Investigation of Calcium-Silicate Surfaces with UHV-IRRAS to understand the First Step in Corrosion of Concretes

C. Natzeck, P. Weidler, C. Wöll, P. Thissen*

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Motivation

➢ The surface chemistry of the mineral Wollastonite as a real model sample for Calcium-Silicate (CS) phase has been studied using infrared reflection-absorption spectroscopy under ultrahigh-vacuum conditions (UHV-IRRAS) using water and methanol as probe molecules.

➢ This is the **first application of IRRAS to** a **crystalline**, yet **multi-domain mineral surface** of natural origin - The assignment of the vibrational bands is supported by a **first-principles theoretical study**.

Wollastonite as real model sample

Part of natural stone – mechanical preparation [1]

- Embedded into resin
- Grinding / polish steps
- Removal resin

➢ Sample surface breaks into lath- or needle shaped (acicular) particles with preferred orientation along the b-axis

Characterization with XRD

➢ specimen is pure Wollastonite and no other mineral phase is present

Fig. 1: Wollastonite crystal representation [3]

Cleaning with XPS-monitoring in situ under UHV condition

- moderate Heating (400 K, 1 h), gentle sputtering (Ar, 15 min)
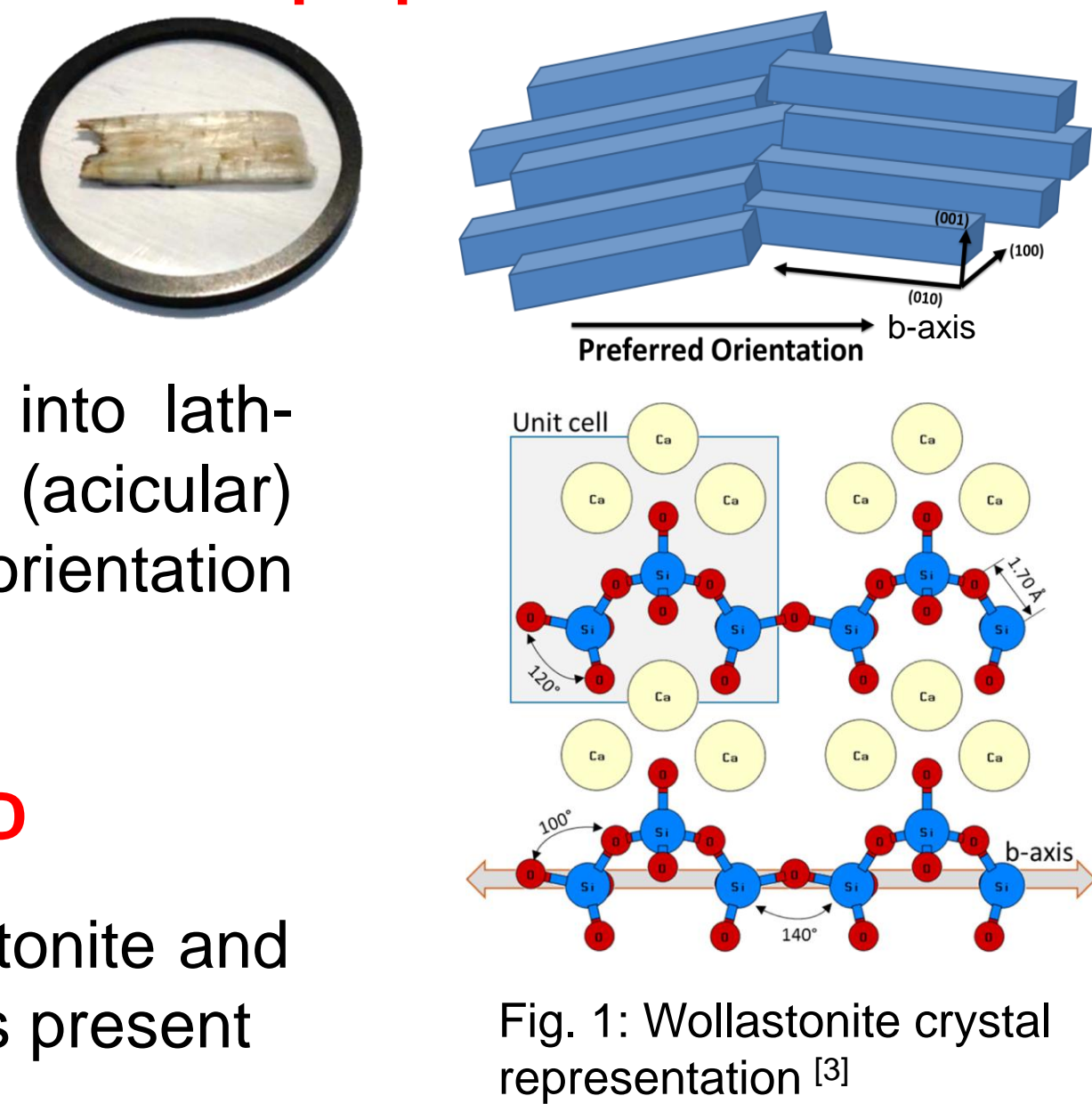
Infrared Reflection Absorption Spectroscopy (IRRAS)

