Karlsruhe Institute of Technology

Structure and reactivity of ceria single crystal surfaces studied by IR spectroscopy

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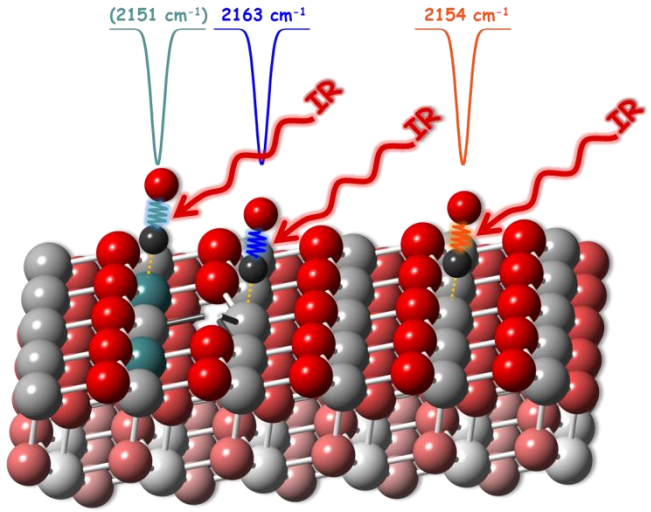
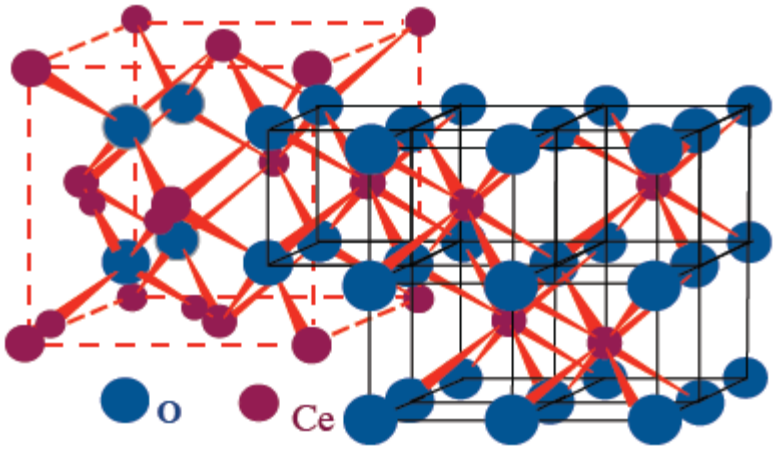
Institute of Functional Interfaces (IFG)

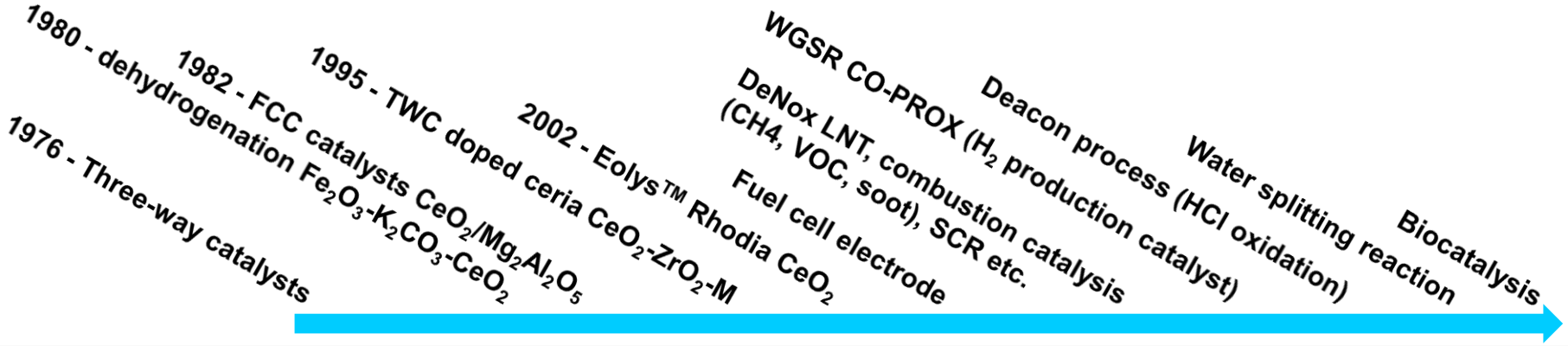


Why ceria (CeO_2, cerium dioxide) is interesting?



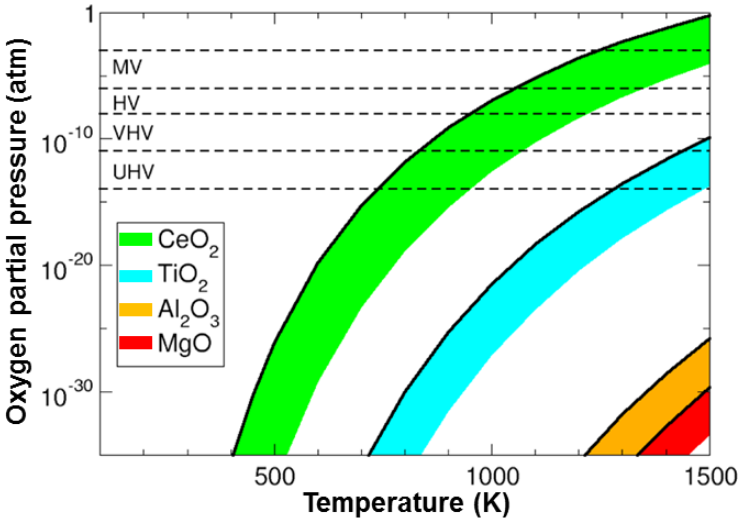
- **Reducibility, storage/release of oxygen atoms – oxygen storage capacity (OSC).**
- **Interconversion between $4f^1$-Ce(III) and $4f^0$-Ce(IV) oxidation states.**
- **Defects can be created by oxygen release and electron transfer.**
- **Promote electron and oxygen transfer.**
- **Promote dispersion of noble metals and thermal stability of the support.**

