EXPERIMENTAL MID-INFRARED SPECTROSCOPIC ANALYSIS: ITS APPLICATION AND POSSIBILITY

室内実験における赤外分光分析の利用法と可能性

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Outline

- Introduction
  --- IR spectroscopy
- IR spectroscopic measurements
  --- IR spectroscopy
      * Function
      * Aerosol spectroscopy
      * In situ FTIR spectroscopy
      * IR ellipsometry
  --- Sample preparation
      * Pellet
      * Aerosol spectroscopy
      * On substrate
- Measurements & data analysis
- Astronomical application
- Possibilities for future
- Summary

Introduction

◆*What is the IR spectroscopy?*

An analytical technique to identify substances

Quartz (SiO_2)

Corundum (Ruby: Al_2O_3)

Olivine ($Mg_{1.9}Fe_{0.1}SiO_4$)

Kyanite (Al_2SiO_5)

Aquamarine ($Be_3Al_2(SiO_3)_6$)

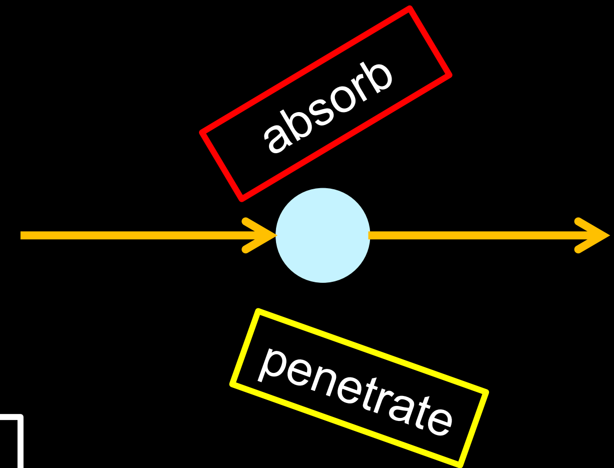
Enstatite ($MgSiO_3$)

Amo-$MgSiO_3$

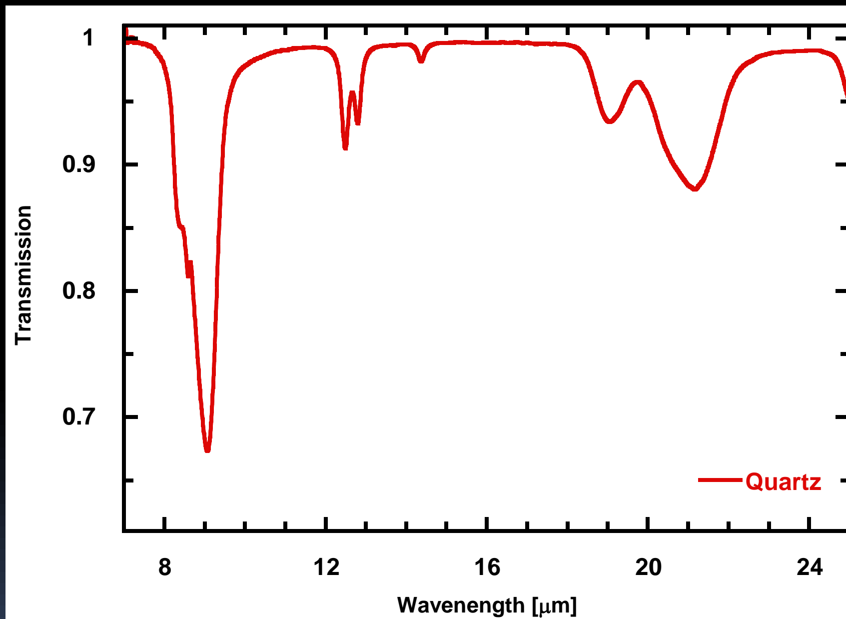
Fayalite (Fe_2SiO_4)

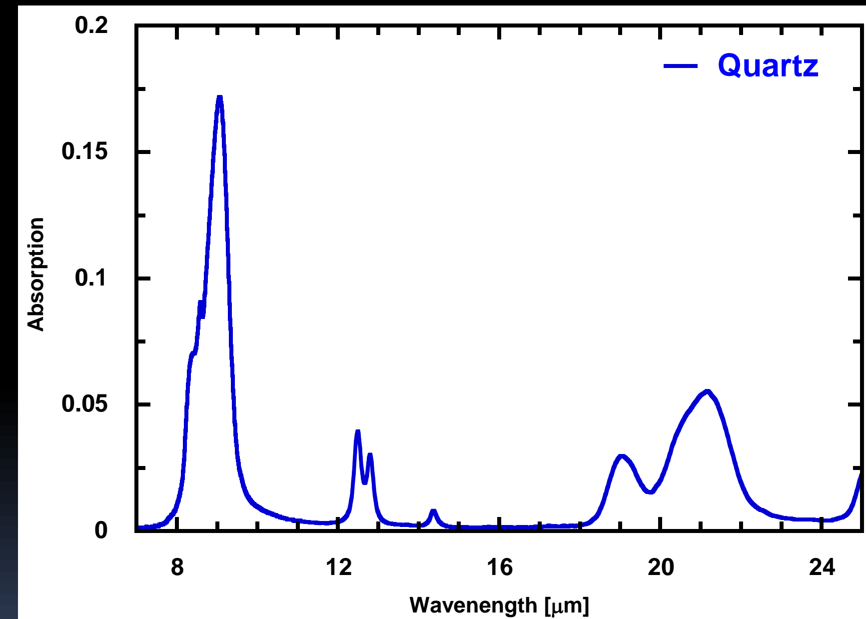
What can we obtain?