- Measurements at 10^{-10} mbar pressure and RT or 100 K sample temperature
- beam path: grazing incidence (80°) in direction of preferred orientation (b-axis)
- Exposures of water or methanol in situ in Langmuir units (L) from 1 mL to 1000 mL

On dielectric surfaces, the surface selection rule does not apply!

Consequences:

➢ both s- and p-polarized light can couple to adsorbate vibrations:

Experimental Challenge: very low reflectivity of dielectrics!

- Using the standard optical path within the IR-spectrometer without any additional optical element
- Attach spectrometer directly to Ultra High Vacuum (UHV) chamber

Fig. 2: UHV-IR/XPS-chamber at the IFG: "THEO"
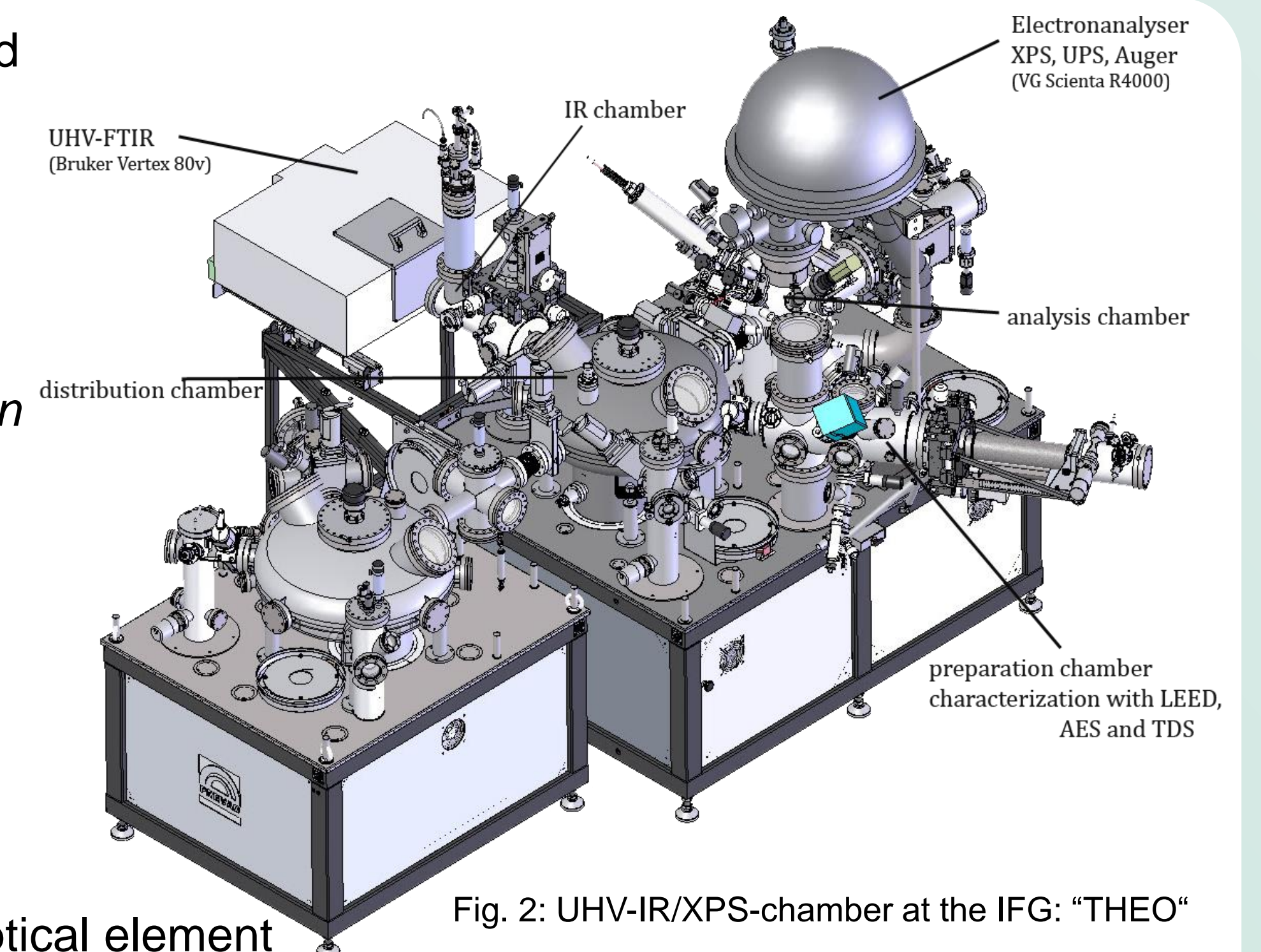
Water on Wollastonite Surface

