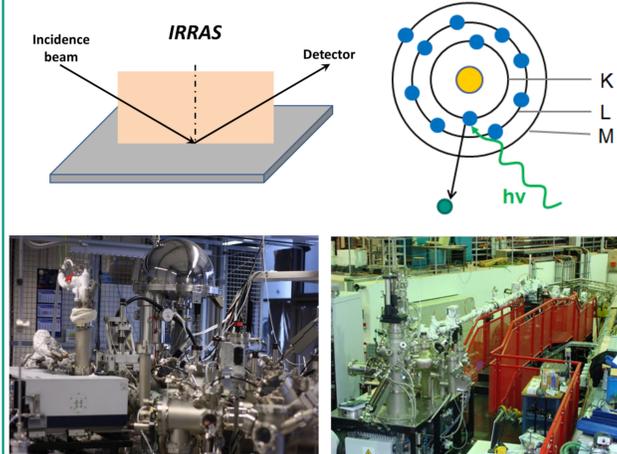


Introduction

The interaction of water with metal oxide surfaces is of interest because of the versatile roles of water in astrophysics, electrochemistry, geochemistry and heterogeneous catalysis. In contrast to water/metal systems, atomic scale information on water/oxide interfaces is limited, regardless of their abundance and rich chemical functionality. The reactivity of oxide surfaces toward water depends on various parameters, such as the ionicity of the metal-oxygen bond, the lattice constant, the defect structure and the surface orientation.^[1-4] In this work we present a surface-scienc study on the interaction of water with well defined Fe₂O₃(0001) single crystals by employing infrared absorption reflection spectroscopy (IRRAS) in conjunction with X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). The experimental results provided deep insights into the electronic, structural and chemical properties of various surface species, which were further corroborated by theoretical calculations.

Equipments

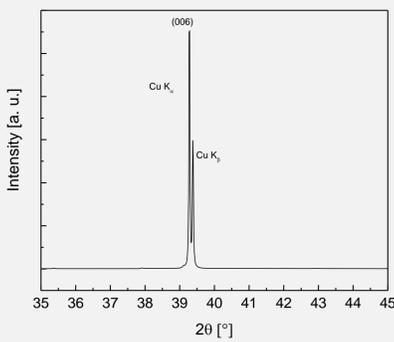


Experimental

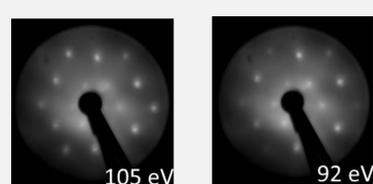
IRRAS measurements were conducted in the UHV-apparatus „Theo“ with a base pressure of 10⁻¹⁰ mbar. The IR-spectrometer contains an internal polarizer module, which is dedicated for orientational studies of adsorbed molecules on oxide single-crystal surfaces. The X-ray spectroscopic experiments were carried out at BESSY on a modern endstation at HESGM-beamline. The Fe₂O₃(0001) single crystal was mounted on a sampleholder with e-beam heating and cleaned by repeated cycles of annealing with stepwise heating from 850 K and 950 K in oxygen atmospheres of 10⁻⁵ mbar to obtain a single Fe surface termination. Water (D₂O) was purified by repeated freeze-pump-thaw cycles. Exposure to water was carried out by backfilling the analysis chamber through a leak-valve based directional doser. Gas dosages are quoted in Langmuir (L). The vibrational analysis was performed with vienna ab-initio simulation package (VASP) for two water molecules per unit cell with a 2x2 superstructure. The exchange-correlation function was PBE.

Structural characterization of Fe₂O₃(0001)

XRD

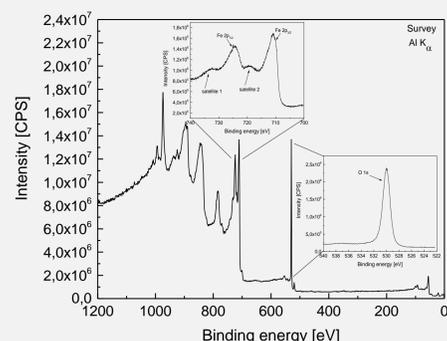


LEED



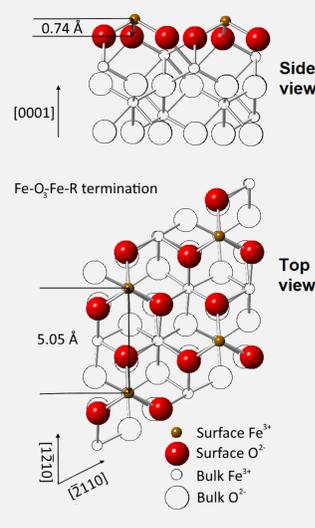
LEED exhibits threefold symmetry as expected for spacegroup R $\bar{3}c$

XPS



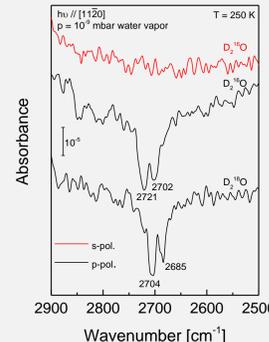
Selected core-levels	Peak position Fe ³⁺ and O ²⁻ [eV]
Satellite 1	733.2
Fe 2p _{1/2}	724.5
Satellite 2	719.1
Fe 2p _{3/2}	710.9
O 1s	530.0