Detecting absorption and transmission bands due to vibrational transitions of atomic bonds



Crystalline SiO_2

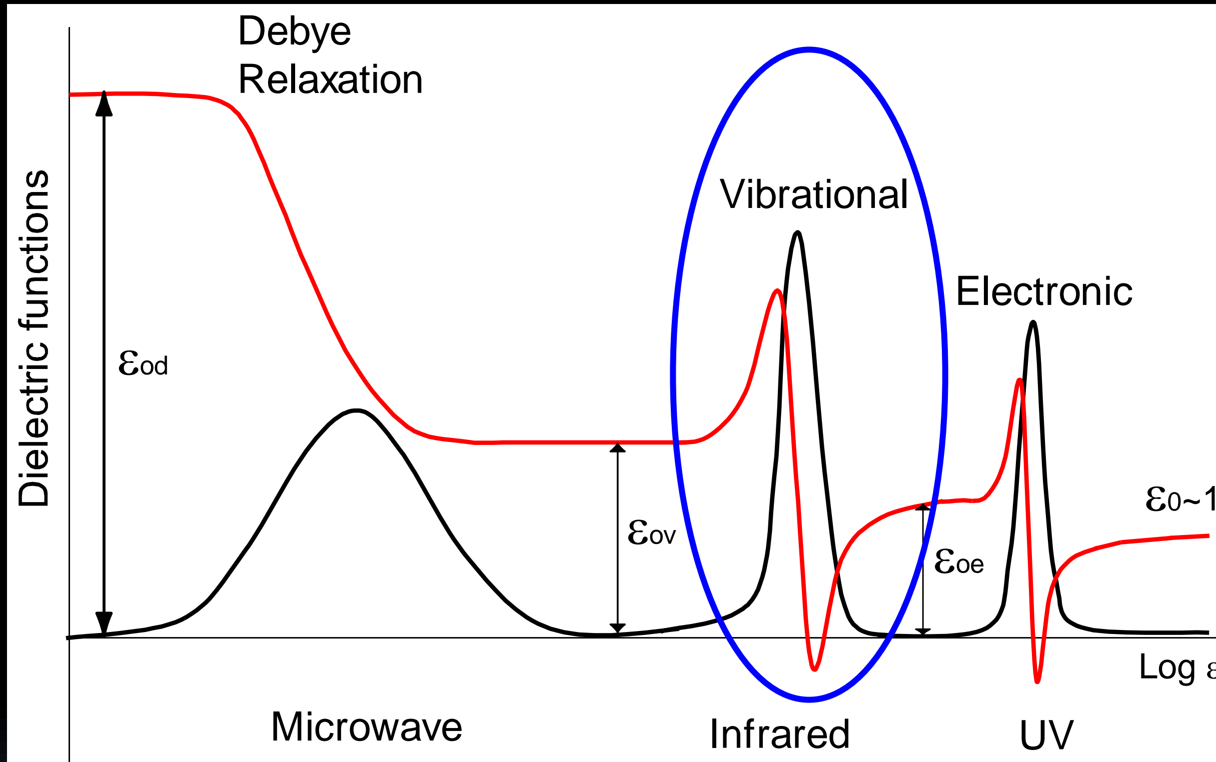




Absorbance = -log (transmittance)
Transmittance = $10^{-absorbance}$

Fingerprint of the material along with absorption peaks

Optical constant & Absorption



Describing optical properties

$$m = n + ik$$

n: real part
directly relate to refraction

k: imaginary part
relate to absorption

In microscopic mechanisms → Dielectric function

$\varepsilon = \varepsilon' + i\varepsilon'' = (n + ik)^2$

$\varepsilon' = n^2 - k^2$

$\varepsilon'' = 2nk$

Electronic transitions inside atoms and molecules →UV regions
Rotational spectra → far-IR & microwave regions
Vibrational spectra → near- & min-IR

How can we do the IR spectroscopic measurements?

IR spectroscopy

- FTIR spectrometer
- Aerosol spectroscopy
- In-situ FTIR spectroscopy
- IR ellipsometry

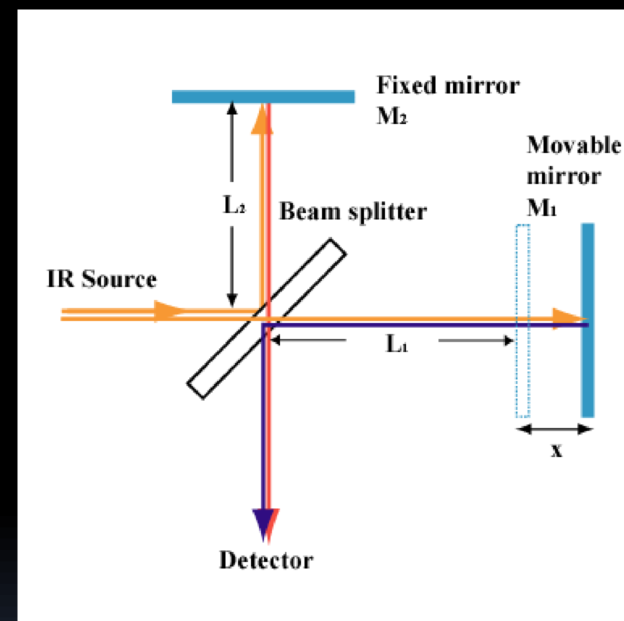
Sample preparation

- Pellet technique
- Aerosol technique
- On substrate
  - evaporation
  - spin coating