40 years of catalysis by ceria

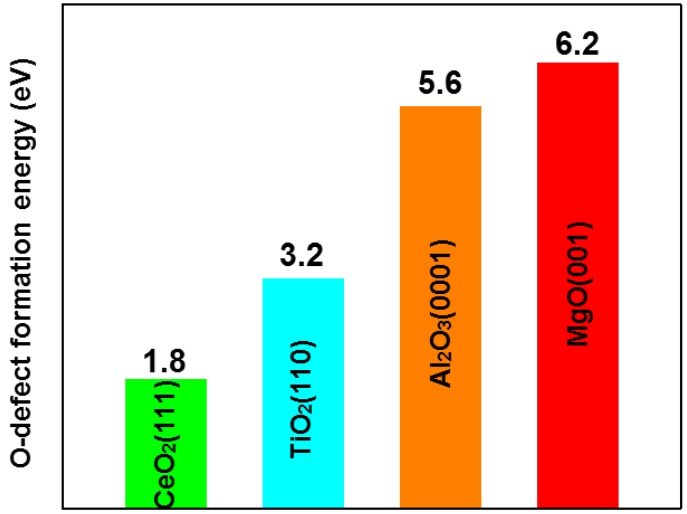


H. S. Gandhi, A. G. Piken, M. Schelef, R. G. Delosh, *SAE Paper*, 1976, 55, 760201.

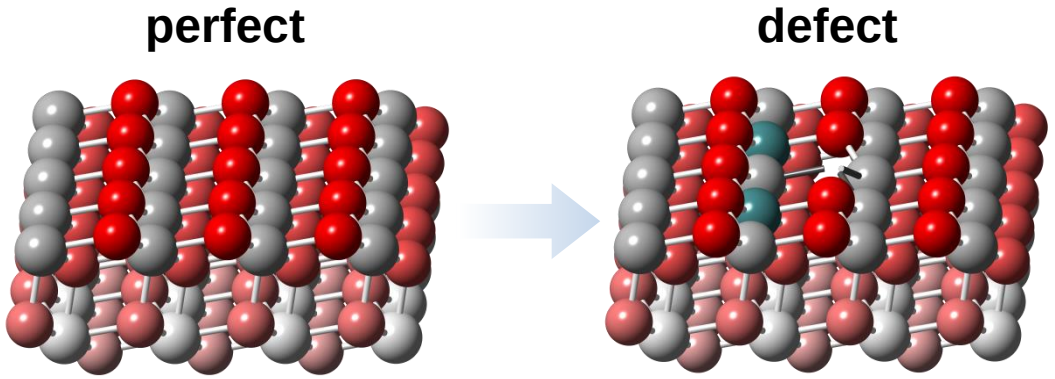
Ceria has low oxygen vacancy formation energy



p(O_2) vs T phase diagram.



Calculated oxygen defect formation energy.



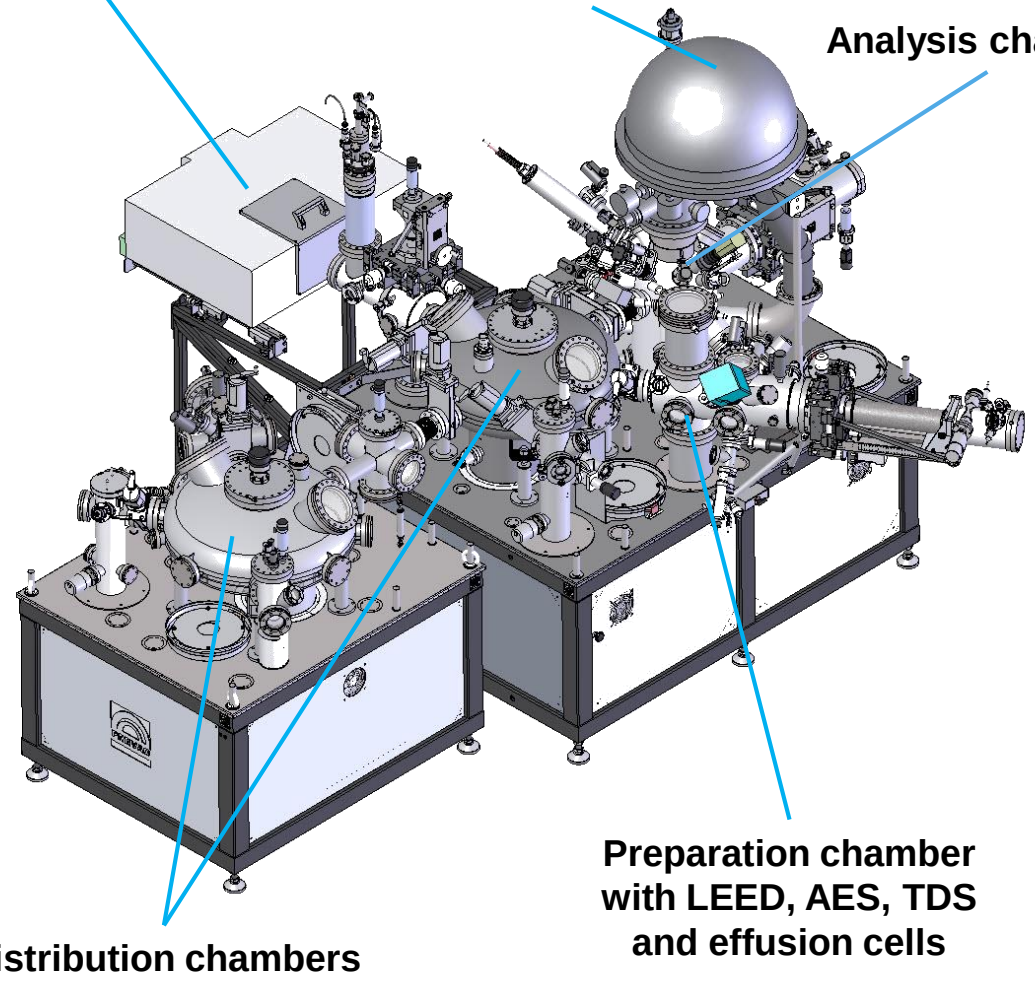
Stability and reducibility of ceria surfaces

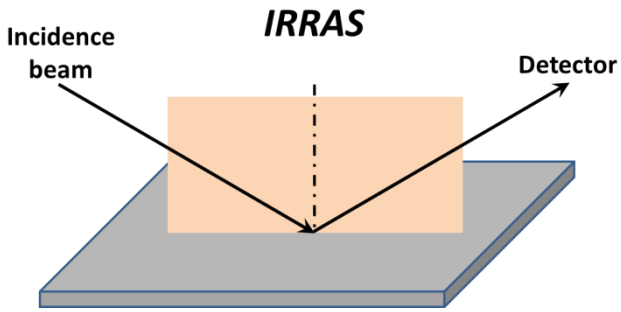
Surface	Surface energy (J·m^{-2})	O-vacancy formation energy (eV)
(111)	0.68	2.60
(110)	1.01	1.99
(100)	1.41	2.27

