Karlsruhe Institute of Technology

Spectroscopic investigation on interactions of water with the α-Fe_2O_3 (0001) surface

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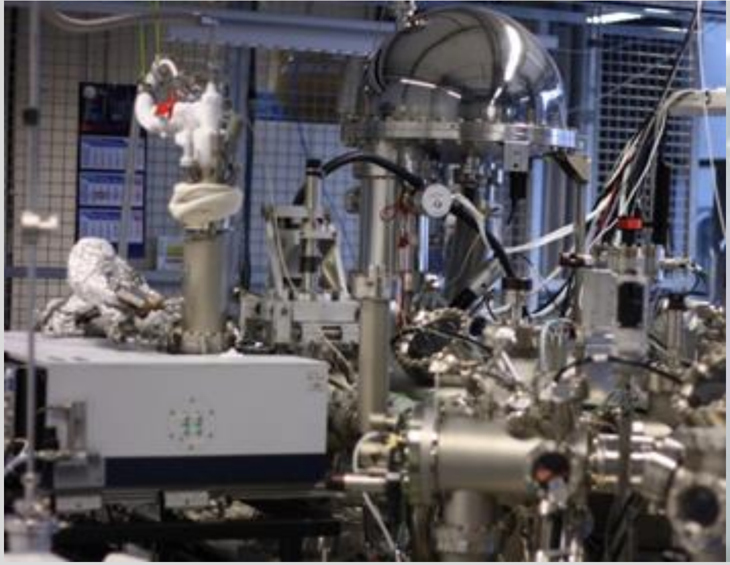
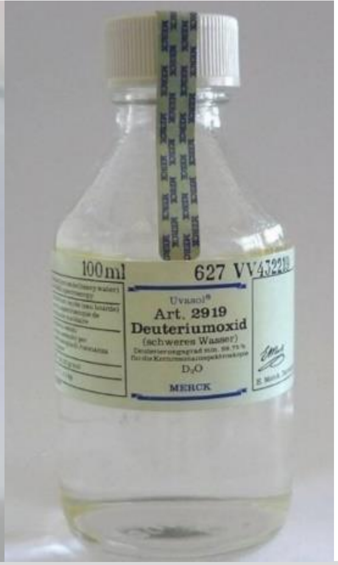
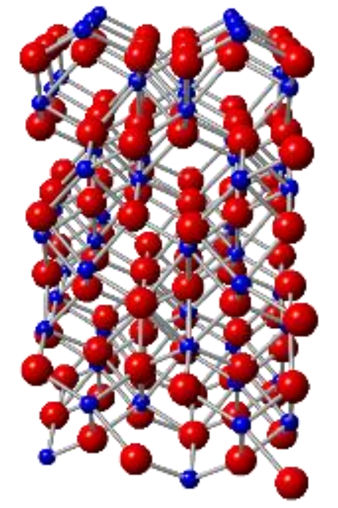
254th ACS Meeting Washington D.C., 20.8.2017

Institute of functional interfaces (IFG), Helmholtz-Research-School „Energy related catalysis“

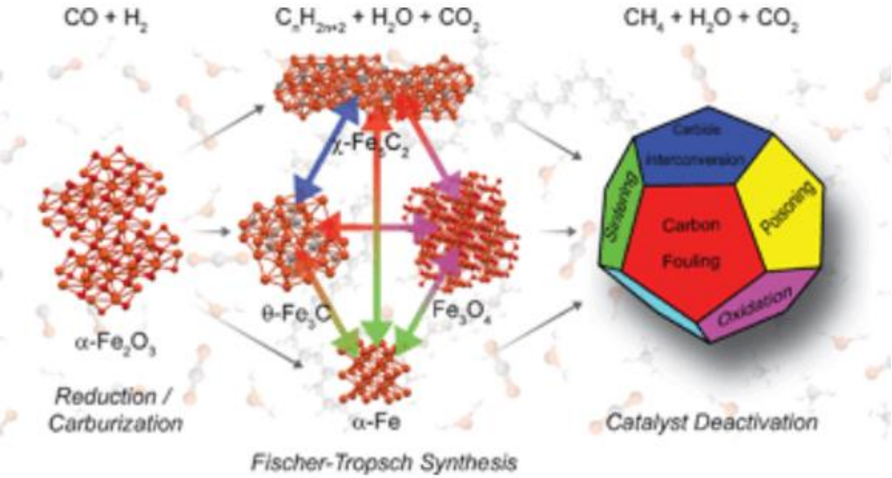




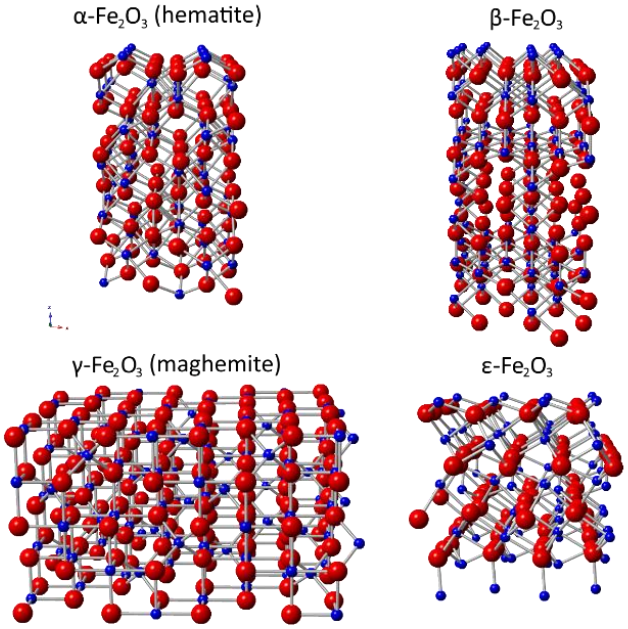


Motivation and concepts

- Central processes in geology/mineralogy (oxides, hydroxides, oxide hydroxides)
- Corrosion and its relevance for industrial manufacturing
- Heterogeneous catalysis



Iron oxide in catalysis
Adopted from: E. de Smit, B. Weckhuysen,
Chem. Soc. Rev., **2008**, 37, 2758-2781



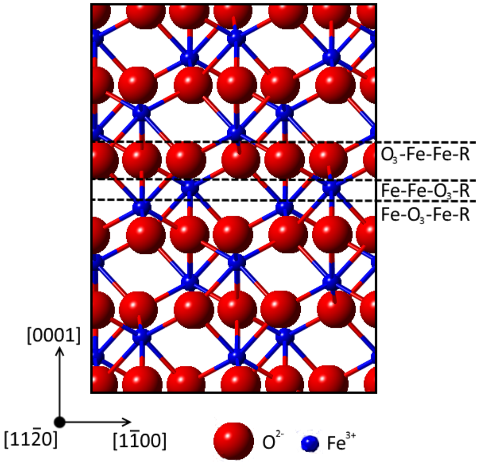
Graphical representation of fundamental crystal structures of Fe_2O_3