FTIR Spectrometer

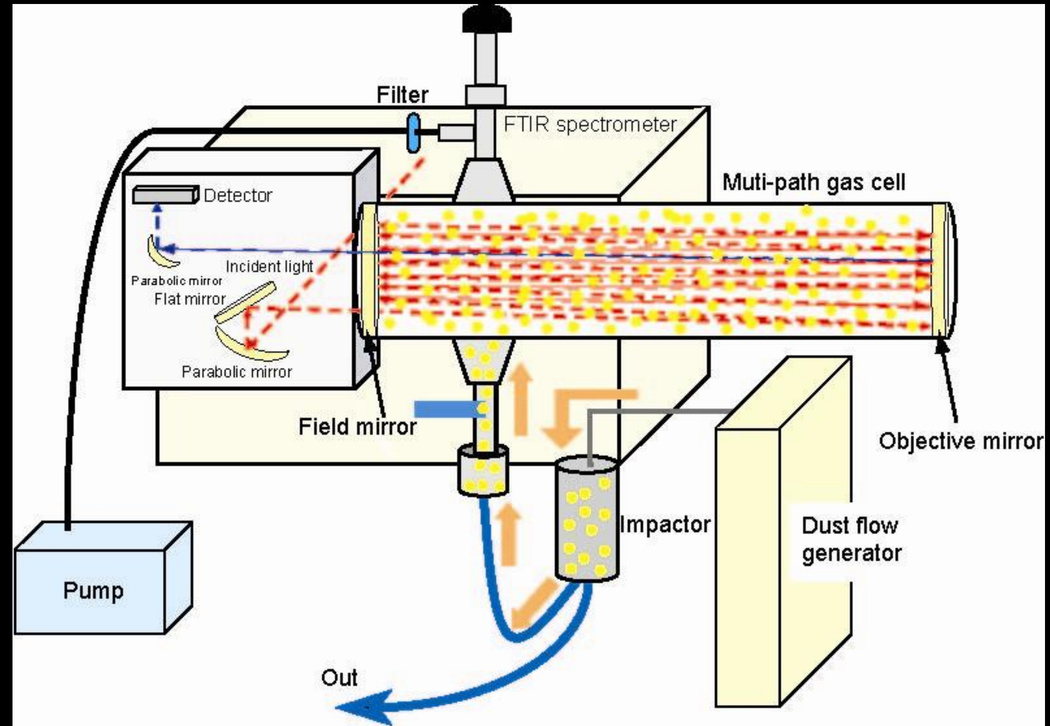
Fourier Transformation Infrared Spectroscopy (FTIR)

Michelson interferometer → the heart of FTIR & using for encoding a composite signal that contains all of the IR frequencies present in order to measure all of the IR frequencies at the same time



- ✓ A beam-splitter (w/ an orientation angle of 45° relative to the 2 mirrors) to divide an incident beam into 2 beams
- ✓ A fixed mirror is located at // to the incident beam w/ a distance L_2 from the splitter
- ✓ A movable flat mirror is placed at ⊥ to the beam with a distance (L_1+x) from the splitter
- ✓ ½ of the beam reflects off the splitter and travels to the fixed mirror M_2
- ✓ The other half of the beam passes through the beam splitter and reflects off the movable mirror M_1 precisely moves back and forth along the direction of the incident beam within a distance x
- ✓ After both beams reflect off the mirrors respectively, they recombine at the beam splitter
- ✓ As a result of a phase difference between these 2 beams, they interfere w/ each other either constructively or destructively depending on the additional path difference

