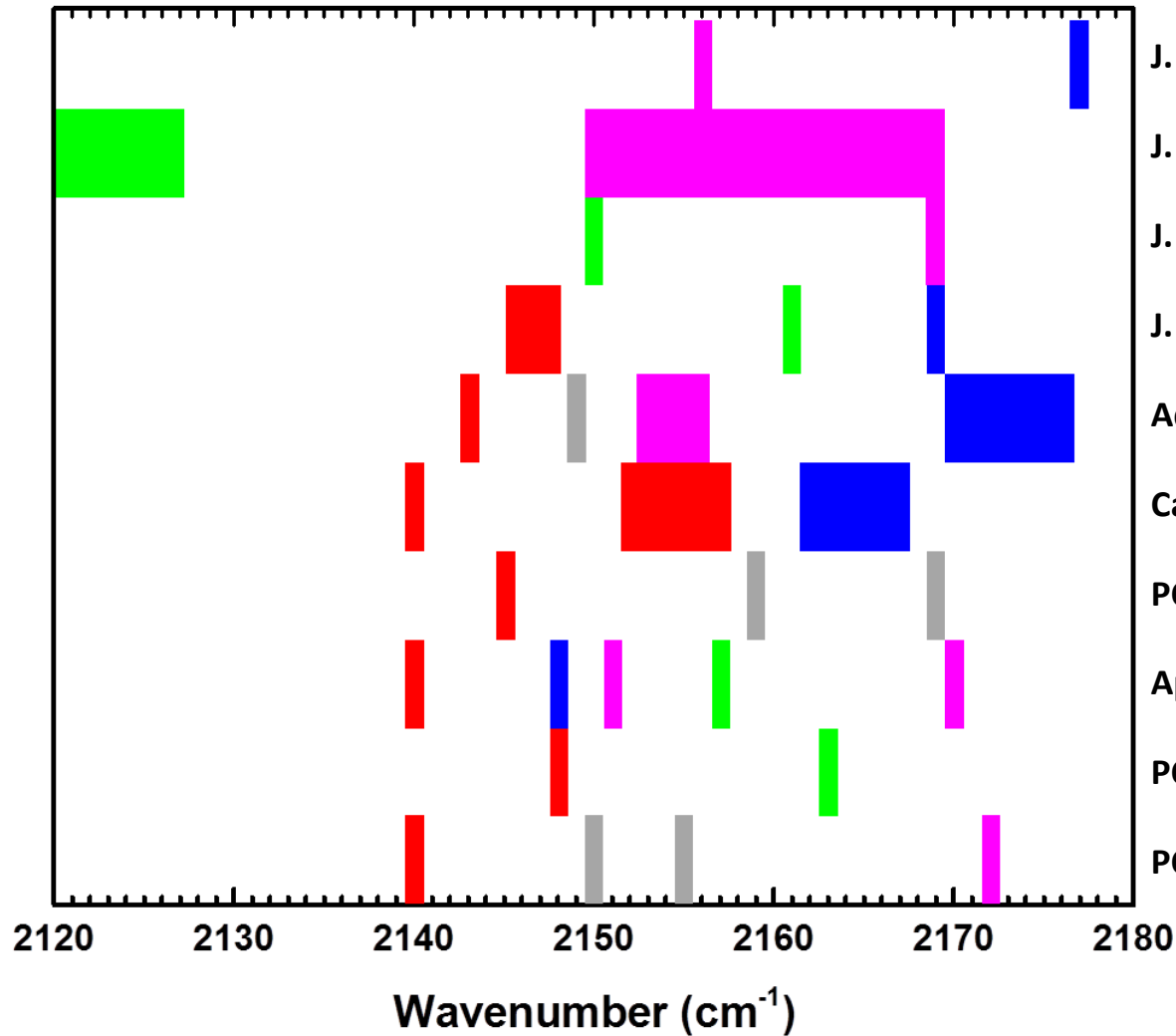
CO on ceria powders



Wulff construction



Assignments of CO bands of ceria powders



J. Chem. Soc., Faraday Trans., 1989, 85, 929.

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J. Phys. Chem., 1986, 90, 3176.

J. Chem. Soc., Faraday Trans., 1996, 92, 1603.

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PCCP, 2005, 7, 187.