Surface orientation and termination of hematite

- Compared to other faces, the (0001) surface orientation possesses the most thermal inert structure

Facets of hematite	Surface energy [J/m^2]
(0001)	4.38
$(1\bar{2}10)$	2.40
$(1\bar{1}00)$	1.46
$(10\bar{1}2)$	2.44
$(11\bar{2}3)$	0.89

Table of surface energies for various hematite faces

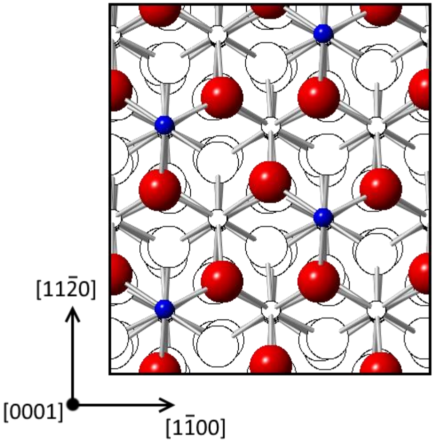


Schematic representation of various surface terminations on hematite (side view).

- Fe-termination has a lower surface energy than O-Fe-Fe-R, but the autocompensation principle predicts it as the energetically favorised termination on α-Fe_2O_3(0001)

- For the O-terminated surface of α-Fe_2O_3(0001) a substantial increase in covalent character results from interlayer relaxations->loss of ionic character in top-layer

- <u>Preparation</u>: *O=Fe(IV)-O_3-Fe-R:* 10^{-3}-1 mbar O_2, 1050 K
  Fe-O_3-Fe-R: 10^{-5} mbar O_2, 850-950 K

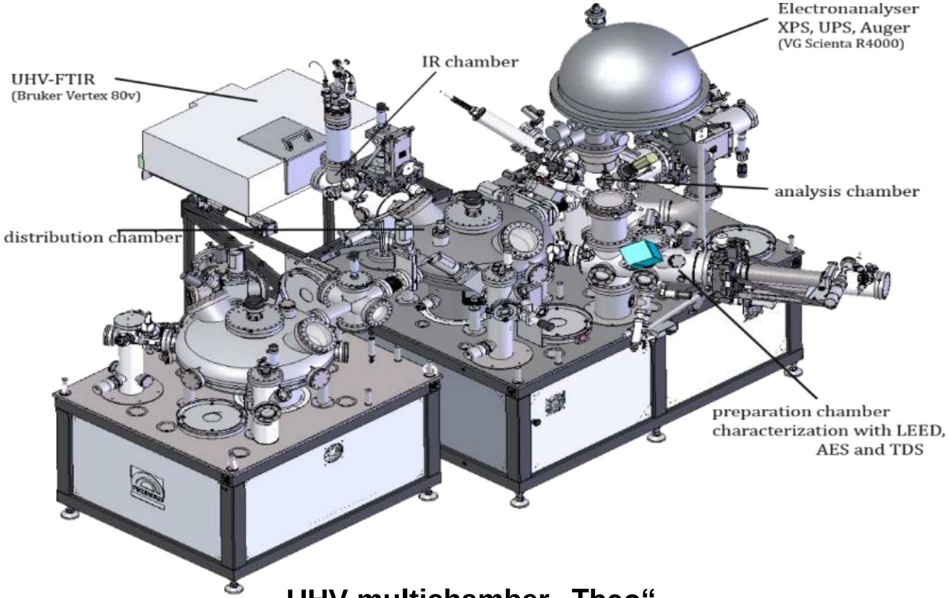


Model of (2x2) hematite unit cell with Fe-O_3-Fe-R termination (top view). Surface atoms are inked.

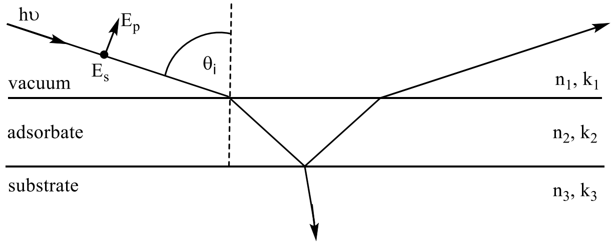
N. Bulgakov, V. Sadykov, *React. Kinet. Catal. Lett.* **1996**, 58, 2, 397-402.
S. Chambers, S. Yi, Surf. Sci. **1999**, 439, 785-791.
C. Lemire, S. Bertarione, A. Zecchina, D. Scarano, A. Chaka, S. Shaikhutdinov, H.-J. Freund, *Phys. Rev Lett.* **2005**, 66101

Methodology and equipments

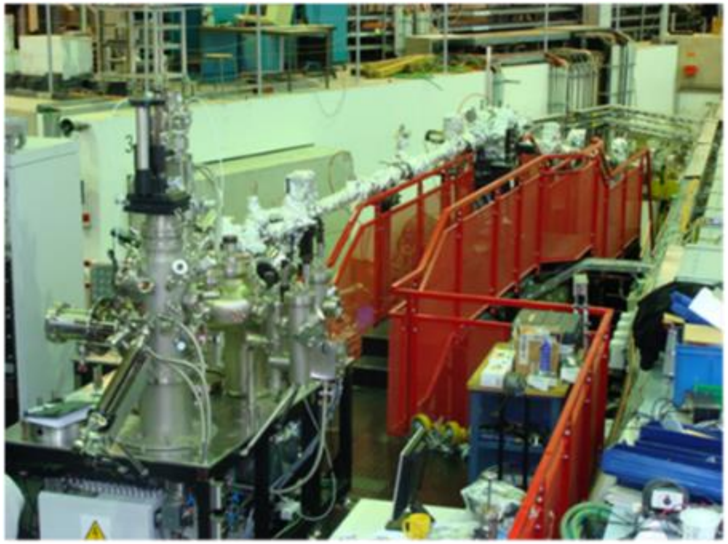
- IRRAS on metal oxide single crystals with low reflectivity (Absorbance: 10^{-5})
- Pressure: $< 1 \cdot 10^{-10}$ mbar
- Grazing incidence (θ=80°)
- Sample cooling down 60 K (LHe)
- Integrated polarizer for s- and p-IR beams allows orientational studies of molecules deposited on surfaces