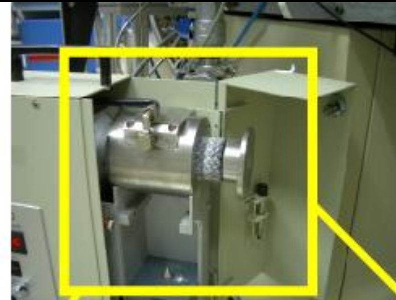
Aerosol spectroscopy

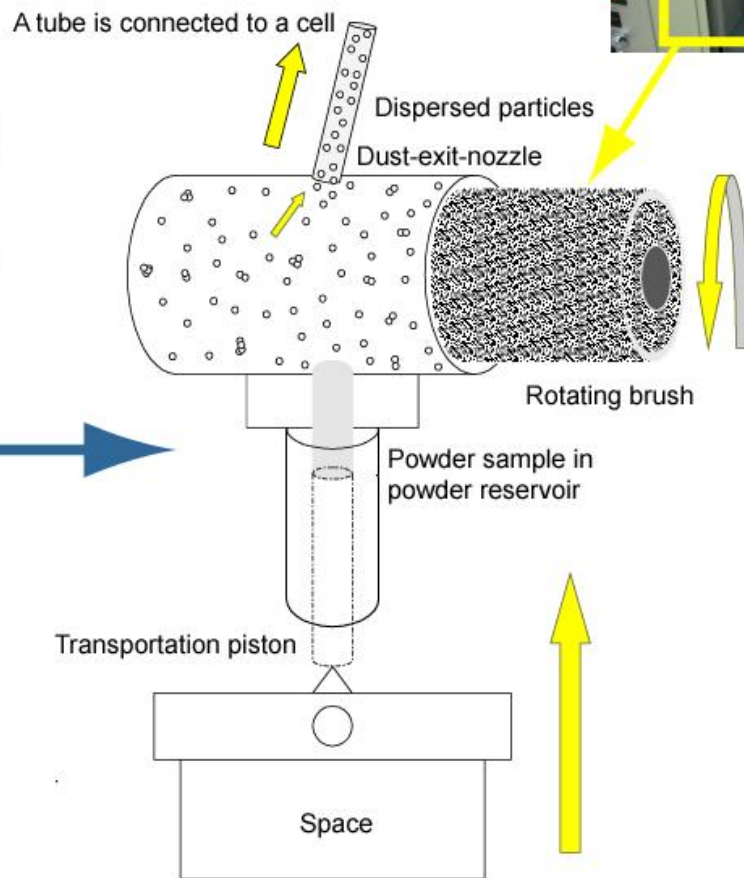


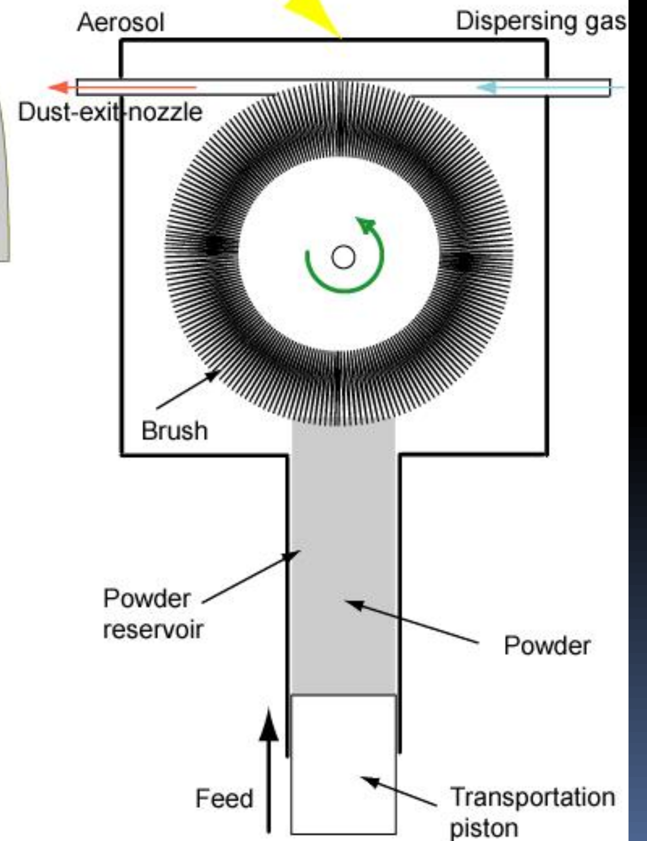
- Particle size: <1μm
- N_2-gas
- Path length: ~18m
- Wavelength range: 2-50 μm
- Sampling:
  Polyester capillary pore membrane filters

AIU Jena
More details in Fundamentals and Applications in Aerosol Spectroscopy, Tamanai & Mutschke 2010

Aerosol Generator







Impactor

Inlet aerosol
1000 l/h

Retaining very big particles

Retaining next large particles
8 nozzles with Ø = 1.4mm

Concentrating aerosol particles
14 nozzles with Ø = 0.6mm

Outlet gas 910 l/h

Outlet aerosol 90 l/h

In situ FTIR spectroscopy

Condensation experiment

UHV chamber
(base pressure < 10^{-10} mbar)

gas system

LEED

sample attached
to cryostat/heater
(40 - 1300 K)

FTIR-spectrometer
(Bruker IFS66v)

IR beam

detector
(MCT/DTGS)

triple evaporator
- 3 independent cells filled with SiO, Mg and Fe, for example
- Co-evaporation or layer by layer deposition

quartz crystal
microbalance (QCM)

quadrupole mass
spectrometer (QMS)

Triple evaporator for preparation of different types of thin films:

Diagram by Wetzel (KIP)

IR Ellipsometry

Ellipsometry measurements?

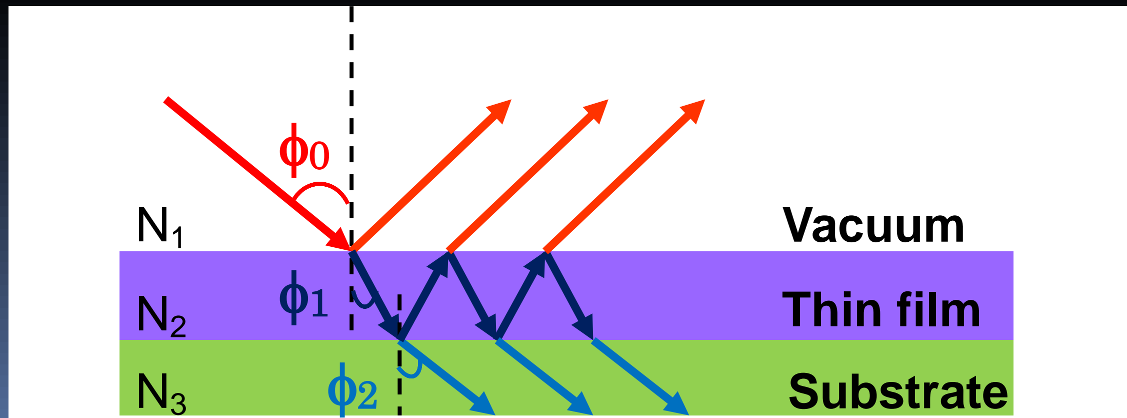
--- Possible to investigate the optical and physical properties of thin films and bulk materials

- ❖ Film thickness
- ❖ Dielectric constant

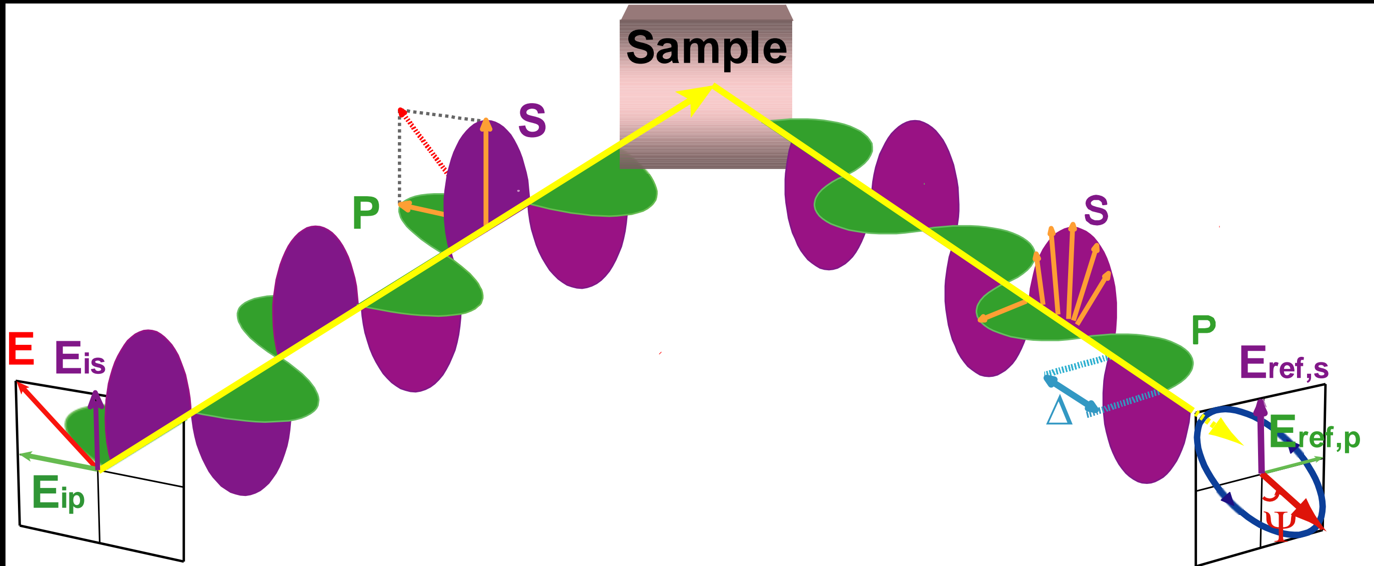
What can we measure with an Ellipsometor?