- Water dissociate in interaction with Wollastonite surface – early stage hydration or **Metal Proton Exchange Reaction (MPER):**

  - lead to partial leaching of Ca from the near surface reaction [1] and depend on the pH value of aqueous environment [2]
  - first step is the proton exchange between adsorbed molecular species and the mineral surface – leading to the formation of surface OH species
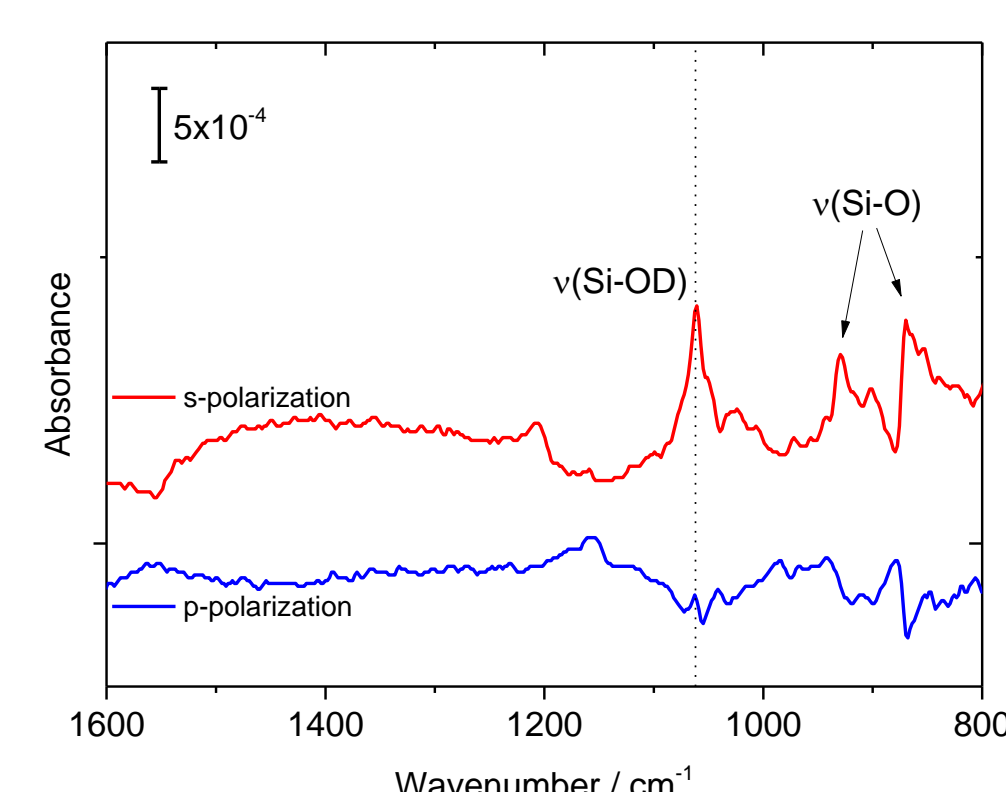 - lead to strong deformation of Si-O-tetrahedra keeping the same volume