UHV multichamber „Theo“
IR/XPS apparatus@IFG/KIT

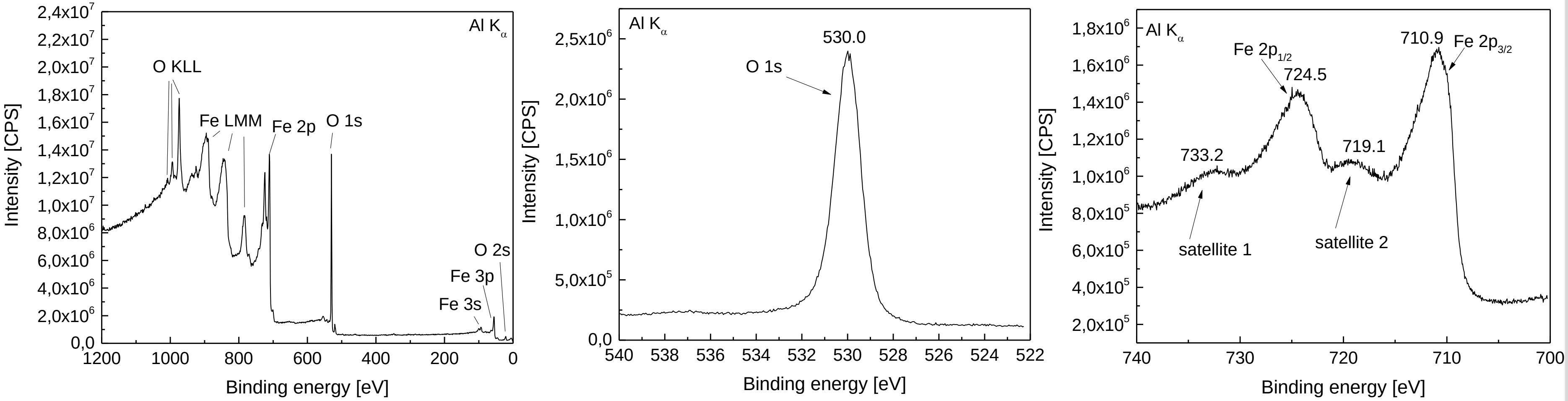


Schematic illustration for the beampath of light in IRRAS experiments

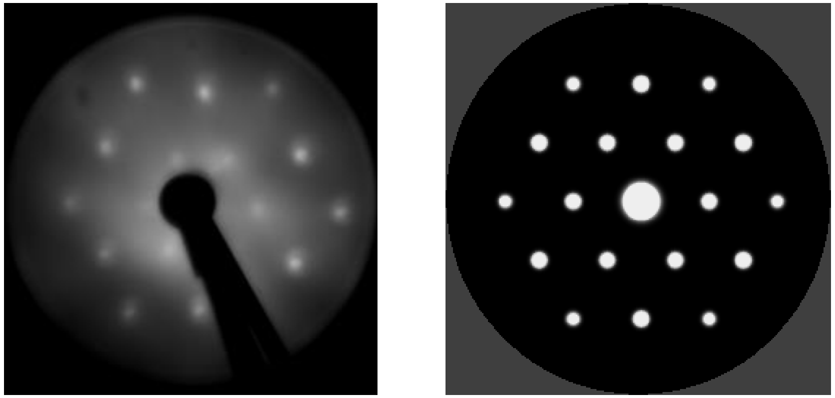


HE-SGM beamline for NEXAFS/XPS@BESSY

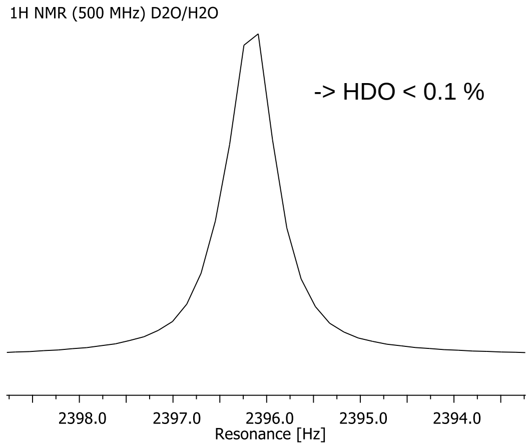
Structural properties of well-defined Fe_2O_3(0001)



XPS core level emission



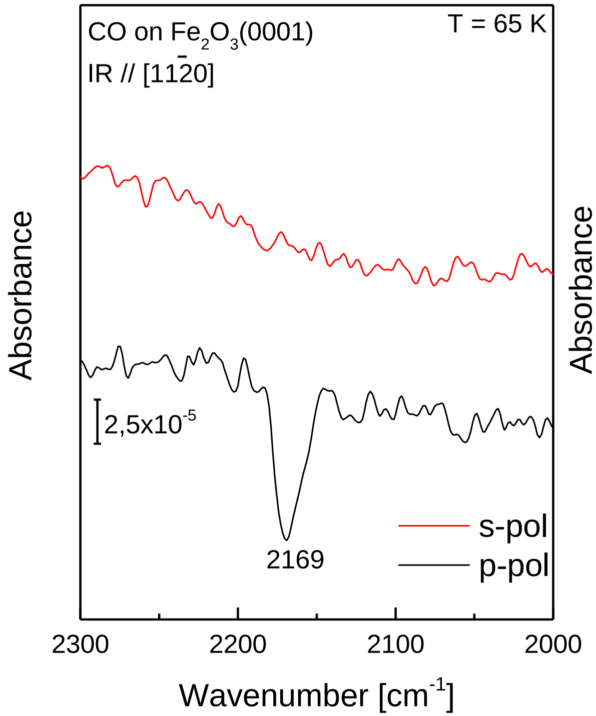
Obtained and simulated (1x1)-LEED pattern at 105 eV