PCCP, 2013, 15, 3454.

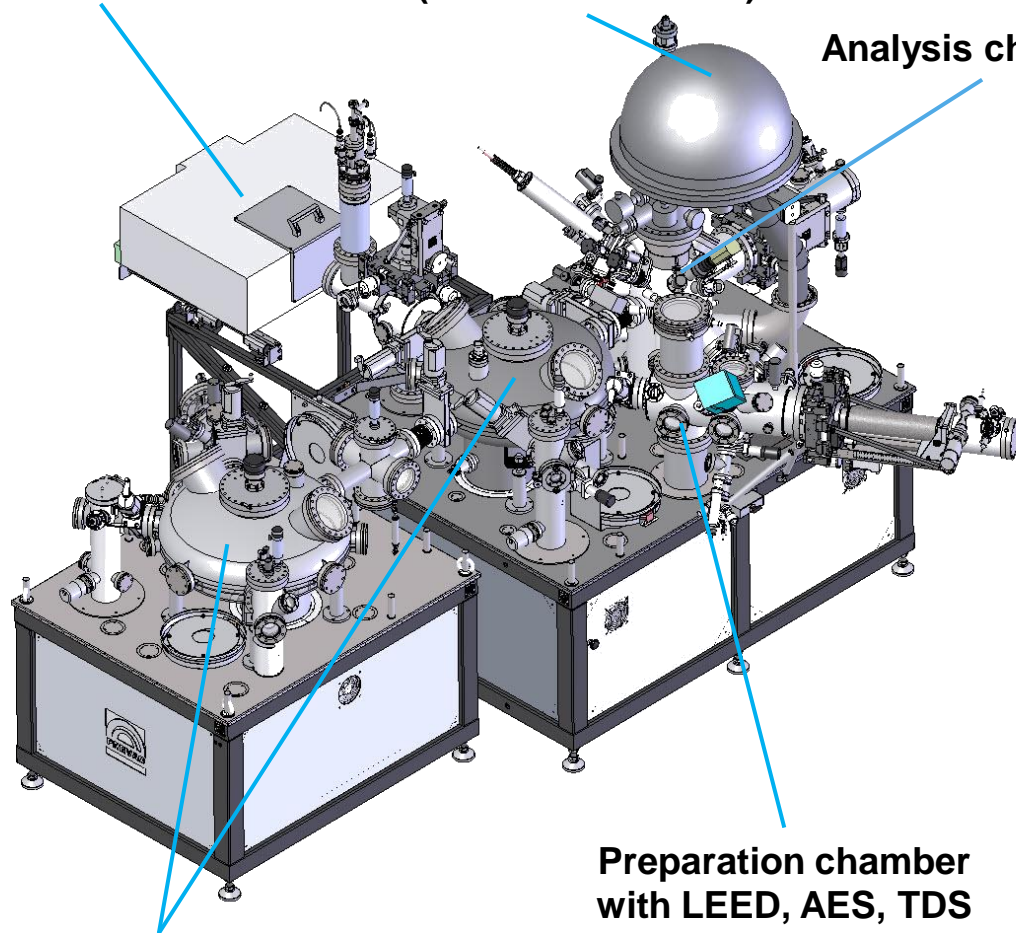
█ physisorbed CO
 █ CO/Ce⁴⁺
 █ CO/Ce⁴⁺_{cus}
 █ CO/Ce³⁺
 █ other assignments

UHV-FTIR apparatus

UHV-FTIR
(Bruker Vertex 80v)

XPS, UPS and AES analyzer
(VG Scienta R4000)