Fig. 3: Differential infrared absorption spectra of D_2O adsorbed on Wollastonite referenced to the clean surface before exposure in s- and p-polarization modes
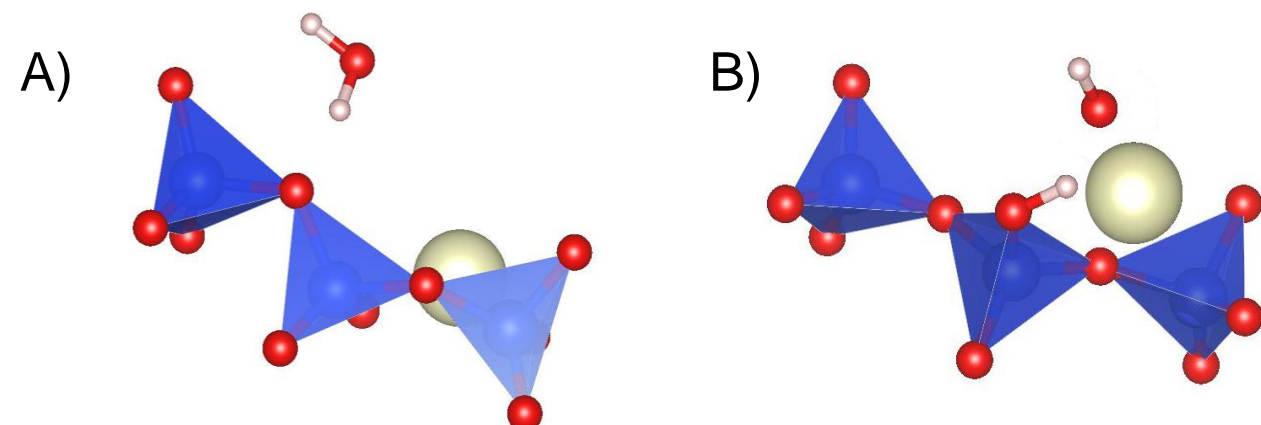
Fig. 4: (A) and (B) present the proton exchange during the water adsorption on the clean Wollastonite(001) surface. Gray spheres represent Ca, red spheres represent O, and blue spheres represent Si

➢ Si-OD stretching vibration is the strongest mode and is formed by transfer of a proton from water

➢ no vibrational modes from molecular D_2O are observed (D_2O at 1250 cm^{-1})

➢ a further OD-binding on Ca species is with 350 cm^{-1} (Ca-OD) outer limit

➢ in comparison to the sensitivity of the Si-OD vibration, the intensity of surface O-D (2690 cm^{-1}) is very low

First-principles theoretical study [3]