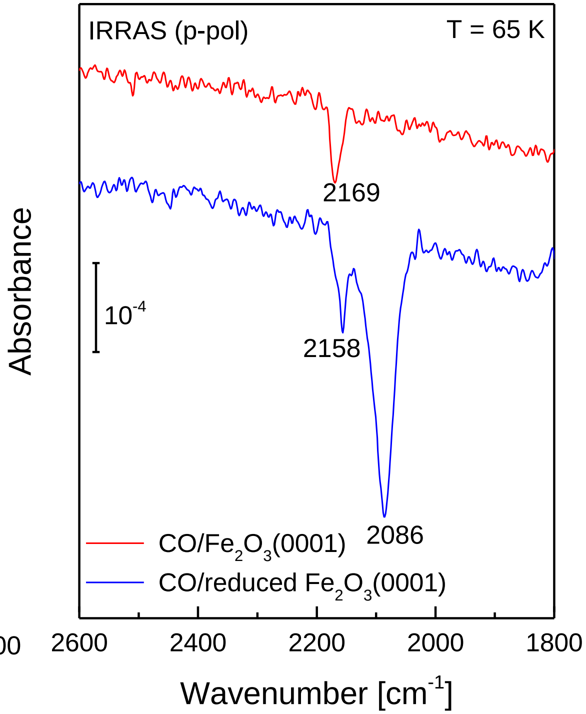


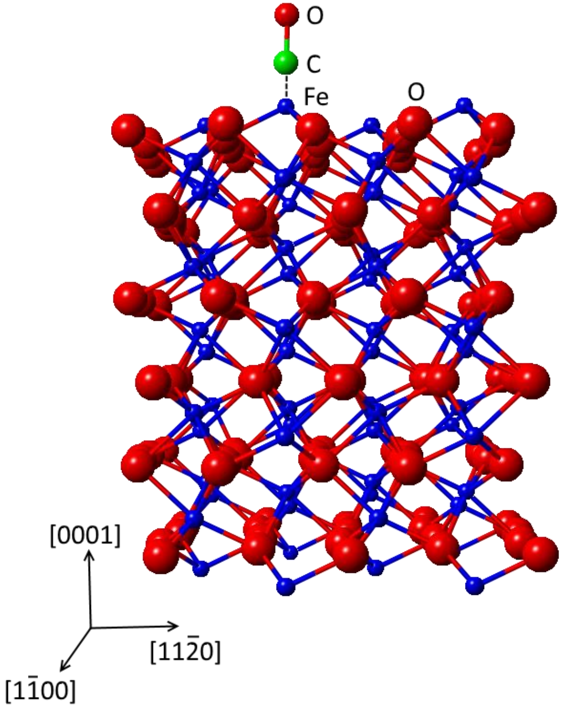
^{1}H-NMR of employed heavy water

T. Yamashita, P. Hayes, *Appl. Surf. Sci.* **2008**, 254, 2441-2449.

IRRAS: Probing the surface termination of Fe_2O_3(0001) by CO adsorption



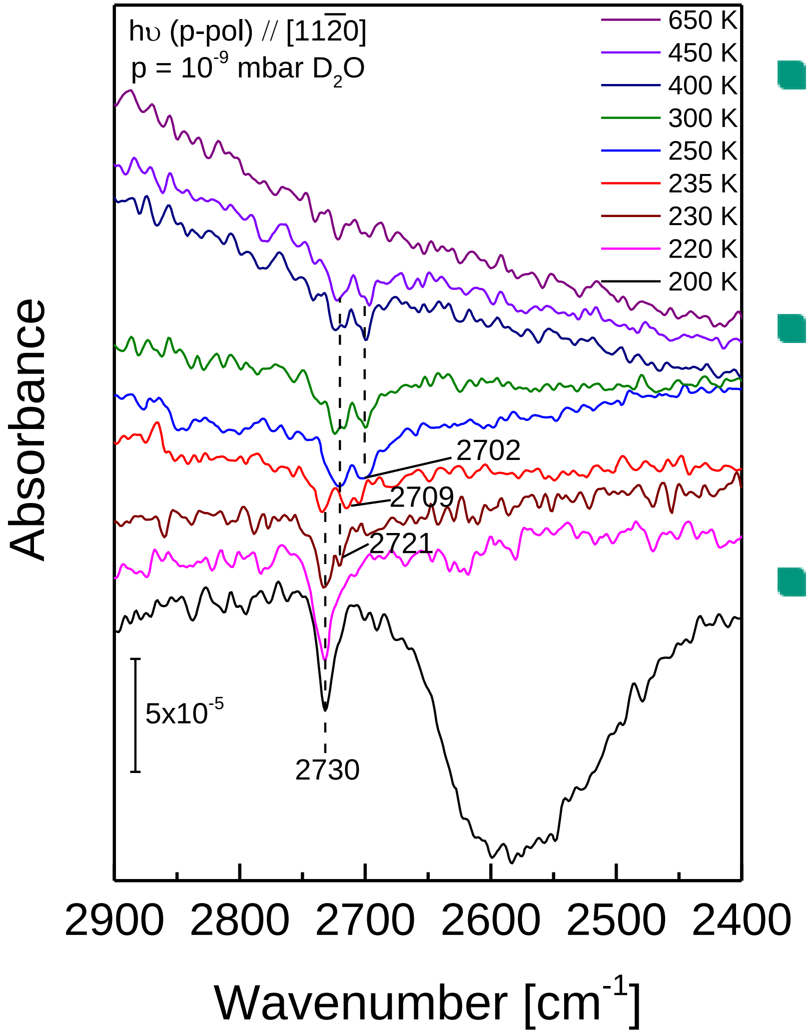




- The surface structure of Fe_2O_3(0001) is not defective after preparation on the deployed crystal as obtained by a sharp negative CO stretch vibration band at 2169 cm^{-1}

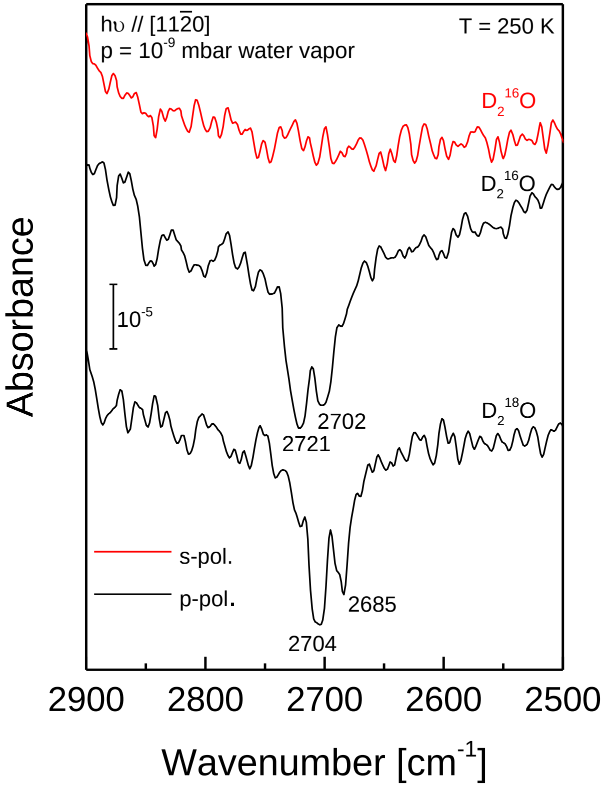
- Comparative CO probing on hematite and reduced hematite confirms a trivalent Fe^{3+} surface species on clean Fe_2O_3(0001)