M. Nolan et al., *Surf. Sci.*, 2005, 576, 217.
M. Nolan et al., *Surf. Sci.*, 2005, 595, 223.

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

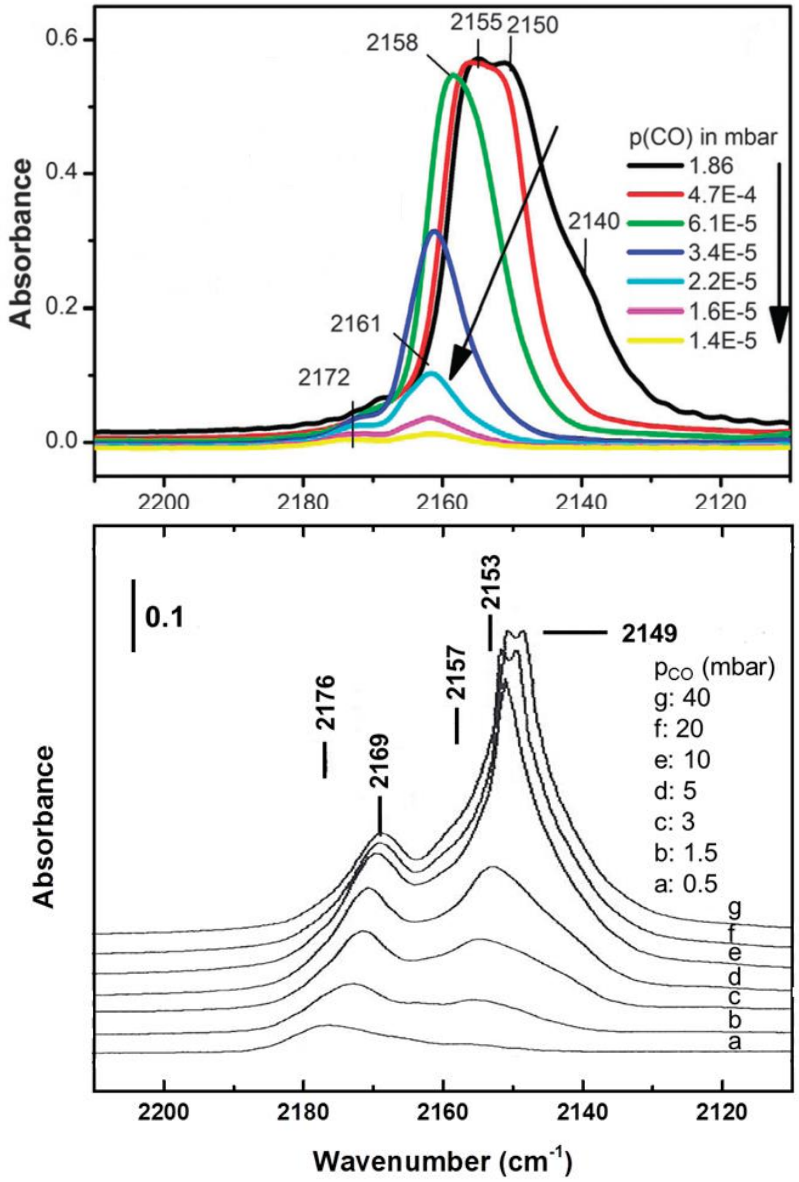
UHV-FTIR apparatus

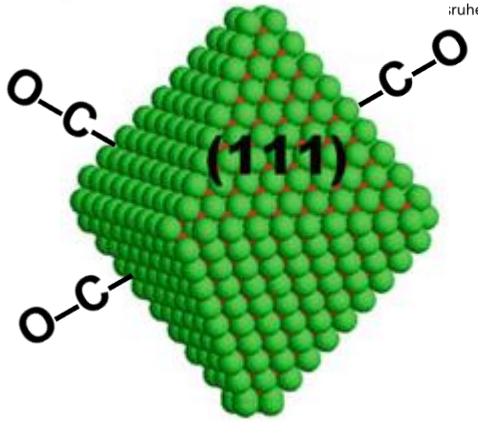




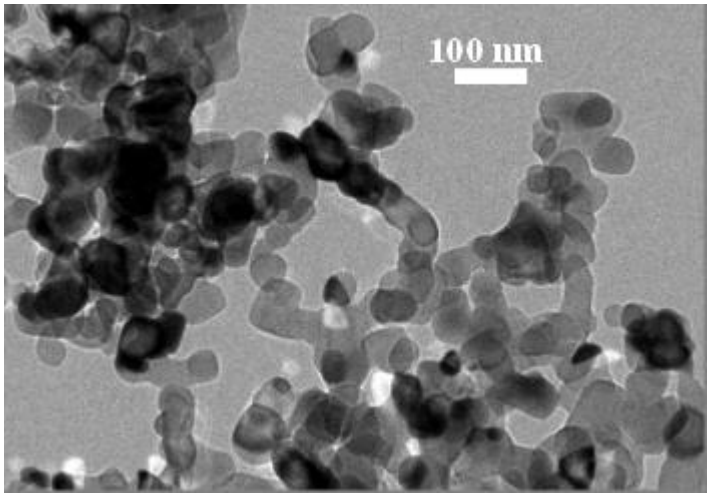
Enable routine measurements of IRRAS on oxide substrates