Changes in the polarization state of light when it is reflected from a surface of a sample

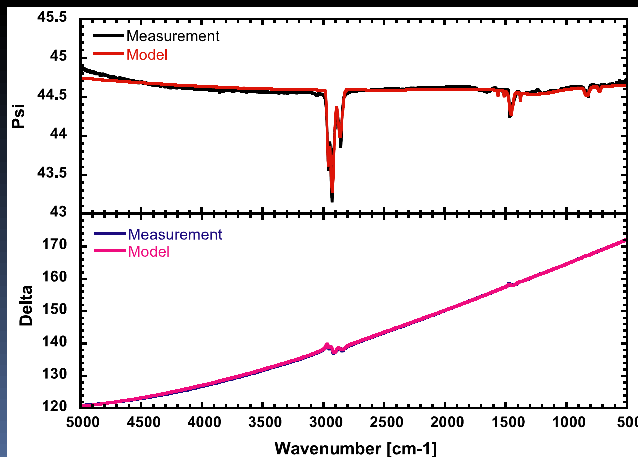
- ❖ The ratio of the amplitude reduction (Ψ)
- ❖ The phase shift induced by the reflection (Δ)



IR Ellipsometry -- Ψ & Δ --



Ψ→ the ratio of the amplitude reduction (偏光の振幅比(屈折率))
Δ → the phase shift induced by the reflection (偏光の位相差（減衰係数))



- Ψ and Δ spectra of P3HT on an evaporated Au substrate prepared by spin coating (1000 rpm: concentration 2.5%)
- Measured with the incident angle of 60°
- Poly(3-hexylthiophene) (P3HT)
  (thiophene ring with 6 carbons in the alkyl side chain)
- Type: p-type semiconductor
- Chemical formula: $(C_{10}H_{16}S)_x$

Ellipsometry -- Modeling --

These parameters are related to the Fresnel reflection coefficient R_p(p-polarized) and R_s (s-polarized). The fundamental equation for ellipsometry (the complex reflectance ratio ρ) can be described as

$$\rho = \frac{\tilde{R}_p}{\tilde{R}_s} = \tan(\Psi) e^{i\Delta}$$

- A pseudo-dielectric function can be derived by the measured values Ψ & Δ

$$\varepsilon = \varepsilon' + i\varepsilon'' = \sin^2(\Phi_1)\left\{1 + \tan^2(\Phi_1)\left(\frac{1-\rho}{1+\rho}\right)^2\right\}$$

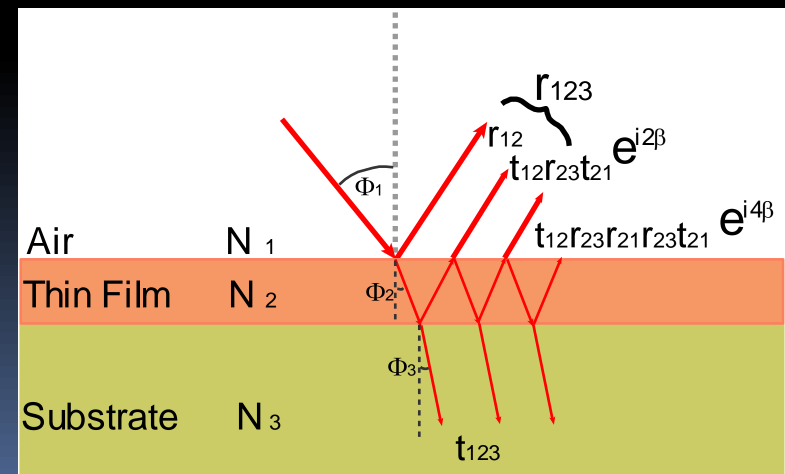
ε': real part
ε'': imaginary part
Φ_1: the angle of incidence

Film Thickness

Film thickness can be determined by interferences between light reflected from different surfaces:

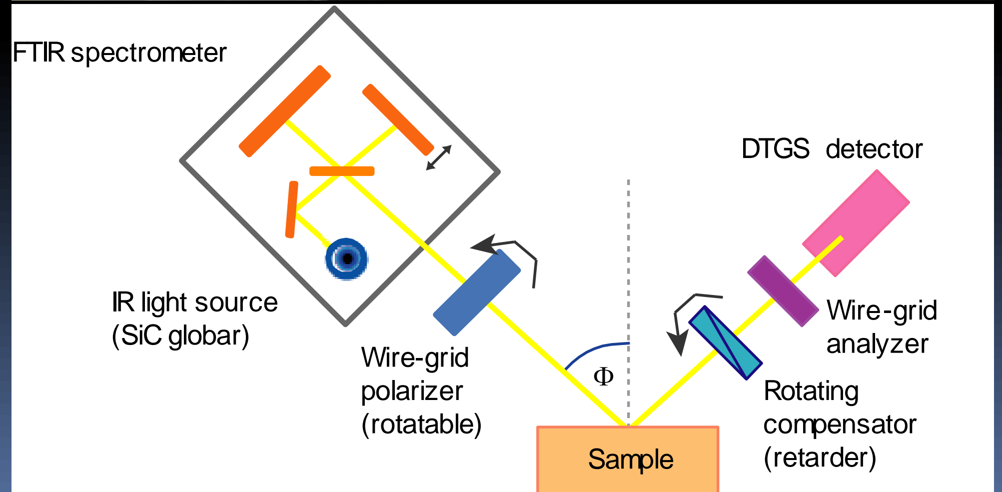
$$\mathbf{d} = \beta \frac{\lambda}{2\pi\sqrt{N_2^2 - N_1^2 \sin^2(\Phi_1)}}$$

d: the film thickness
β: the phase factor
Φ_1: the angle of incidence
λ: the wavelength of light



cont. IR Ellipsometry

- A rotating compensator IR Ellipsometer from J.A. Woollam Co., Inc (IR-VASE)
- In the spectral range of 333 to 5900 cm^{-1} (30 – 1.7 μm)
- The angle of incidence can be adjusted the range between 26° and 90°
- Ψ & Δ measurements



