Wollastonite ($CaSiO_3$) as model surface of Calcium-Silicates
Methanol adsorption studied by IRRAS

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Motivation

- Wollastonite is a chemically well characterized mineral ($CaSiO_3$) with versatile physical properties for use in industry reaching from medicine with the formation of artificial bones to construction chemistry with Calcium-Silicates (CS) as model system for cement and concrete.
- Because of the rather complicated structure of Calcium-Silicates (CS) important key information about surface chemistry going down to the atomic level of detail is missing for mineral surfaces.
- 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**.

Infrared Reflection Absorption Spectroscopy (IRRAS)

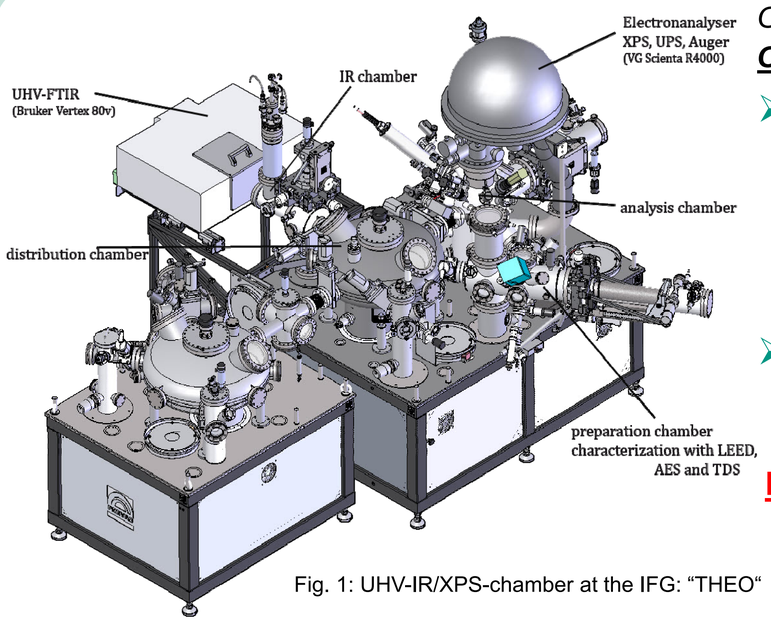
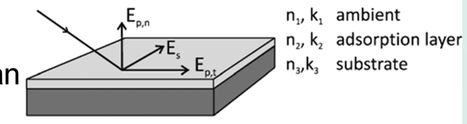


Fig. 1: UHV-IR/XPS-chamber at the IFG: "THEO"

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

***Consequences*:**



- both s- and p-polarized light can couple to adsorbate vibrations:
  - s-polarized light: bands will always be negative
  - p-polarized light: bands can be negative or positive depending on the incidence angle θ and the refractive index n of the substrate
- From considering all three components ($E_{p,n}$, $E_{p,t}$, and s) of the incident polarized light separately, the adsorption structure can be obtained directly

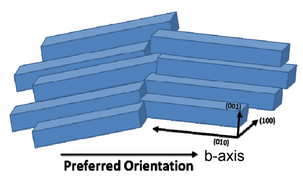
Experimental Challenge: very low reflectivity of dielectrics!

- Attach spectrometer directly to UHV chamber
- Using the standard optical path within the IR-spectrometer without any additional optical element

Wollastonite as 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

- Fit with the Pawley method utilizing data set for Wollastonite
- specimen is pure Wollastonite and no other mineral phase is present

XRD		Data set*)	Fit
lattice /nm	a	0.79258	0.79493
	b	0.73202	0.72876
	c	0.70653	0.70687
angle / °	α	90.055	90.79
	β	95.217	95.002
	γ	103.426	103.05

*) COD-file 0995777

Cleaning with XPS-monitoring in situ under UHV condition

- Cleaning procedure: moderate Heating (400K, 1h), gentle sputtering (Ar, 15min)