- Calculations are performed with Vienna Atomic Simulation Package (VASP)
- **Basis Set:** Plane Waves, Supercell Approximation: Periodic Boundaries
- **Exchange-Correlation Functional:**
  - Generalized Gradient Approximation (Perdew and Wang '91)
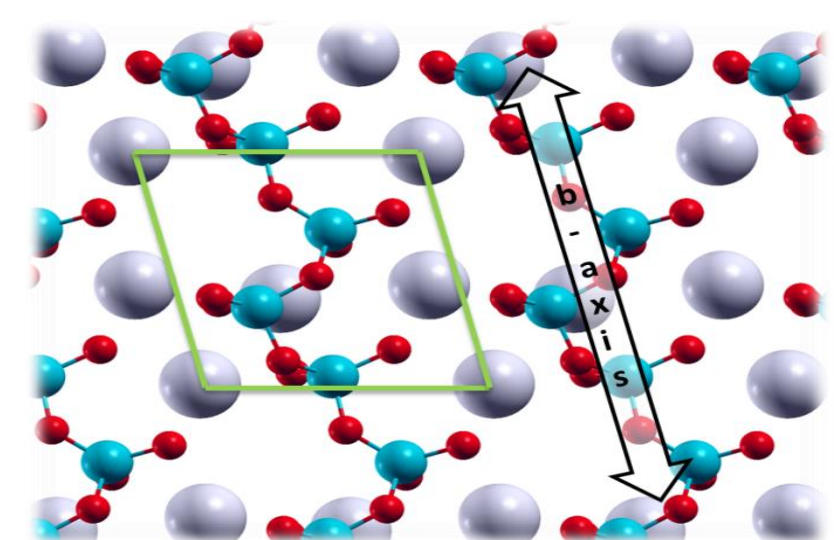 - Ultrasoft Pseudo Potentials
- **Kinetic Energy Cut-off:** 360 eV

Fig. 5: Top view on the clean wollastonite(001) surface. The surface unit cell is highlighted. The arrows indicate the chains formed by Si-O tetrahedra along the crystal b-axis. Grey spheres represent Ca, red spheres represent O and green spheres represent Si

Methanol on Wollastonite Surface

- Methanol does not dissociate in interaction with Wollastonite surface – no proton transfer take place and weakly chemisorbed molecular Methanol is present:

  - lead to no Metal Proton Exchange Reaction: no formation of Si-OH or Ca-OH species
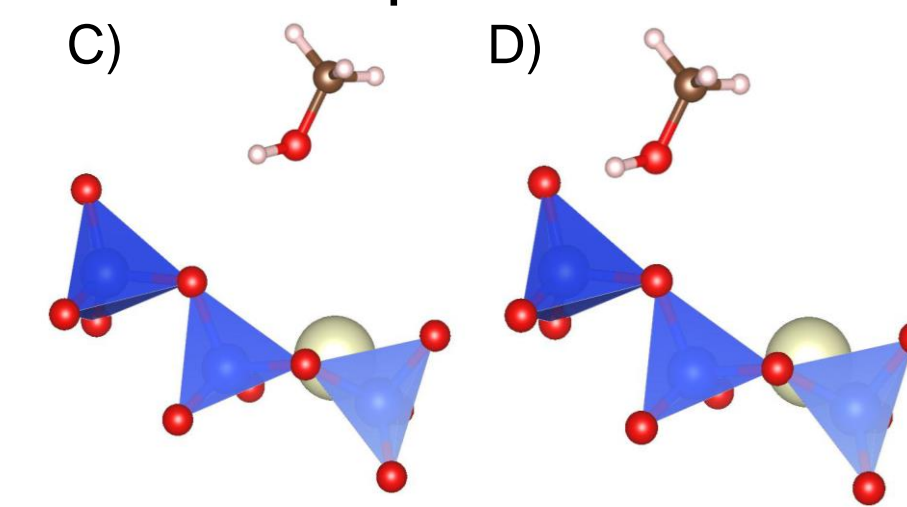 - weakly deformation of Si-O-tetrahedra