Analysis chamber

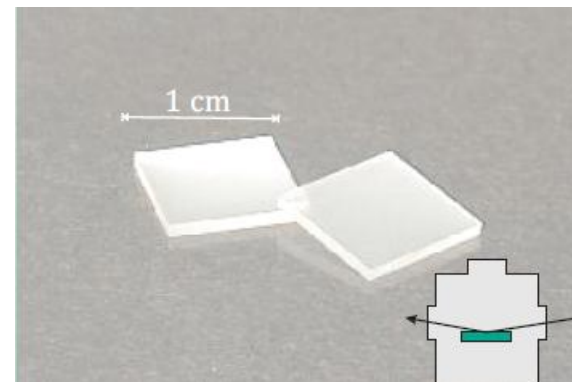


Distribution chambers

Preparation chamber
with LEED, AES, TDS
and effusion cells



Powder IR measurements
in transmission mode



Oxide SXs IR measurements
in reflection mode

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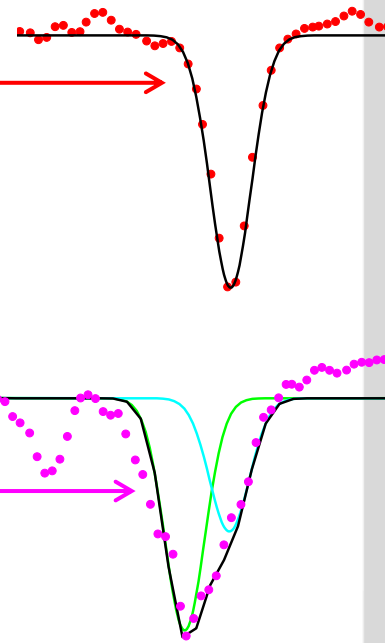
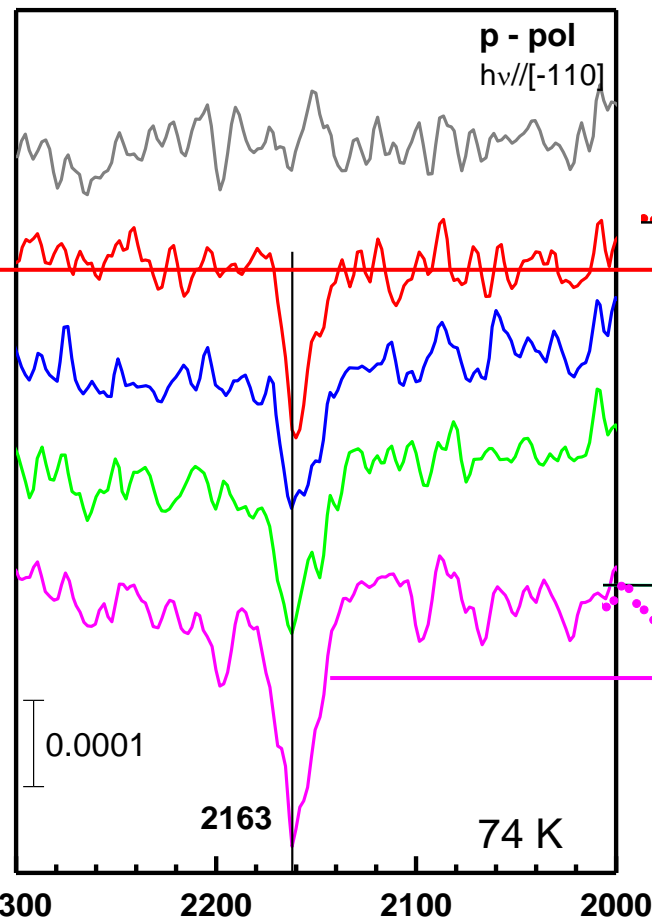
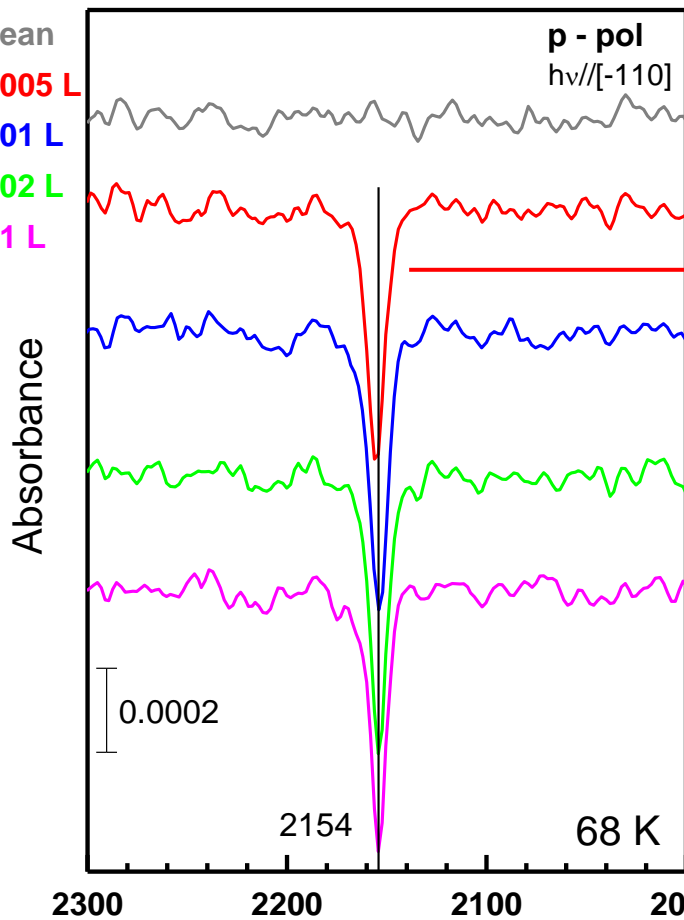
■ Summary