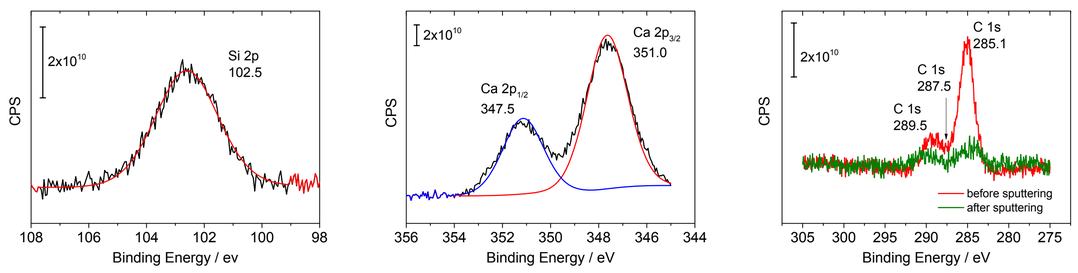


Fig. 2: XPS detail spectra of the Wollastonite surface

- Ratio of Ca : Si = 1 : 1, carbonate film on surface is removed

IRRAS: methanol on Wollastonite Surface

Adsorption of methanol in situ under UHV conditions

- Exposures of methanol in Langmuir units (L) from 1mL to 1000mL (Langmuir unit exposure time of 1 s at $1.33*10^{-6}$ mbar)
- Measurements at 10^{-10} mbar pressure and 100K sample temperature (liquid N_2)
- beam path: grazing incidence (80°) in direction of preferred orientation (b-axis)

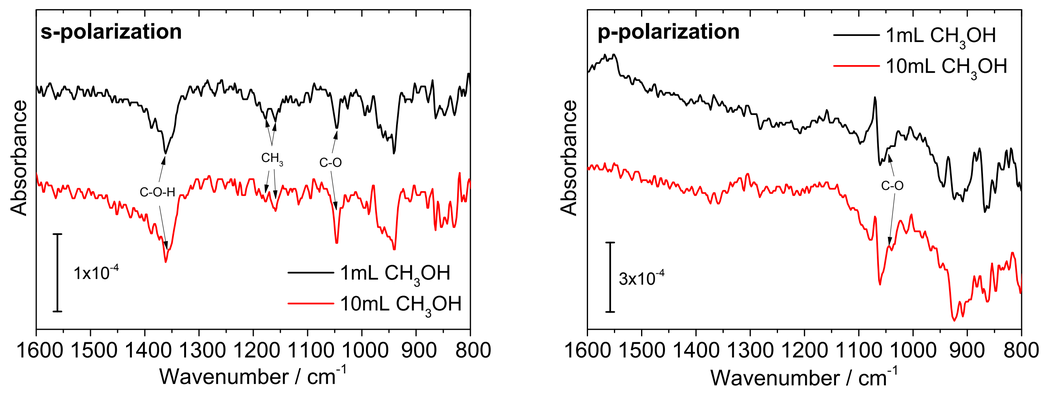


Fig. 4: Differential infrared absorption spectra of CH_3OH adsorbed on Wollastonite referenced to the clean surface before exposure in s- and p-polarization modes

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

Assignment of Structures

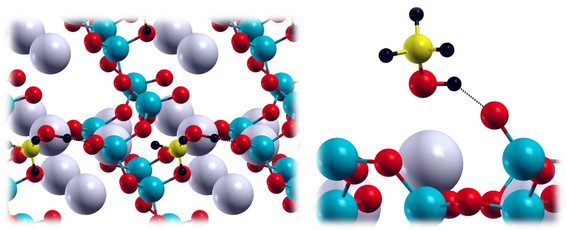


Fig. 5: Side- and top-view of energetically favorable structures modeling the adsorption of CH_3OH on Wollastonite(001)

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		

Structural information concerning the CH_3OH adsorbed on Wollastonite(001)

- 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

First-principles theoretical study – DFT [3]

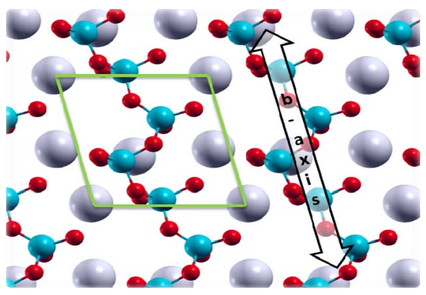


Fig. 3: Top view on the clean wollastonite(001) surface. The surface unit cell is highlighted. The arrows indicate the chains formed by Si-O tetrahedra along the crystal b-axis. Grey spheres represent Ca, red spheres represent O and green spheres represent Si.

- Calculations are performed with VASP
- **Basis Set:**
  - Plane Waves,
  - Supercell Approximation: Periodic Boundaries
- **Exchange-Correlation Functional:**
  - GGA (PW91)
  - Ultrasoft Pseudo Potentials
- **Kinetic Energy Cut-off:** 360 eV

Conclusion

Investigations on Wollastonite surface have been done by Infrared Reflection Absorption Spectroscopy allowing for consideration of all components of the incident polarized light separately. Appearance of the C-O-H deformation mode was proofing the methanol still to be molecular after adsorption. The appearance of the C-O-H deformation mode in s polarization but not in p polarization gives evidence for a strong orientation of the methanol along the b-axis. With the help of first principles calculations, a model of the Wollastonite(001) surface satisfying most points of the IRRAS could be developed.

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References

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