CO on ceria powders





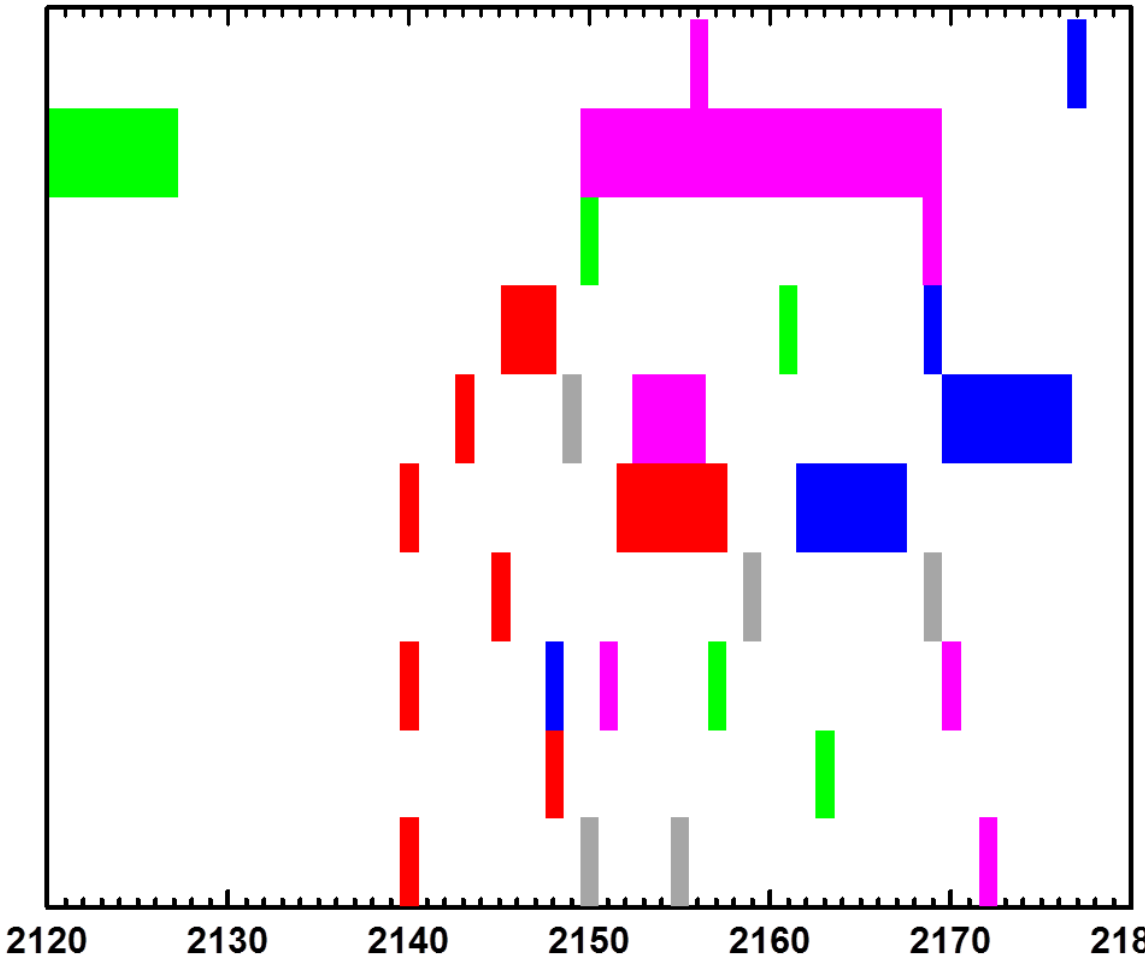
Wulff construction



How to assign the CO IR-bands?

R. Farra et al., *PCCP*, 2013, 15, 3454.
G. A. H. Mekhemer, M. I. Zaki, *Adsorpt. Sci. Technol.*, 1997, 15, 377.

Controversial assignments of CO IR-bands on ceria powders



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

J. Chem. Soc., Faraday Trans., 1994, 90, 653.

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

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

Adsorpt. Sci. Technol., 1997, 15, 377.

Catal. Today, 1999, 50, 207.

PCCP, 1999, 1, 5717.

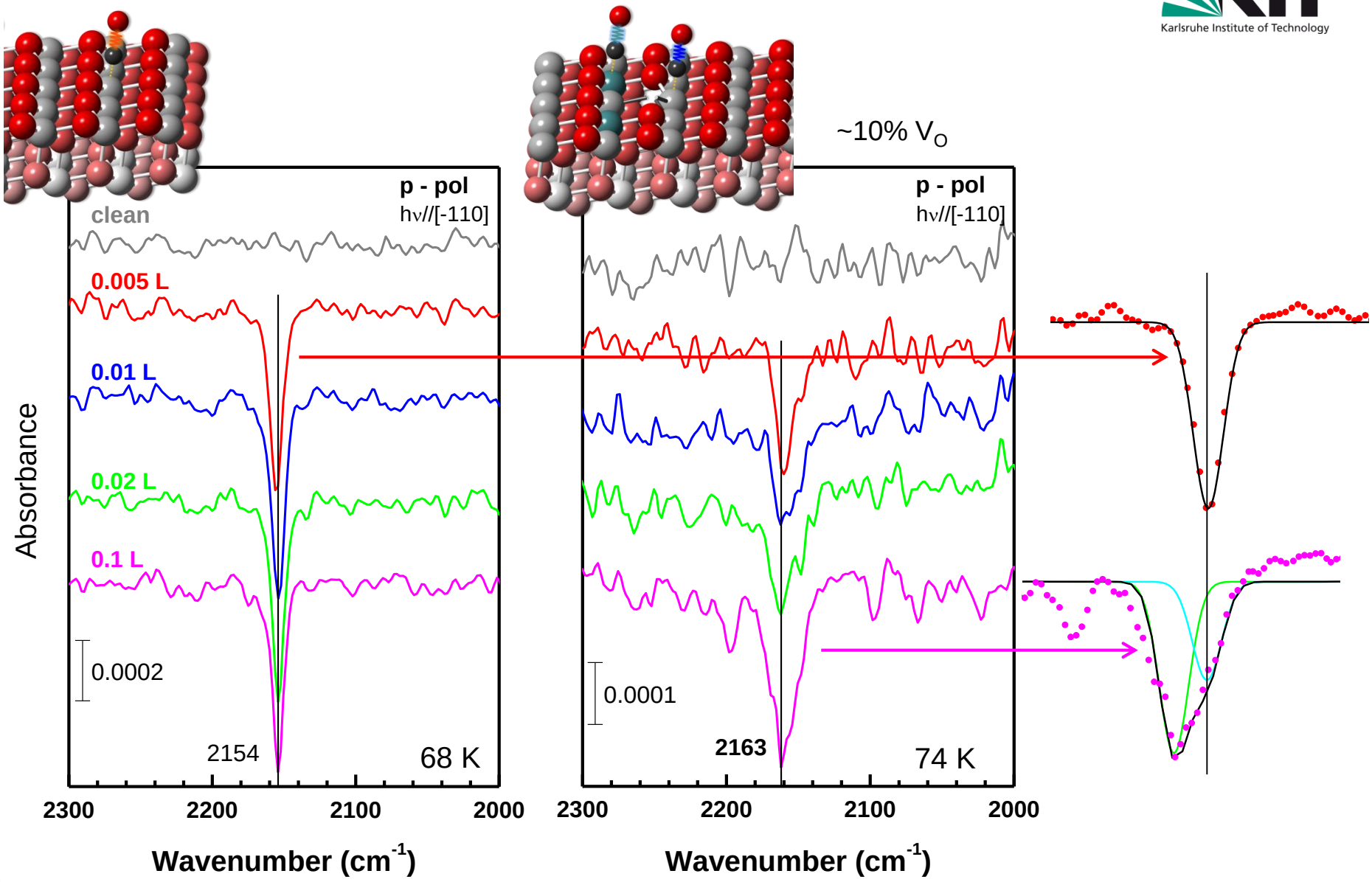
Appl. Catal. A: Gen., 2003, 252, 385.

PCCP, 2005, 7, 187.

PCCP, 2013, 15, 3454.

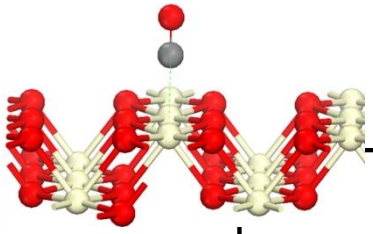
physisorbed CO | CO/Ce^{4+} | CO/Ce^{4+}_{cus} | CO/Ce^{3+} | other assignments

CO on single crystal CeO_2(111)