Surface termination

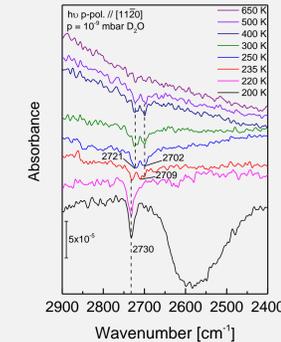


Water adsorption on the Fe₂O₃(0001) surface

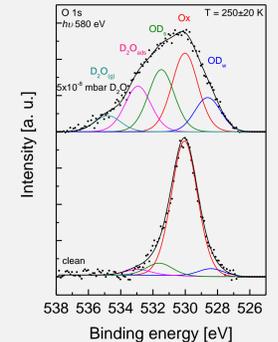
IRRAS



IRRAS



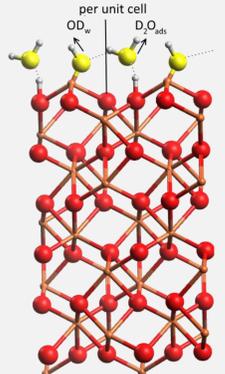
XPS



Peak assignment and adsorption model

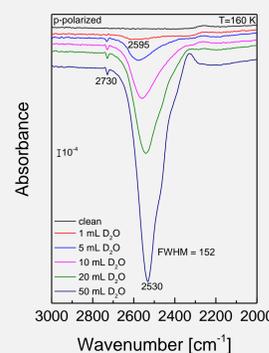
Oxygen containing species	Observed IR wavenumber [cm ⁻¹]	Calculated wavenumber [cm ⁻¹]
¹⁶ OD _{Fe-d}	2721	2757
¹⁶ OD _{S-d}	-	2660
D ₂ ¹⁸ O _{d-d}	2702	2729
¹⁸ OD _{Fe-d}	2704	2740
¹⁸ OD _{S-d}	-	2644
D ₂ ¹⁸ O _{d-d2o}	2685	2712

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 ₂ O _{h-h}	533.0	-0.8
Ox	530.0	0.0

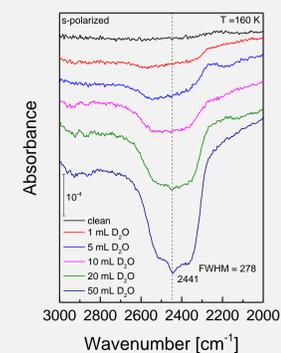


Water multilayers on Fe₂O₃(0001)

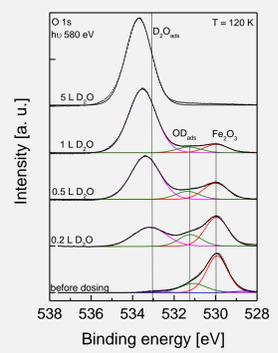
IRRAS



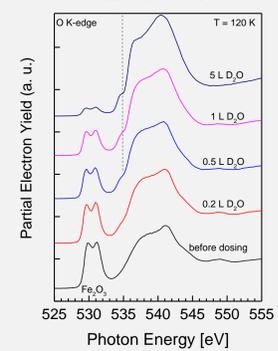
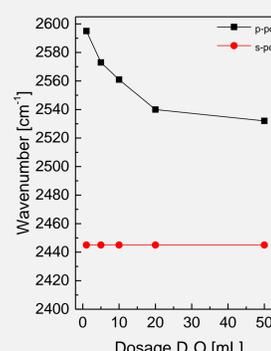
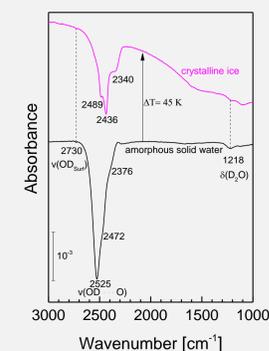
IRRAS



XPS



NEXAFS



Conclusions

- The clean Fe₂O₃(0001) is primarily Fe-terminated confirmed by the (1x1) LEED pattern.
- After water (D₂O) exposure on the cleaned sample at 250 K, two OD bands were observed at 2721 and 2702 cm⁻¹ with IRRAS, which are stable during annealing upon 500 K.
- The isotopic substitution experiments with D₂¹⁸O show that both bands are red-shifted by 17 cm⁻¹ indicating that no hydroxy species originate from D transfer to the surface oxygen (¹⁶O).
- Under same conditions water dissociation was detected by synchrotron XPS.
- The combined experimental and theoretical results reveal, that water is stabilized as a partially dissociated OD_{Fe-d}-D₂O_{d-d} dimer species on the Fe₂O₃(0001) surface.
- Multilayer growth of water was monitored by IRRAS at temperatures below 160 K: The sharp IR band at 2730 cm⁻¹ was assigned to the OD vibration of terminal water groups (non-H-bonded OD). For p-polarized IR excitation, bulk water vibrations are redshifted from 2595 to 2525 cm⁻¹ with increasing water exposure, which is contributed to the enhanced H-bonding. In contrast, the s-polarized IR data show a broad band at about 2440 cm⁻¹, which remains constant with D₂O multilayer growth. This is characteristic for the H-bonds parallel to the surfaces.

References

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