IRRAS: Isobaric D_2O adsorption on $Fe_2O_3(0001)$



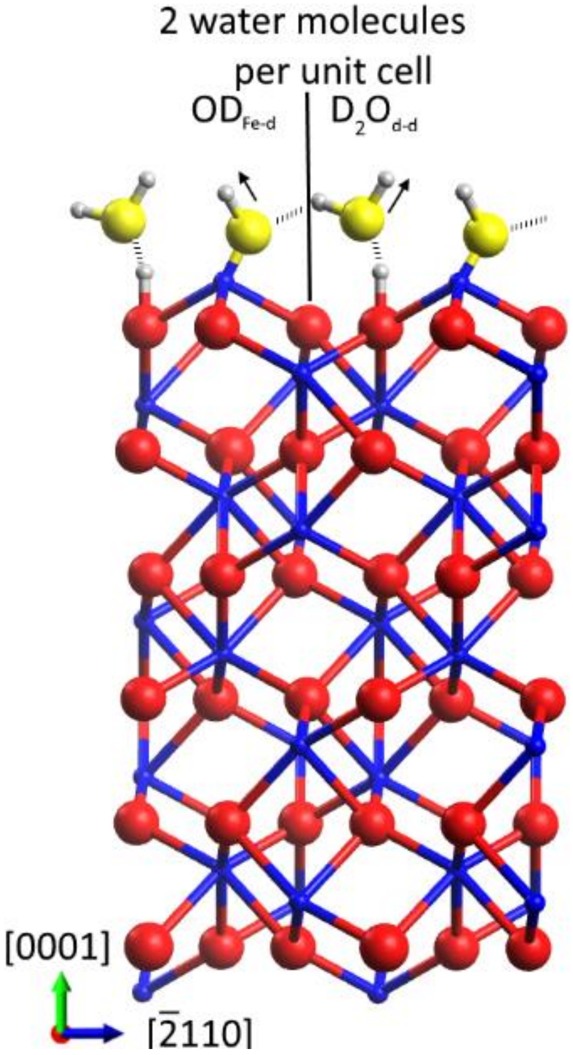
- After water (D_2O) exposure on the clean sample at 250-450 K, two OD bands were observed at 2721 and 2702 cm^{-1} with IRRAS
- The high thermal stability of OD-segments with low surface mobility indicate a hydroxylation of the surface
- For water exposures below 250 K the formation of bilayer /multilayer was observed as characterized by OD-dangling mode at 2730 cm^{-1}

IRRAS: Water monolayer on $Fe_2O_3(0001)$



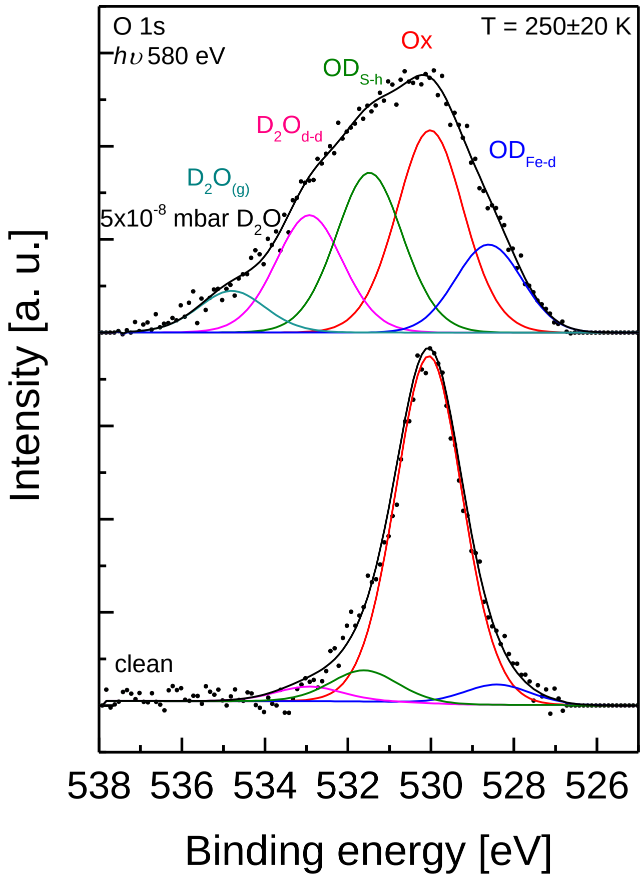
Oxygen containing species	Observed IR wavenumber [cm^{-1}]	Calculated wavenumber [cm^{-1}]
$^{16}OD_{Fe\text{-}d}$	2721	2757
$^{16}OD_{S\text{-}d}$	-	2660
$D_2\,^{16}O_{d\text{-}d}$	2702	2729
$^{18}OD_{Fe\text{-}d}$	2704	2740
$^{18}OD_{S\text{-}d}$	-	2644
$D_2\,^{18}O_{d\text{-}d2o}$	2685	2712

$$\tilde{\nu}_{^{18}OD} = \tilde{\nu}_{^{16}OD}\sqrt{\frac{\mu_{^{16}OD}}{\mu_{^{18}OD}}} = \frac{4\tilde{\nu}_{^{16}OD}\sqrt{5}}{9}$$



- Terminal OD vibrations (assymetric) are perpendicular oriented to the surface
- Isotopic substituion experiments with water clearified that the second OD band does not originate from a transferred deuteron to the oxygen-component from the surface
- OD-Vibrations that are stabilized with deuterium via hydrogenbridgebonding must occur line-broadened and cannot be detected by IRRAS

XPS: D_2O interface species on Fe_2O_3(0001)



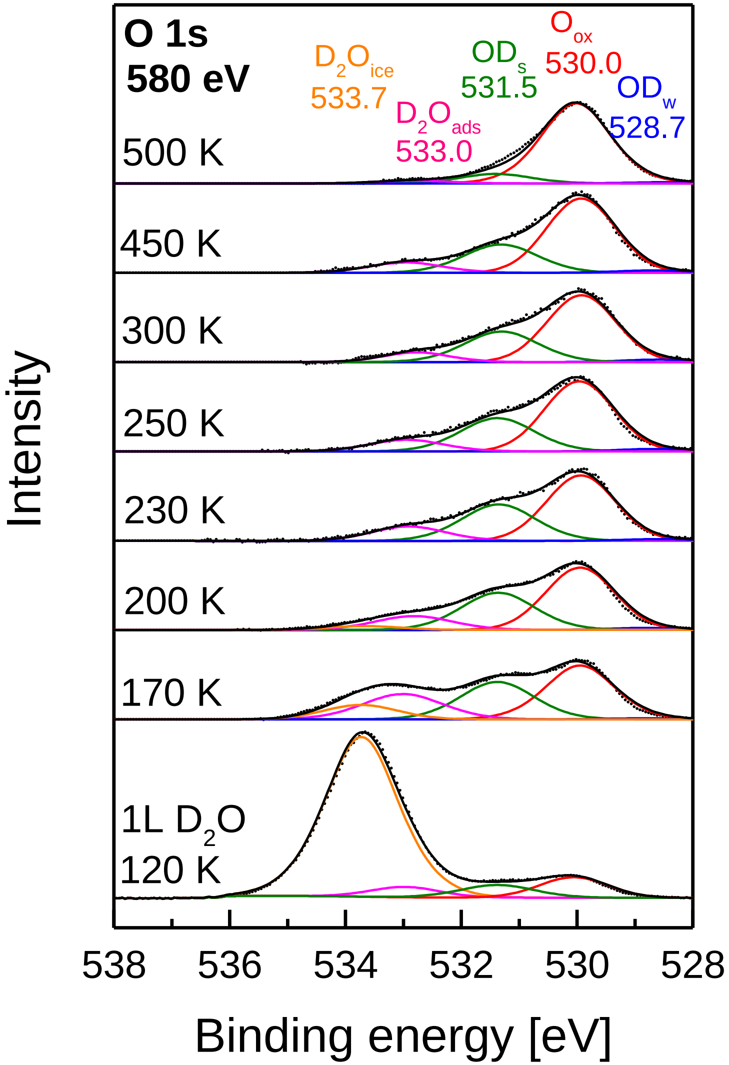
Oxygen containing species	Observed XPS binding energy [eV]	Calculated chemical shift [eV]
OH_{Fe-h}	528.7	+0.3
OH_{S-h}	531.5	-0.7
H_2O_{h-h}	533.0	-0.8
Ox	530.0	0.0