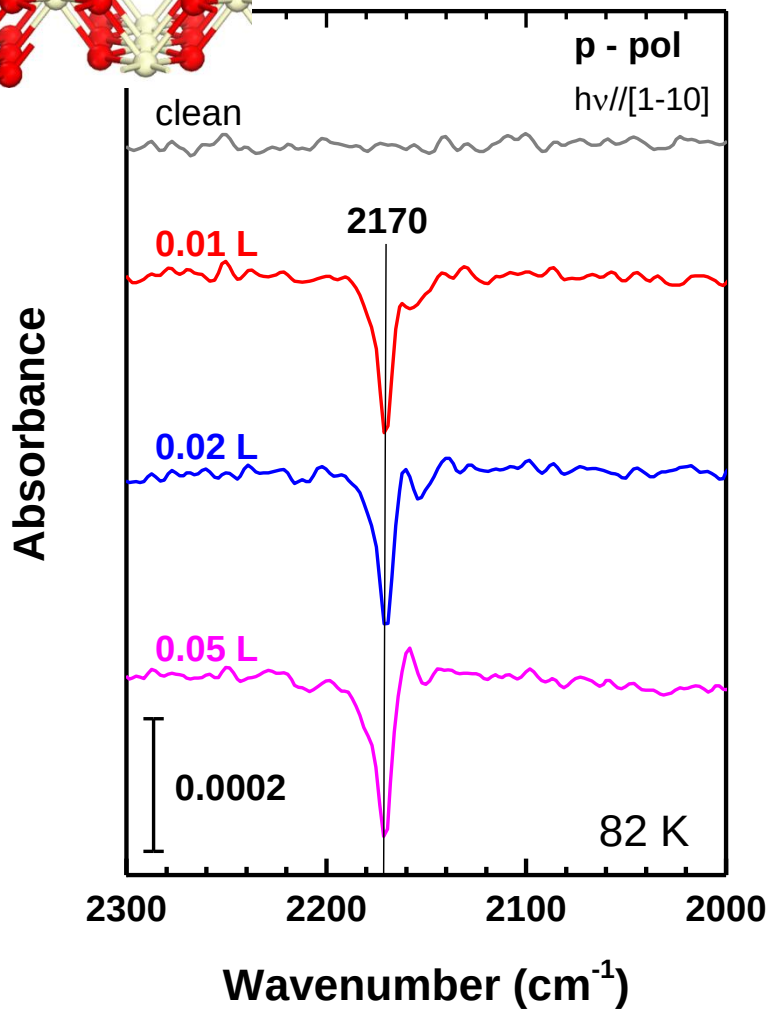


C. Yang, C. Wöll et al., *PCCP*, 2014, 16, 24165.

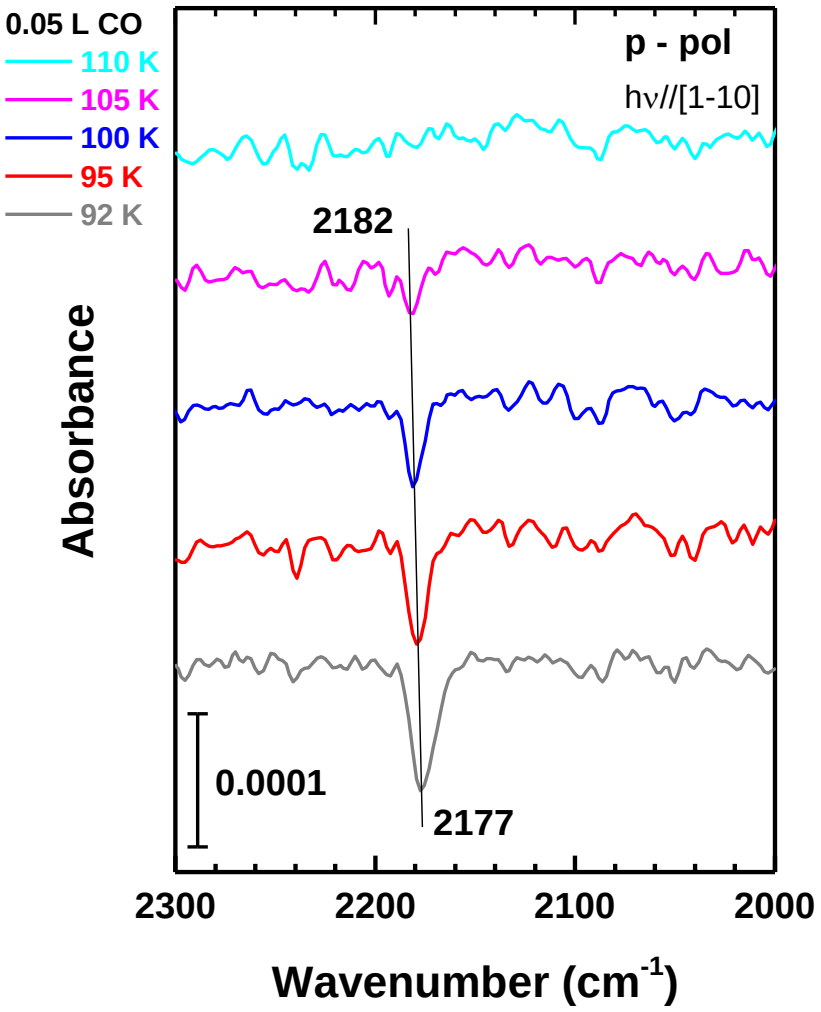
CO on single crystal CeO_2(110)