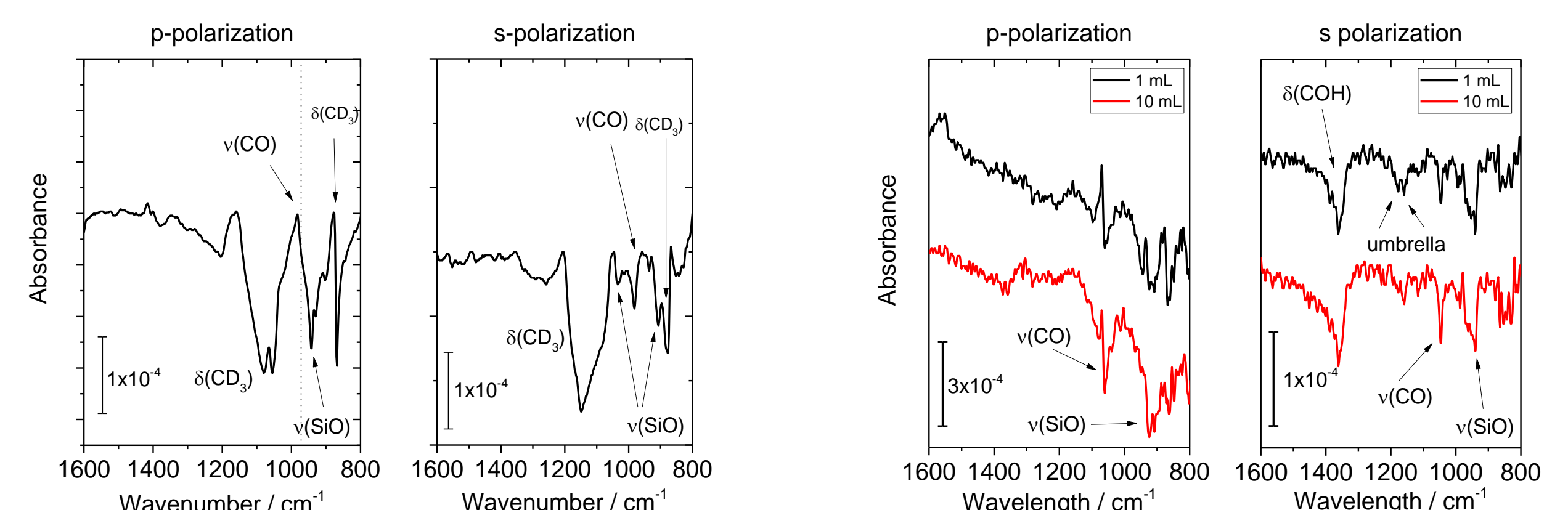Fig. 6 (C) and (D) present the molecular adsorption of methanol on the clean Wollastonite(001) surface