CO on single crystal CeO₂(111)

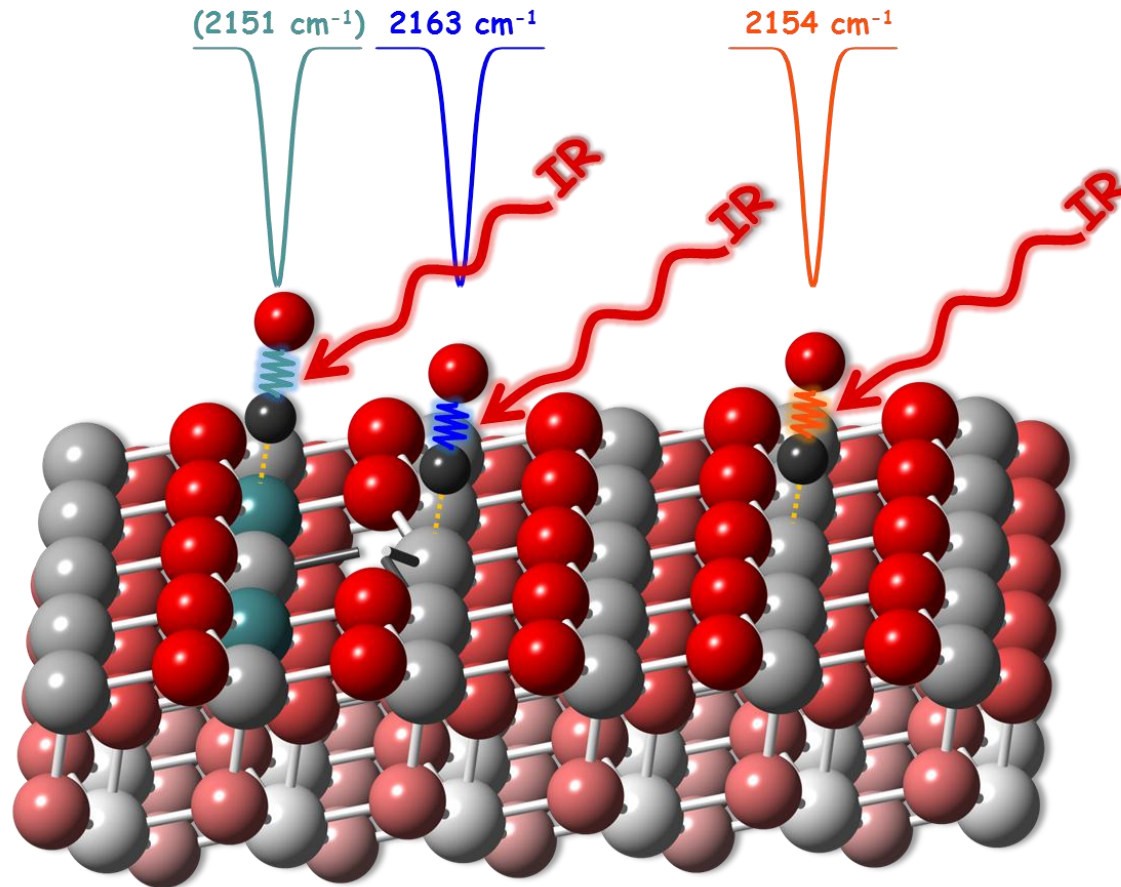
oxidized

reduced ($V_o \sim 10\%$)