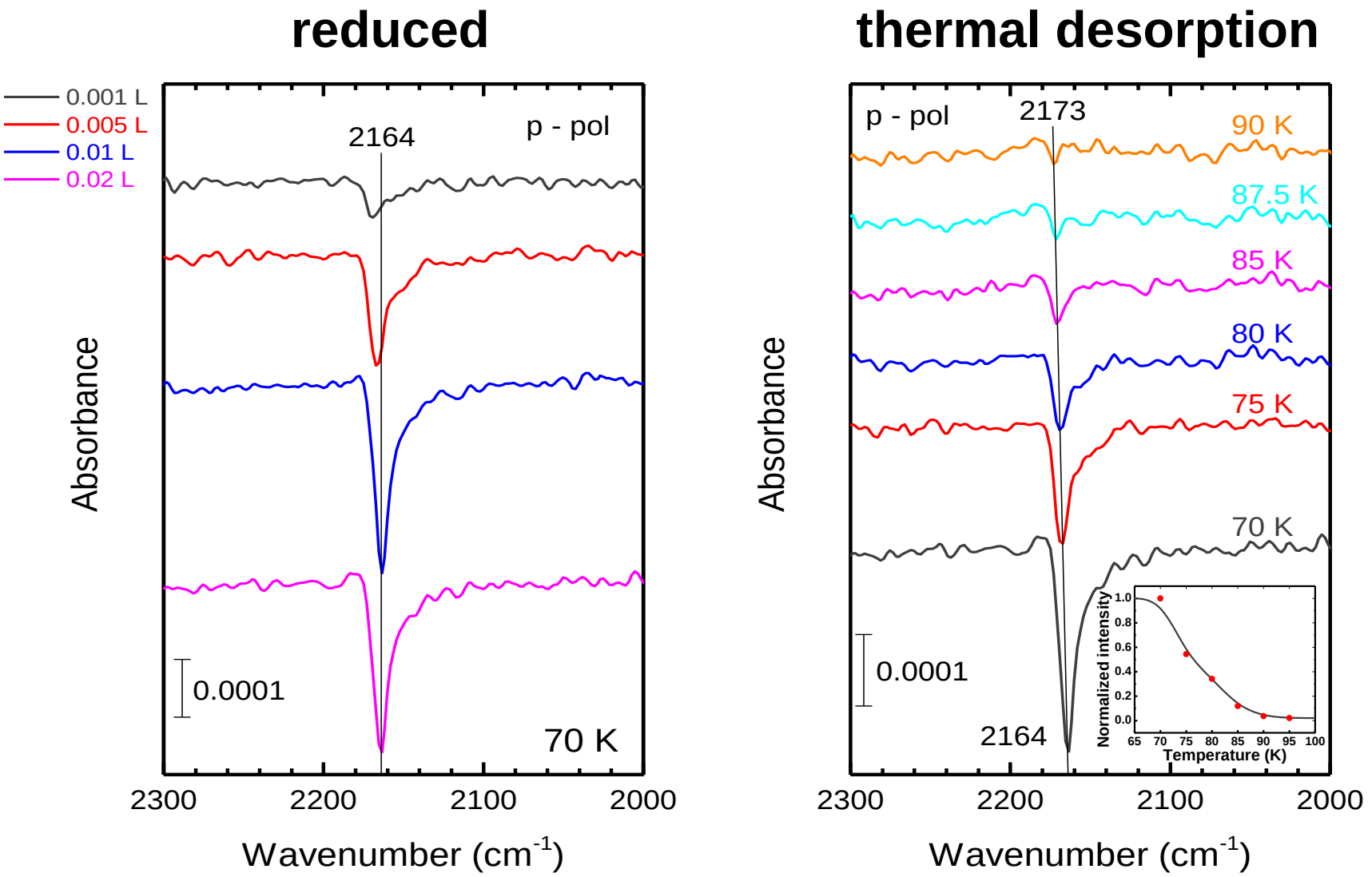
oxidized



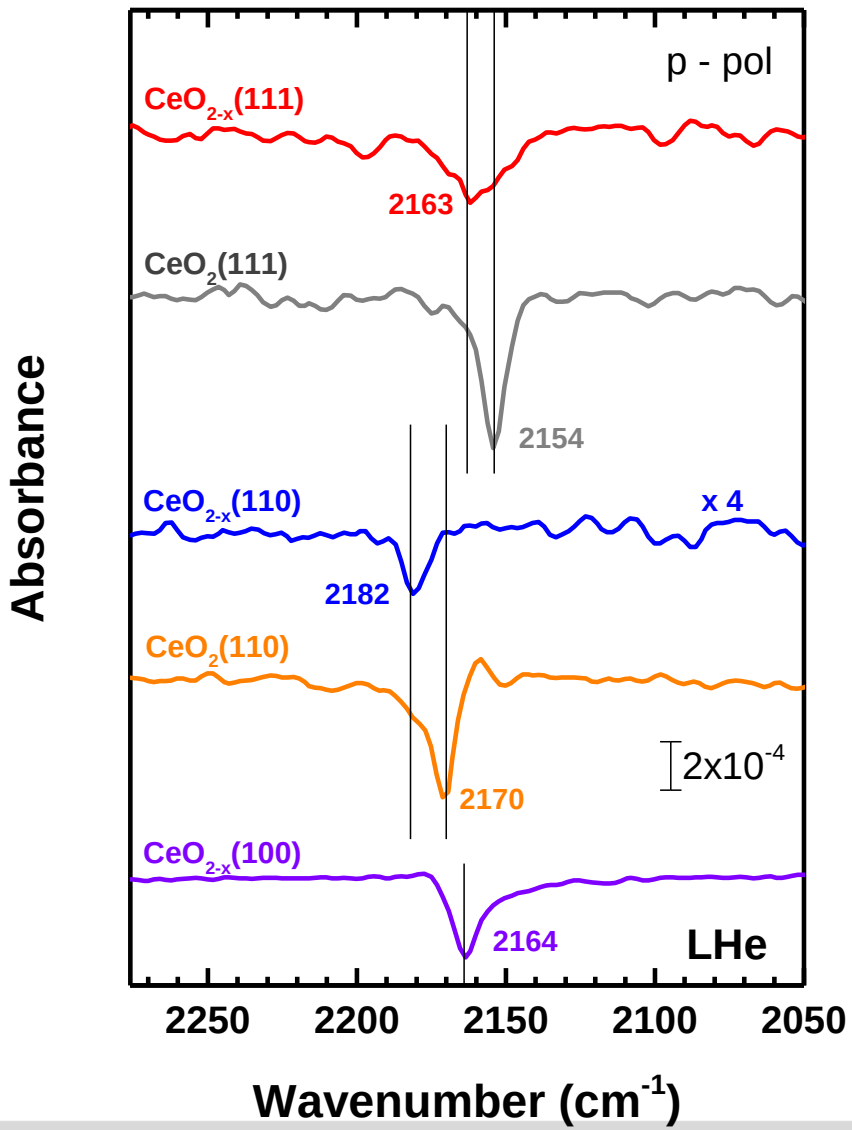
reduced

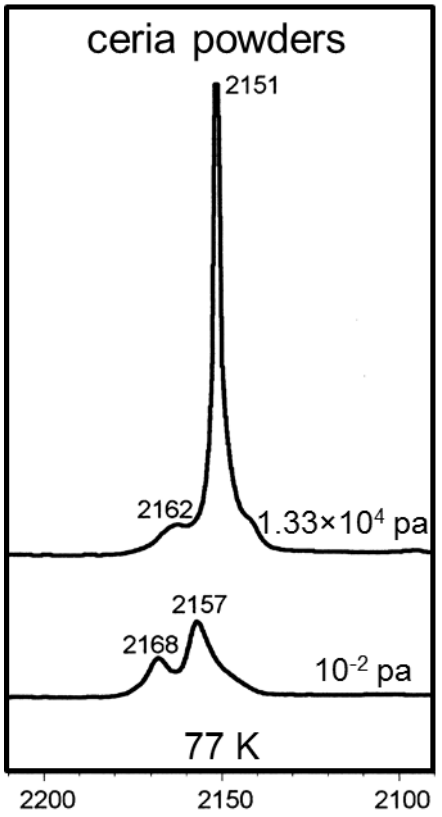


CO on reduced single crystal $CeO_{2-x}(100)$



Reassignment of IR-bands of CO on ceria surface

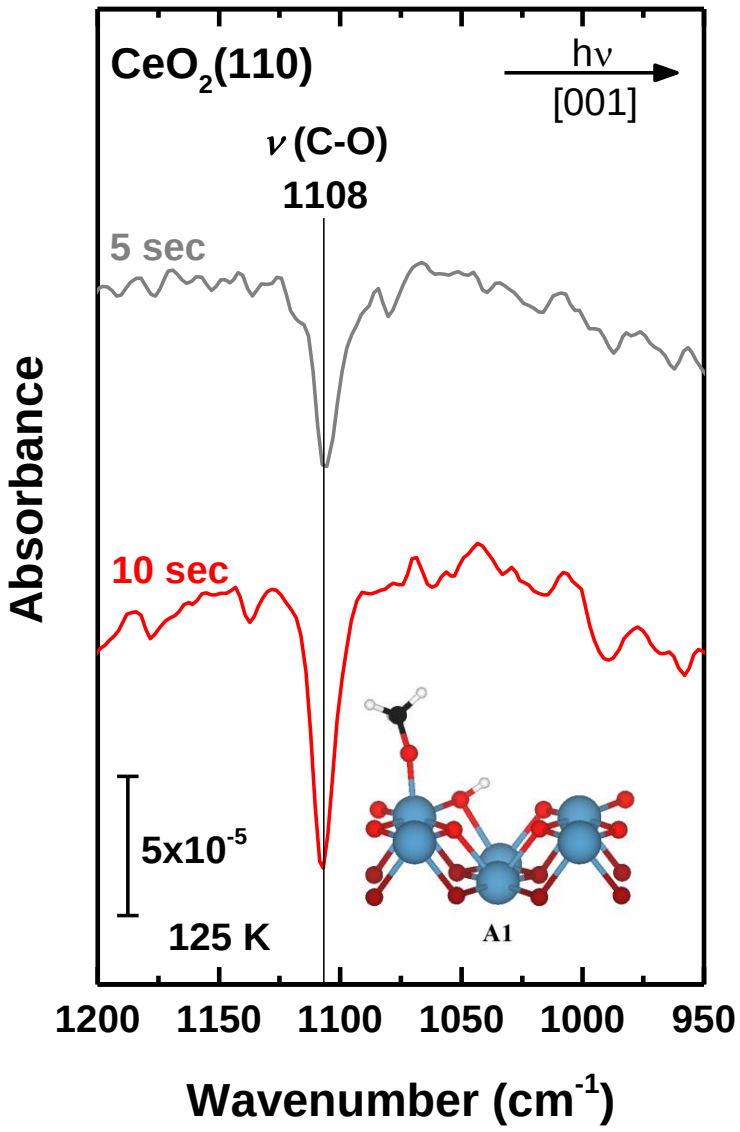