Fig. 7: Differential infrared absorption spectra of CD_3OD (left side) and CH_3OH (right side) adsorbed on Wollastonite referenced to the clean surface before exposure in s- and p-polarization modes
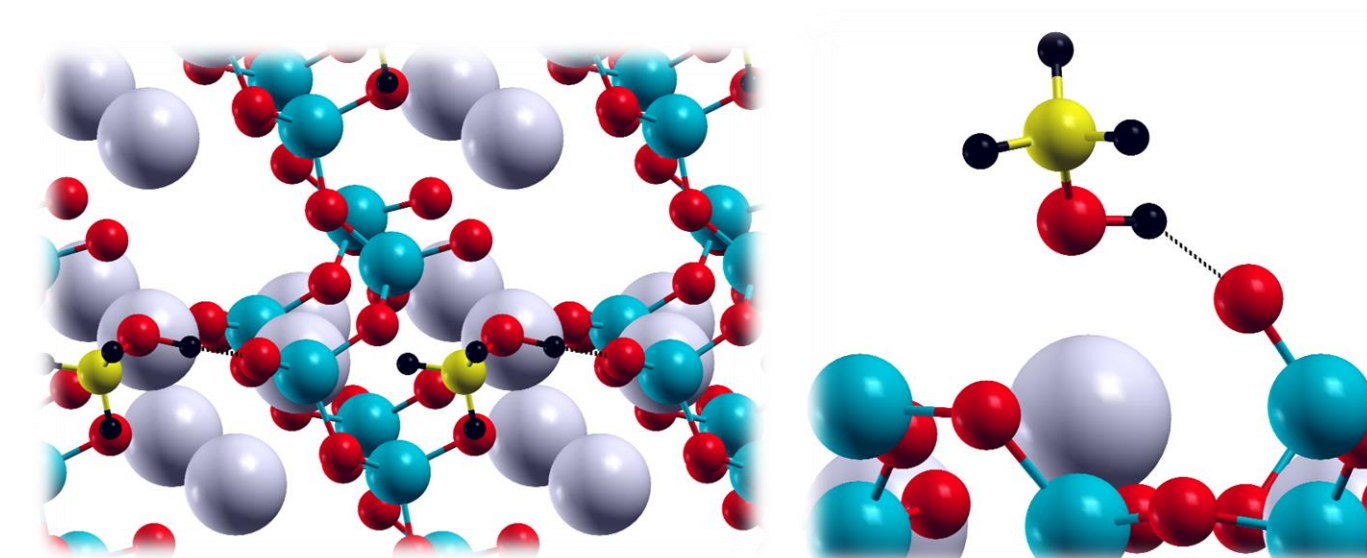
Fig. 8: Side- and top-view of energetically favorable structures modeling the adsorption of CH_3OH on Wollastonite(001)

Structure unit	Distance / Å	Structure unit	Angle / °
Ca-O^{CH3OH}	2.32	C-O-H	113.5
Si-O^{top}	1.57	Ca-O-H	84.8
O^{top}.H^{CH3OH}	1.61	Ca-O-C	136.5
O^{CH3OH}.H^{CH3OH}	1.01	H-C-O-H	169.8
Si-O^{tetrahedron}	1.67		

Vibration mode	Calculation DFT	Experimental p-polarization	Experimental s-polarization
C-O-H-deformation	1380		1360
CH$_3$ umbrella	1167		1177
CH$_3$ umbrella	1146		1157
C-O stretching	1040	1044	1046

➢ C-O-H deformation mode appears in non- und p-polarized mode, but not in s-polarization: gives evidence for a strong orientation of methanol along the b-axis.

➢ Molecular methanol is bond on top of the Ca (Ca-O) and gaining additional orientation along the b-axis by hydrogen-bonding (Si-O-H).

➢ The Ca-O-H angle is 84.4°, and the Ca-O-C is 136.6°, explaining best the appearance of the C-O-H deformation mode in s-polarization but not in p-polarization.

➢ CH$_3$ umbrella can be associated with the intact OH group of the methanol: the CH$_3$ umbrella mode is split.

Conclusion

Investigations of interaction of water and methanol on Wollastonite surface have been done by IRRAS allowing consideration of all components of the incident polarized light separately. With the help of first-principles calculations, a model of the Wollastonite as model surface for concrete satisfying most of the discussed points of the IRRAS could be developed. Surprisingly, methanol did not dissociate during adsorption on the Wollastonite at room temperature. This chemical behavior is in sharp contrast to water, quickly dissociating in contact with CS surfaces as first step of the Metal Proton Exchange Reaction.

* Karlsruhe Institute of Technology, Institute of Functional Interfaces, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-Mail: peter.thissen@kit.edu

References
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[2] Buerger, M. J. Proc. Natl. Acad. Sci. U.S.A. 1956, 42, 113−116
[3] N. Giraudo, P. Krolla-Sidenstein, S. Bergdolt, M. Heinle, H. Gliemann, F. Messerschmidt, P. Brüner, P. Thissen, J. Phys. Chem. C, 2015