— clean
— 0.005 L
— 0.01 L
— 0.02 L
— 0.1 L

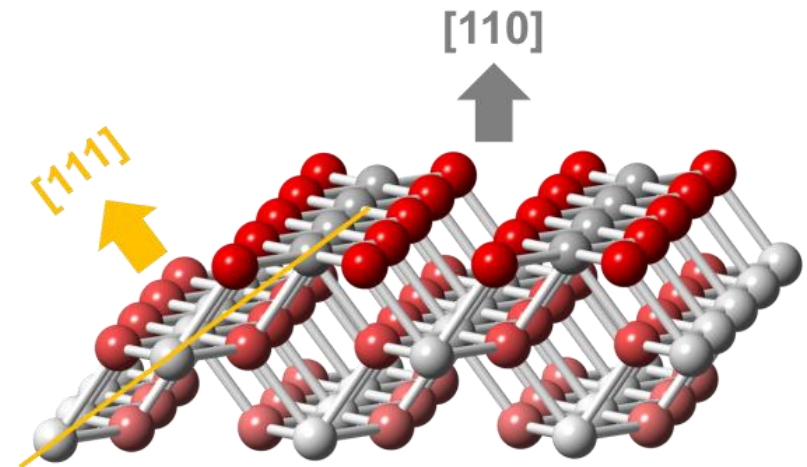
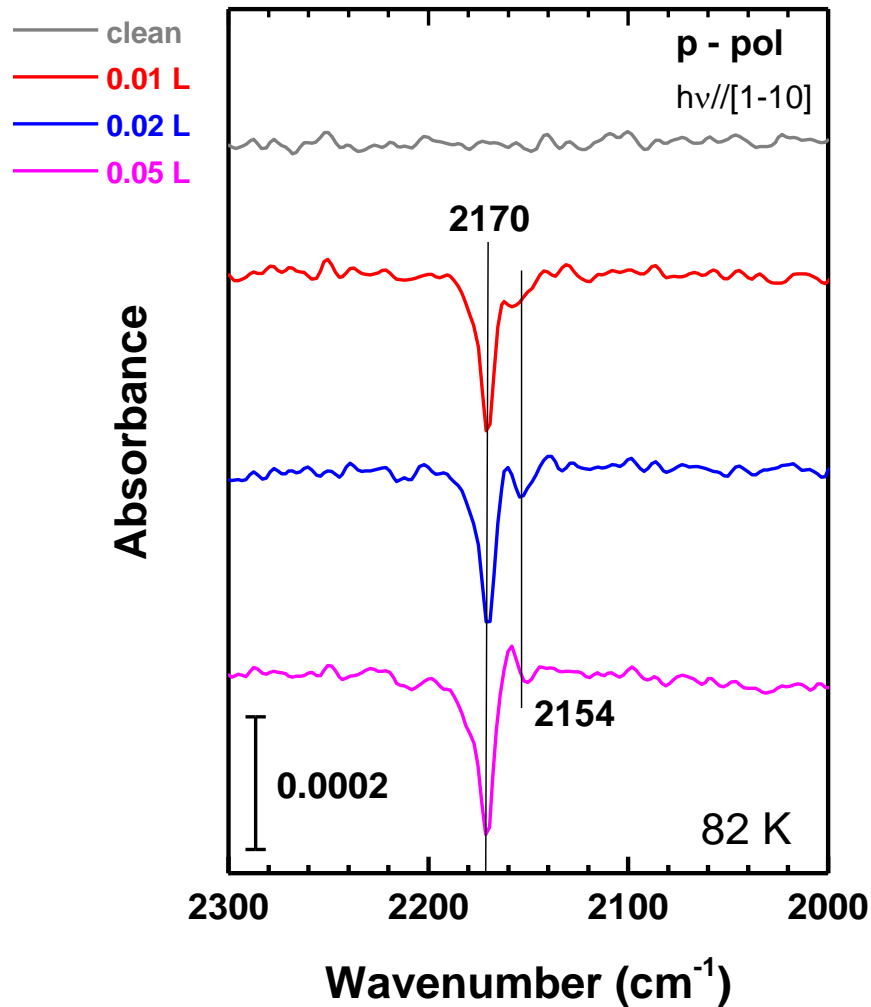