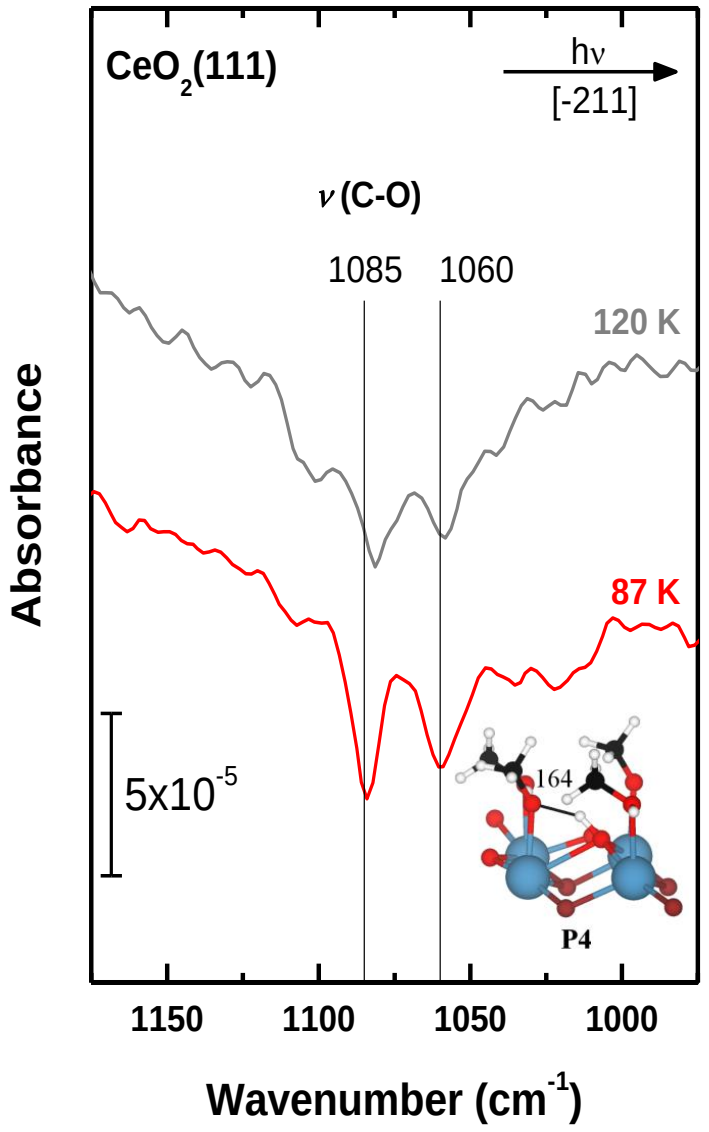


- **2157 cm^{-1}: physisorbed CO**
- **2168 cm^{-1}: CO coordinated with Ce^{4+}**

J.-C. Lavalley et al., *Catal. Today*, 1999, 50, 207. (> 460 citations)

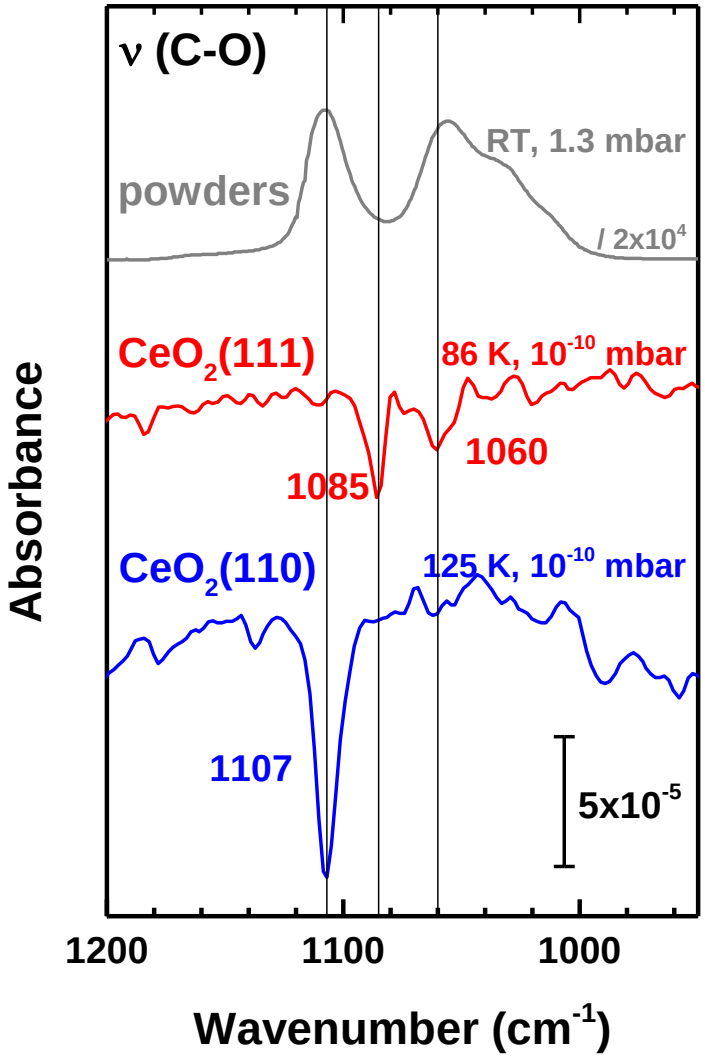
CH_3OH on oxidized monocrystalline CeO_2(110) and (111)