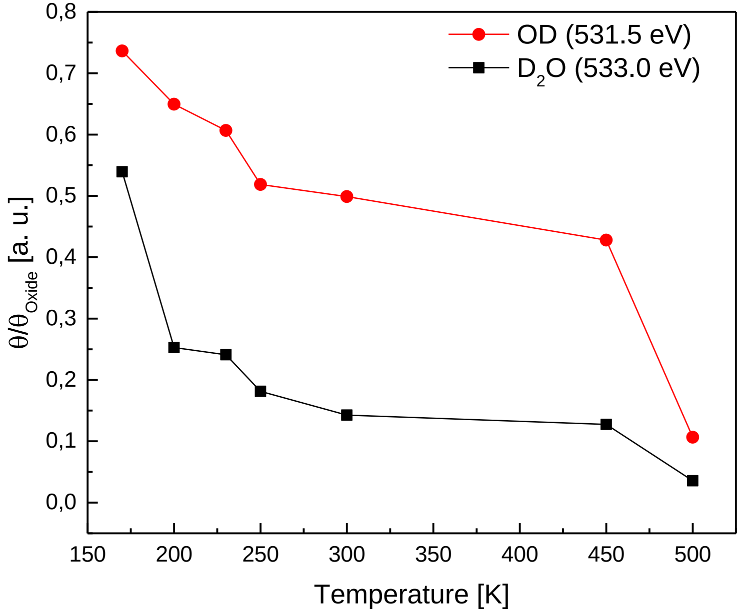
$$D_2O_w + O_s \rightarrow DO_s + OD_w$$

- DFT: Water reacts dissociatively on metal oxides, resulting in a pair of OD containing fragments, that should be specifiable by spectroscopy
- Adsorption measurement at 250 K prohibits the formation of physisorbed water and ice layers
- 2 OD-species with inverse chemical shift were experimentally confirmed in agreement with theoretical calculations
- Presence of molecular water aids the stabilization of surface hydroxyls

S. Yamamoto, T. Kendelewicz, J. Newberg, G. Ketteler, D. Starr, E. Mysak, K. Andersson, H. Ogasawara, H. Bluhm, M. Salmeron, G. E. Brown Jr, A. Nilsson, *J. Phys. Chem. C* **2010**, 114, 2256-2266.
R. Ovcharkeno, E. Voloshina, J. Sauer, *Phys. Chem. Chem. Phys.* **2016**, 18, 25560-25568.

XPS: D_2O heating series on $Fe_2O_3(0001)$

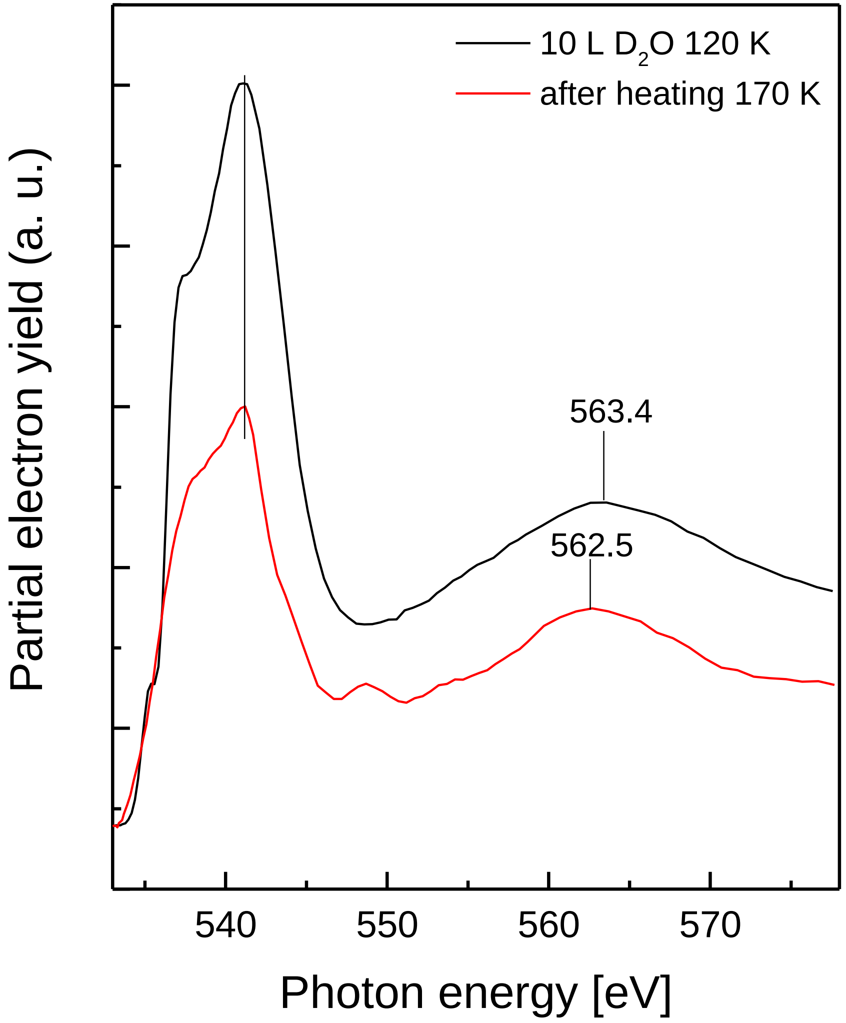




- The peak fit analysis in O1s spectra reveals that D_2O ice and adsorbed D_2O can be distinguished by XPS
- Between 250 K and 450 K there is no significant change in the relative coverage for OD_s and D_2O_{ads} in agreement with IR data
- A nearly hydroxy-free-Fe_2O_3 surface can be obtained for temperatures higher than 500 K