Assignment of CO bands on CeO₂(111) surface

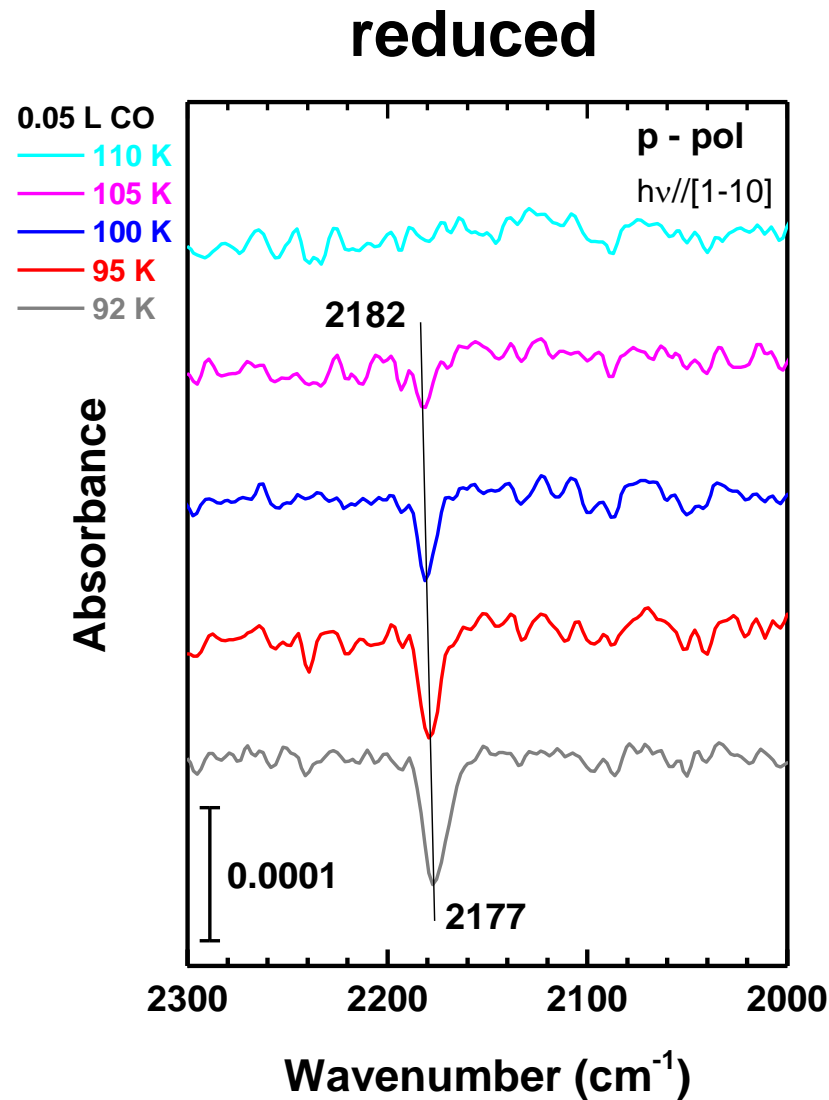


CO on oxidized single crystal $\text{CeO}_2(110)$

oxidized