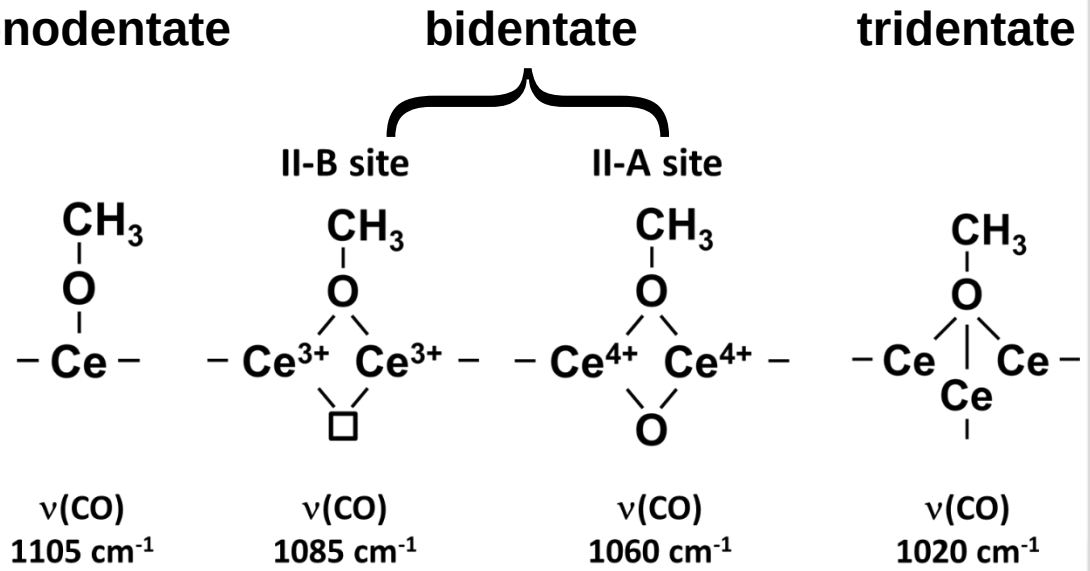
C. Yang, F. Bebensee, A. Nefedov, C. Wöll, T. Kropp, L. Komissarov, C. Penschke, R. Moerer, J. Paier, J. Sauer, *J. Catal.*, 2016, 336, 116.

Reassignment of IR-bands of CH_3OH on ceria surface



previous assignments

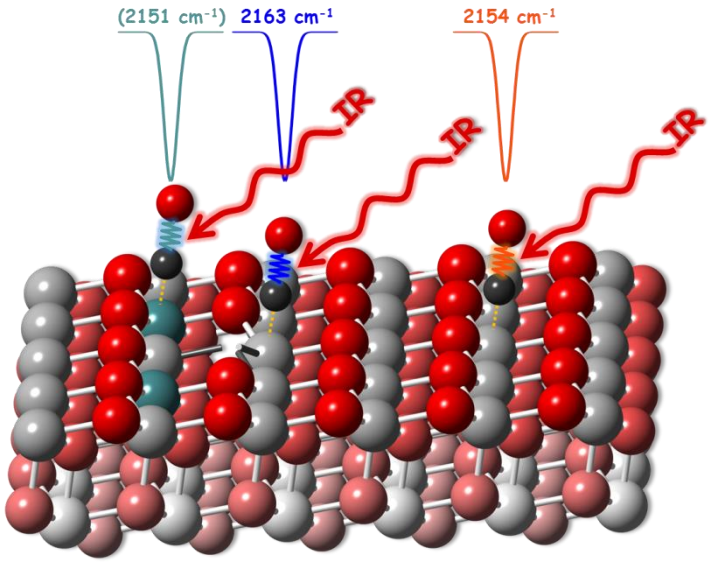
J. C. Lavalley et al., *React. Kinet. Catal. Lett.*, 1988, 36, 113.
J. C. Lavalley et al., *J. Chem. Soc., Faraday T rans.*, 1997, 93. 1159.

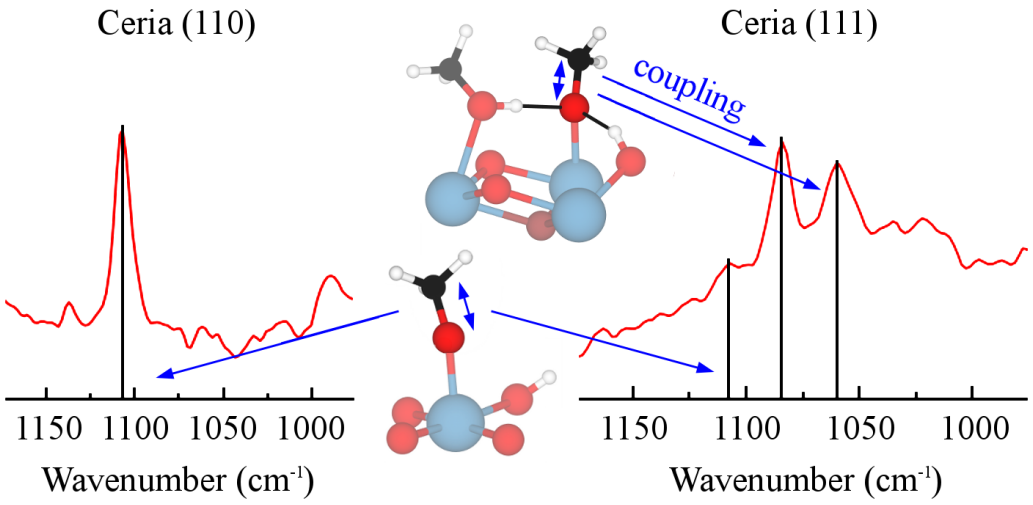


A. Badri, C. Binet, J.-C. Lavalley, *J. Chem. Soc., Faraday Trans.*, 1997, 93, 1159.
C. Yang, F. Bebensee, A. Nefedov, C. Wöll, T. Kropp, L. Komissarov, C. Penschke, R. Moerer, J. Paier, J. Sauer, *J. Catal.*, 2016, 336, 116.

Summary

1. **Using CO and CH_3OH as probe molecules, UHV-IRRAS can distinguish ceria surface orientations and probe oxygen vacancies.**
2. **Based on vibrational frequencies of CO and CH_3OH adsorption on oxidized and reduced ceria single crystals, the controversial assignments of IR-bands of CO and CH_3OH adsorption on ceria powders can be clarified.**





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