J. Blomquist, L. E. Walle, P. Uvdal, A. Borg, A. Sandell, *J. Phys. Chem. C.* **2008**, 112, 16616-16621.

NEXAFS: D_2O on $Fe_2O_3(0001)$



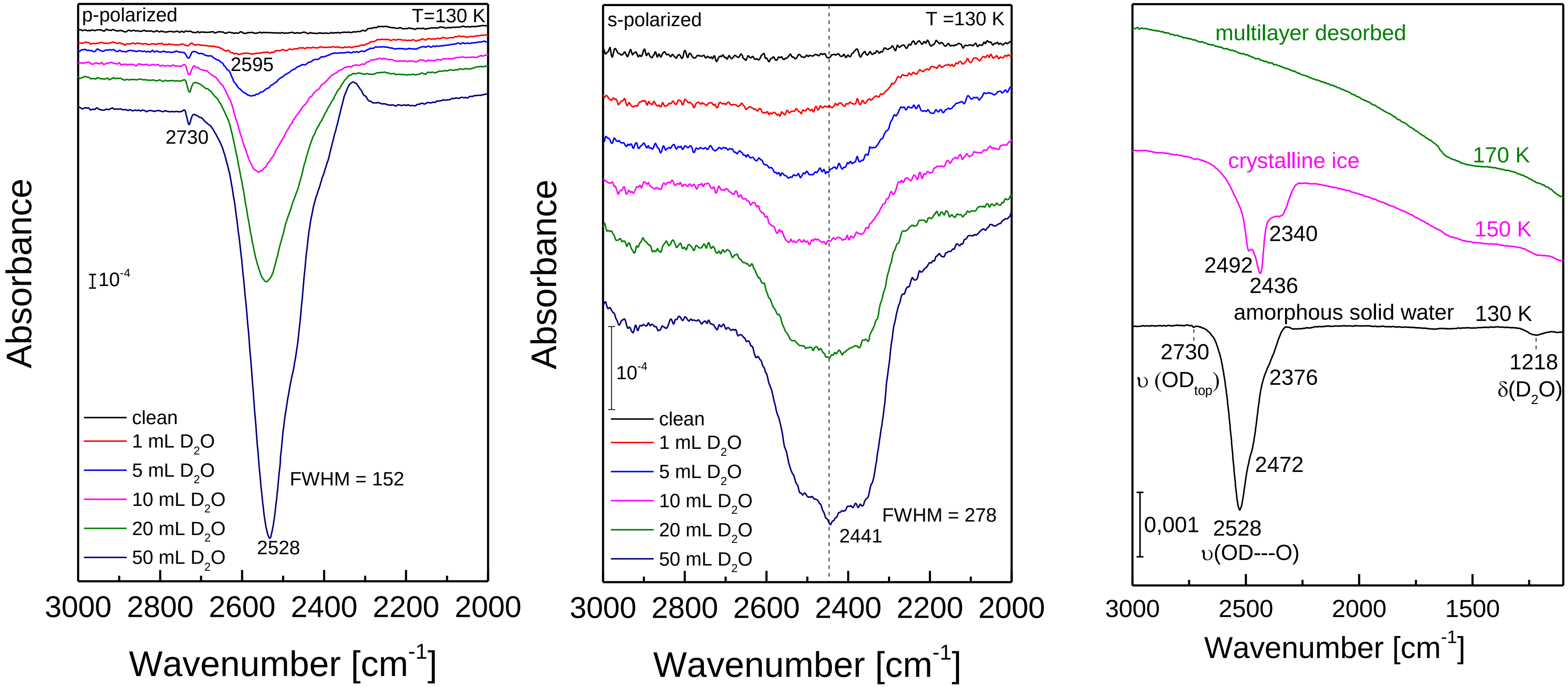
P. Parent, C. Laffon, C. Mangeney, F. Bournel, M. Tronc *J. Chem. Phys.* **2002**, 117, 23, 10842-10851.

- Scattering resonance antiproportional to O-O distance in first coordination shell

$$\sigma^* \sim \frac{1}{R^2}$$

- The lower the σ^* resonance the longer is the O-O distance
- For amorphous ice the O-O length reaches a minimal value for dosages higher than 5 L due to maxed out hydrogen bridge bonding