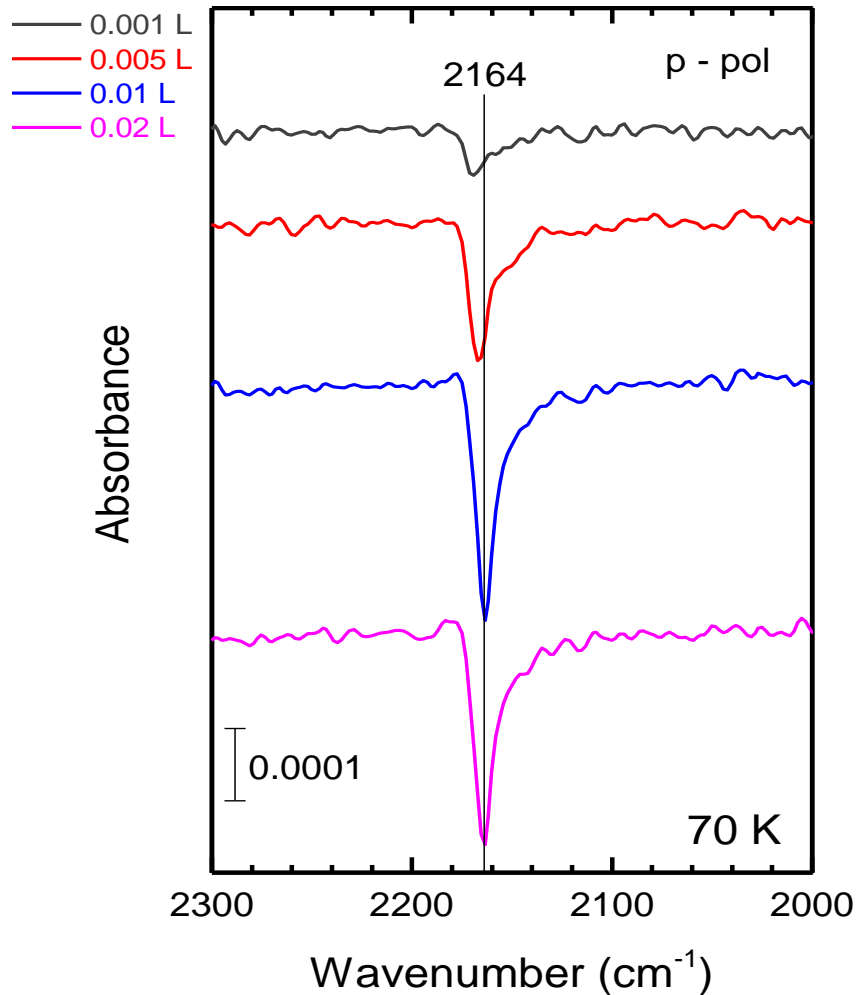


CO on reduced single crystal $\text{CeO}_2(110)$

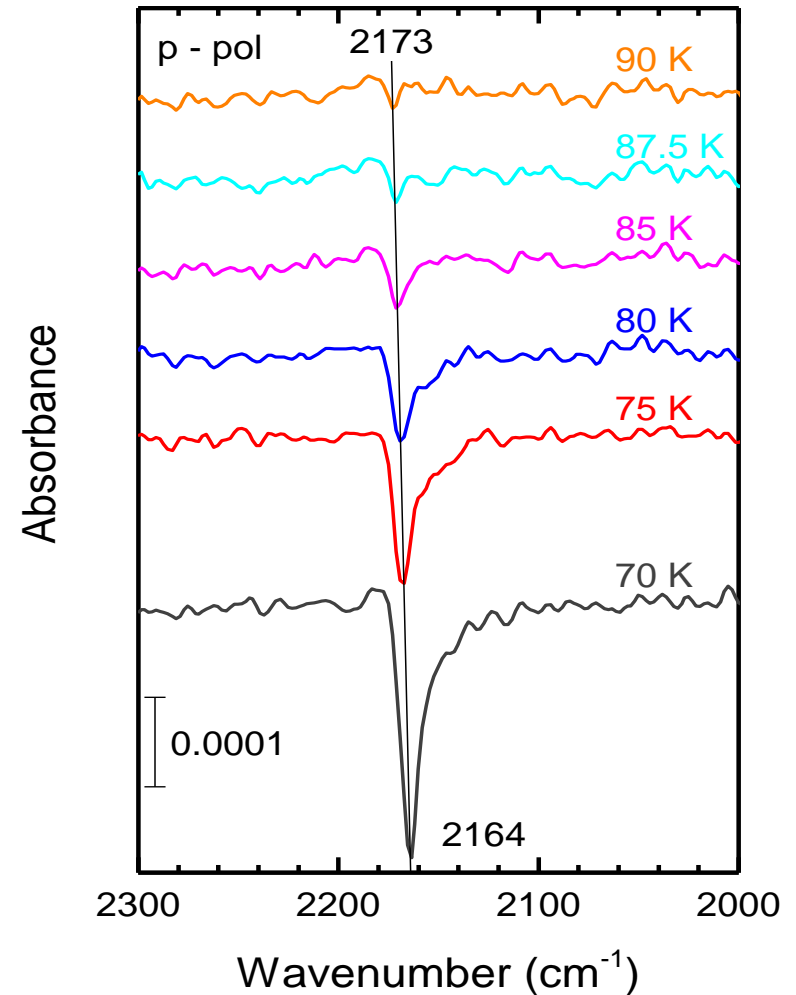


CO on reduced single crystal CeO₂(100)