IRRAS: D_2O ice on $Fe_2O_3(0001)$

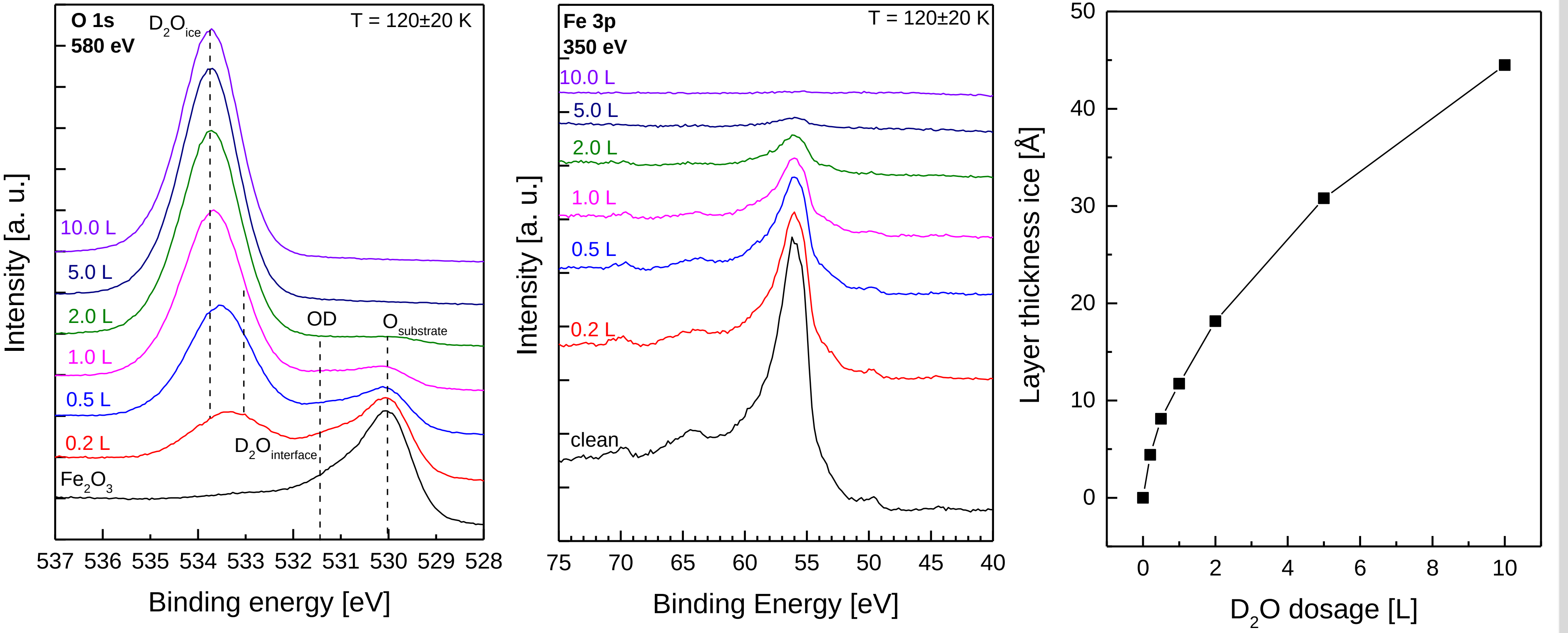


- Hydrogen-bonding is enhanced for increasing dosages and causes a redshift from 2595 cm^{-1} to 2528 cm^{-1} in bulk water vibrations for amorphous solid water excited by p-polarized IR, but remains constant for s-polarized IR at 2441 cm^{-1}

- Transition temperature to crystalline ice (CI) was measured at 150 K within a redshift of 36 cm^{-1} for all broadband species.

Y. Fujimori, X. Zhao, X. Shao, S. Levchenko, N. Nilius, M. Sterrer, H.-J. Freund, *J. Phys. Chem. C* **2016**, 120, 5565-5576.
U. Leist, W. Ranke, K. Al-Shamery, *Phys. Chem. Chem. Phys.* **2003**, 5, 2435-2441.

XPS: D_2O ice growth on $Fe_2O_3(0001)$

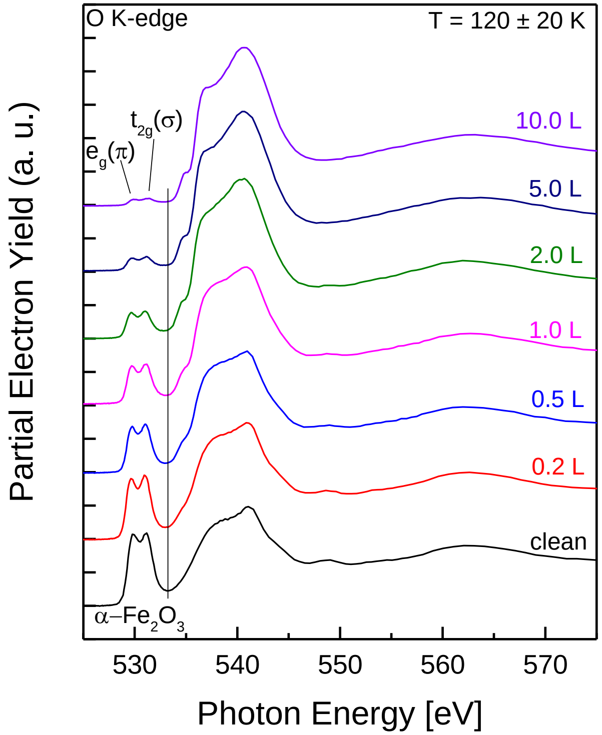


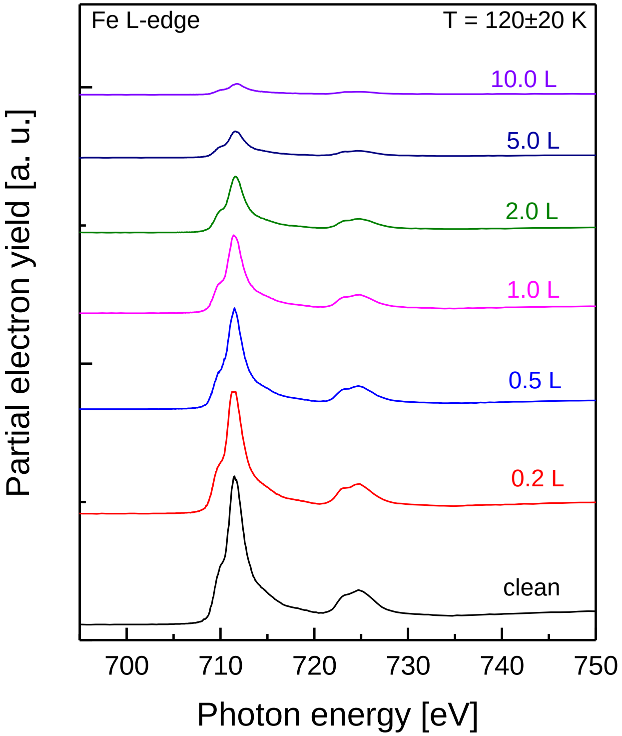
- Layer thickness determination derived from depletion of Fe 3p signal according following equation:

$$d = \lambda_s \cos(\theta) \cdot \ln\left(\frac{I_{S0}}{I_S}\right) \qquad \lambda_s = 8.53\ \text{Å} \qquad \theta = 0^\circ$$

S. Merzlikin, N. Tolkachev, T. Strunskus, G. Witte, T. Glogowski, C. Wöll, W. Grünert, *Surf. Sci.* **2008**, 602, 755-767.
J. L. Junta-Rosso, M. F. Hochella Jr., *Geochem. et Cosmochim. Acta* **1996**, 60, 2, 304-314.

NEXAFS: D_2O ice growth on $Fe_2O_3(0001)$





- The doublet at O K-edge is very well resolved for low coverages and characteristic for hematite. The differences in the energy splitting and intensities are functions of the O-Fe structure: e.g. the energy splitting is larger in hematite than for maghemite

S. Giovannini, F. Boscherini, R. Carboni, L. Signorini, L. Pasquini, N. Mahne, A. Giglia ,M. Pedio, S. Nannarone, M. Benfatto, S. Della Longa, *Phys. Scrip.* **2005**, 115,424-427.

Conclusions

- The adsorption of water on a hematite single crystal was studied by IRRAS for the first time.
- After water (D_2O) exposure on the clean sample at 250 K, two weak and negative OD bands were observed at 2721 and 2702 cm^{-1} with IRRAS.
- Under same conditions water dissociation was detected by synchrotron XPS (OD_w: 528.7 eV, OD_s: 531.5 eV).
- The isotopic substitution experiments with $D_2{}^{18}O$ show that both bands are red-shifted by 17 cm^{-1}.
- For a water splitting model the OD_S vibration seems to be shielded in IRRAS by the adsorbed D_2O-monolayer species.
- The combined experimental and theoretical results reveal that water is stabilized as a partially dissociated $OD_{Fe\text{-}d}$-$D_2O_{d\text{-}d}$ dimer species on the $Fe_2O_3(0001)$ surface.

Thank you for your attention!