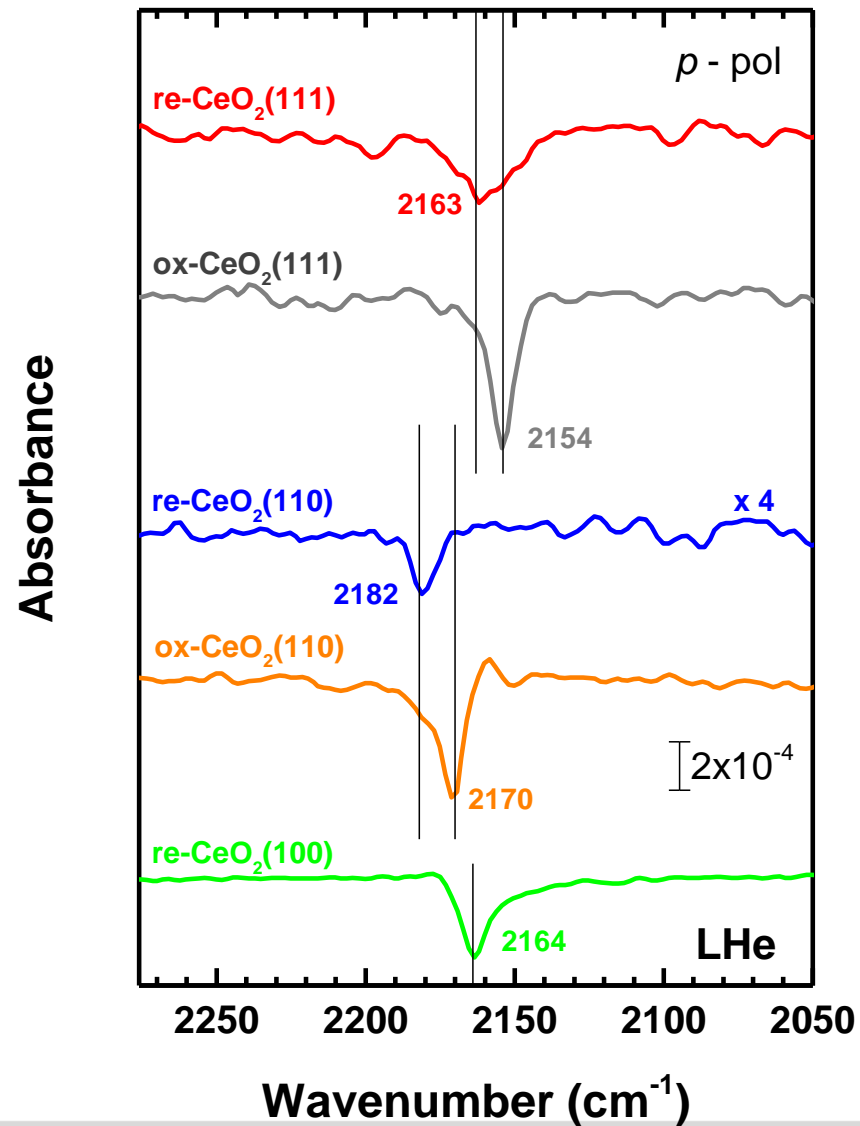
reduced



thermal desorption



Compilation of CO frequencies



- 1. Using CO as probe molecule, UHV-IRRAS can distinguish ceria surface orientations and probe oxygen vacancies.**
- 2. Based on vibrational frequencies of CO adsorption on oxidized and reduced ceria single crystals, the controversial assignments of IR-bands of CO adsorption on ceria powders can be clarified.**

Thank You!!



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Ludger Schöttner

”Theo-Group“

Prof. Christof Wöll

Science and Technology
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Helmholtz Research School
Energy-related catalysis