Uni. Heidelberg, KIP

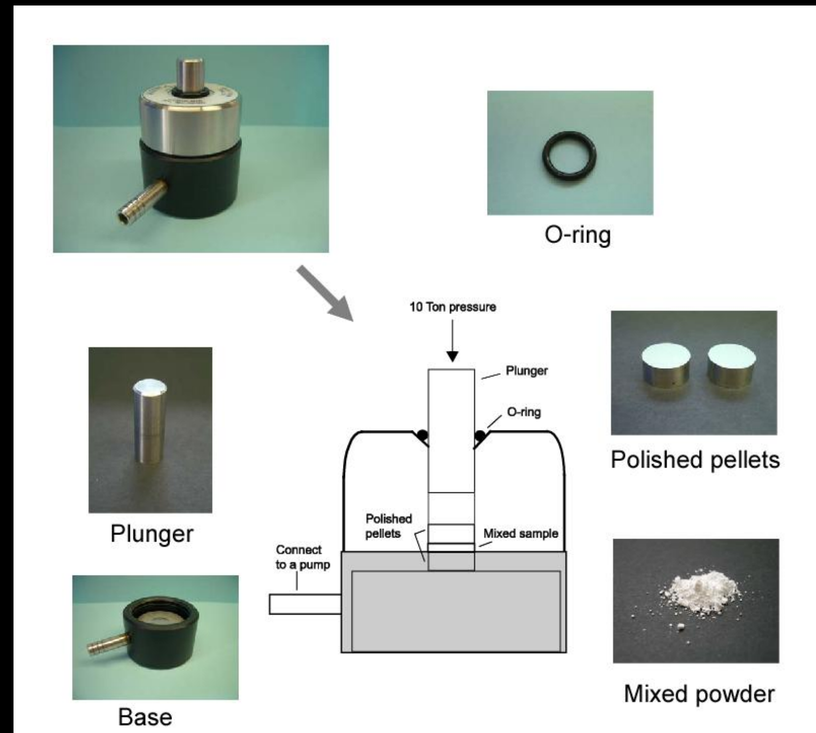
Sample Preparation

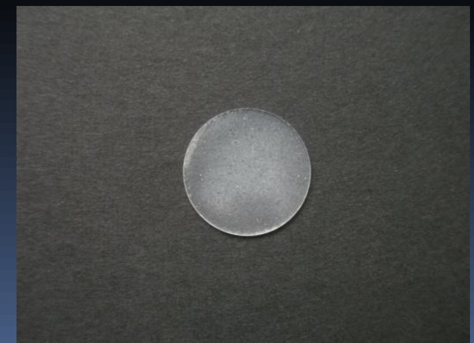
Depending on the experimental purpose and device, the sample preparation changes

- Pellet technique
- Aerosol spectroscopy
- On substrate
  - -- Evaporation
  - -- Spin coating

Pellet Technique

- The ratio of a sample and the KBr powder is 1 to 500 in weight (when a particle size is about 1μm).
- Mixing them well in order to segregate the particle as minuscule as possible.
- For making a 0.55mm thick and 13 mm in diameter pellet, 0.2g of the mixed sample is placed in an evacuatable pellet die.
- Using a hydraulic press, first evacuating all air slowly and applying 10 Ton load to the die for 20-30 min.
- As a medium
  --- KBr (0.23-25 μm)
  --- NaCl (0.18-20 μm)
  --- CsI (0.24-70 μm)





Pellet Technique -- Adv. & Disadv.--

Advantages:

- Low sample consumption
- Possible to keep the pellets in a desiccator
- Quantitative measurement is possible → Possible to calculate an absorption coefficient

κ (absorption coefficinet) = (absorbance*area of the pellet (cm^2))/m

m: mass of the samples in the pellet (mg)

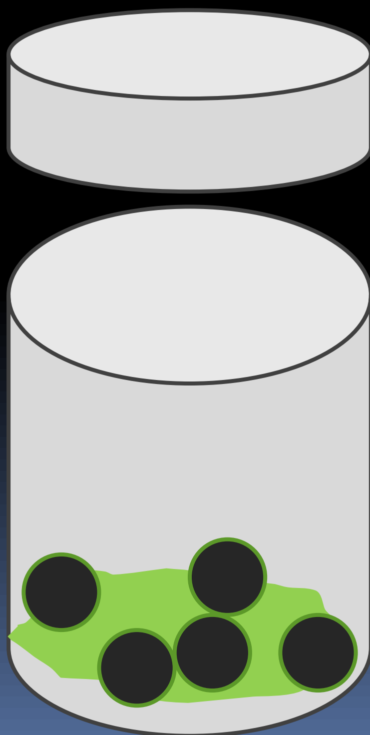
Disadvantages:

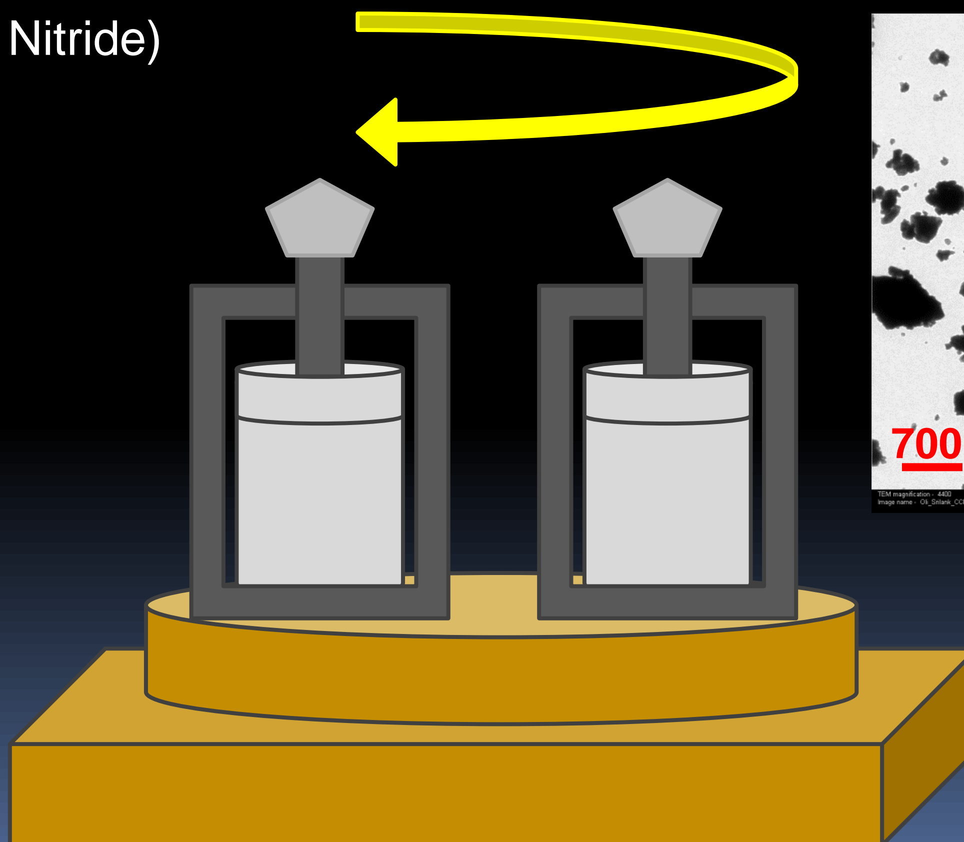
- Particles may transform during the grinding procedure
- A configuration of particles can hardly be visible whether particles are thoroughly isolated in the KBr matrix or not
- There is a risk to cause the powdered sample structure deformation in relation to high pressurization required for the technique

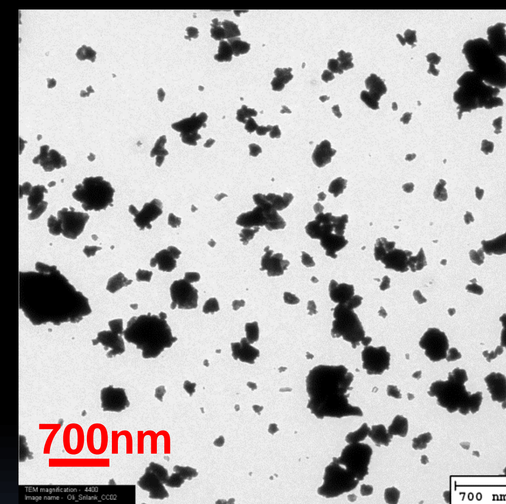
Samples for Aerosol Spectroscopy

Ball mill

→ A grinder --- possible to grind a material into micron-sized particles by making use of centrifugal force







TEM image (Natural olivine)

On Substrate

Transmission:	Reflection:	Substrate thickness:
• Si • Al_2O_3 •Diamond …	• ITO (indium tin oxide) • Au • Ge …	0.7 – 1 mm (Thicker → avoid the intererence, but absorption gets stronger)

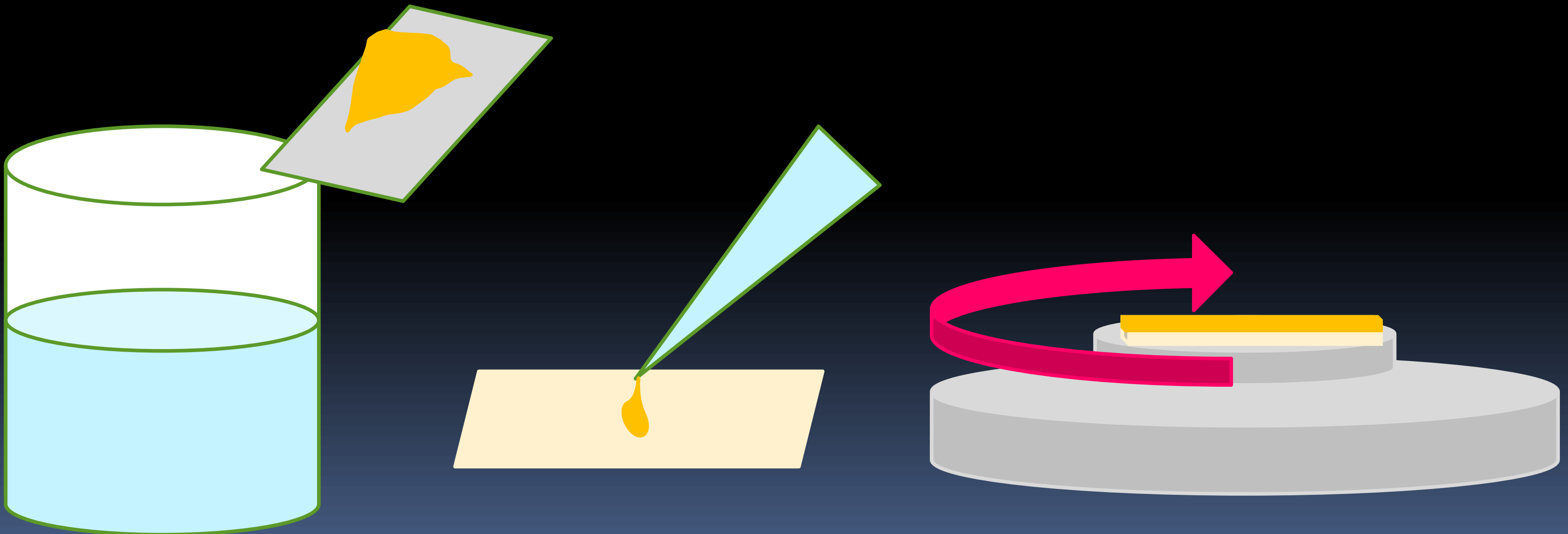
Vacuum evaporation:

- Clean the wafer with ethanol and acetone in order to remove the unnecessary water on the wafer
- Set the pressure 10^{-8} to 10^{-9} mbar and temperature 150°C for 2 to 3 hrs for cleaning the surface of the wafer
- After 30 min. cooling, transfer the wafer to the sample chamber
- Set the pressure 10^{-9} mbar and temperature around 130 to 150 °C
- Switch on the filament for 30 min. Then, put the wafer in the sample chamber
- Bake out the wafer for 2 hrs
- The thickness of the layer is determined by the microbalances in the chamber
- After finishing the bake-out, it is possible to start the spectroscopic measurements for the prepared sample

cont. On Substrate

Spin coating:

- ➢Powdered sample is dissolved in a solvent
- ➢Put a small amount of solution on a substrate
- ➢Transfer the substrate to a spin coating machine
- ➢The substrate is rotated on the machine at high speed, so the solution is uniformly distributed due to centrifugal force
- ➢A film thickness is controlled by a spin speed & concentration of a solute

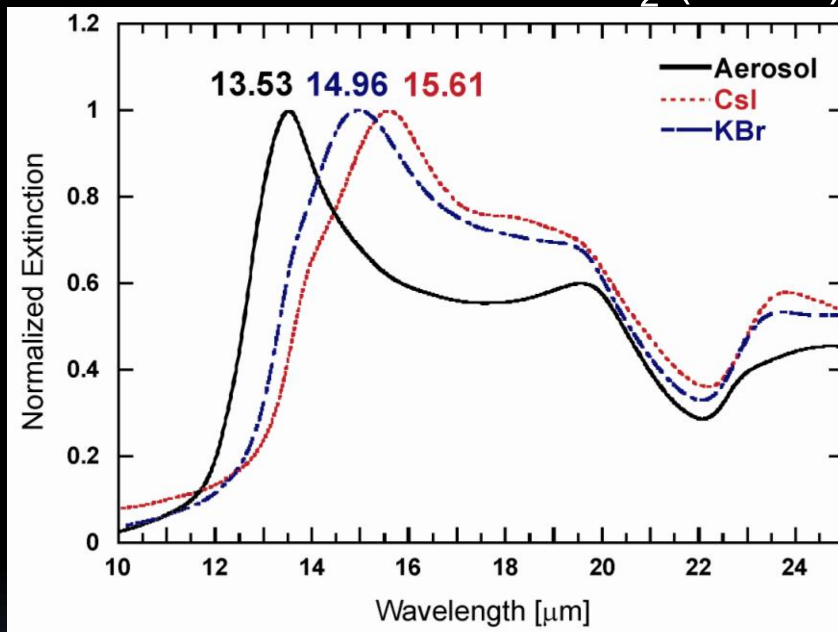


Measurements & Data Analysis

<Pellet vs. Aerosol Measurements>

--Medium effect--

TiO_2 (Rutile)



(Tamanai et al. 2009)

ε_m

N_2 → 1.0

KBr → 2.3

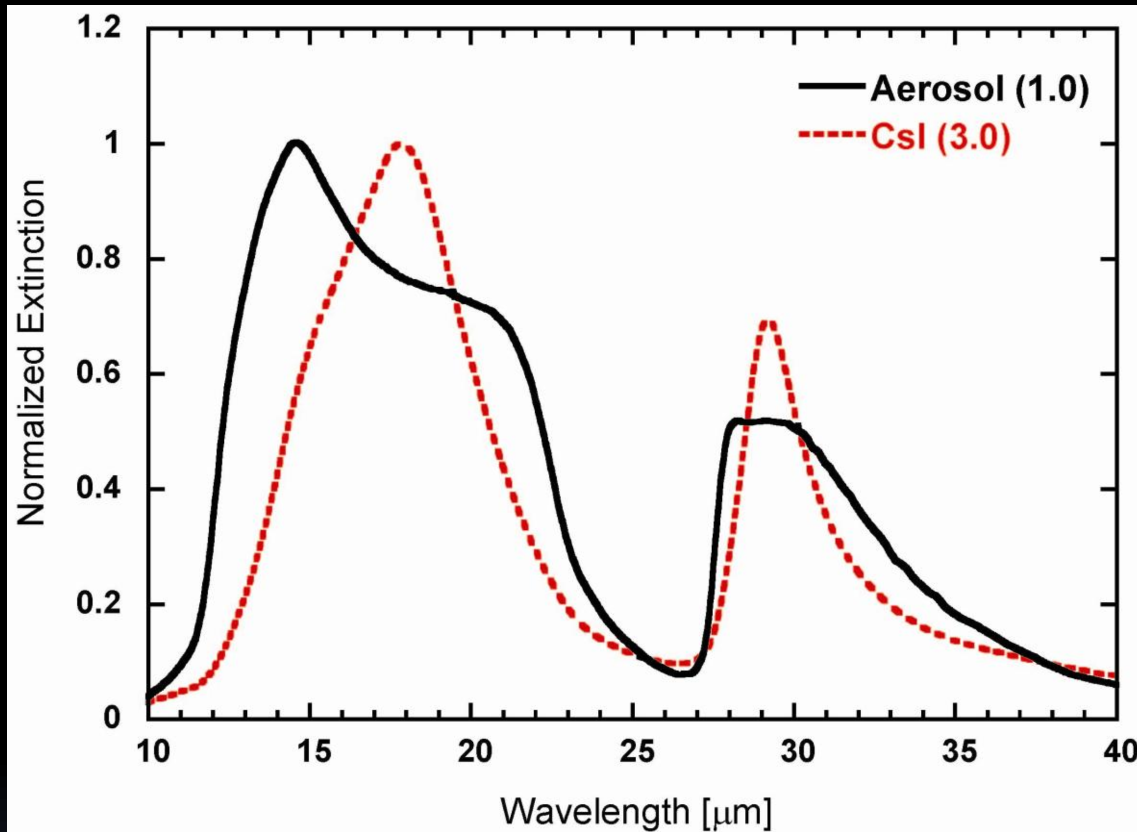
CsI → 3.0

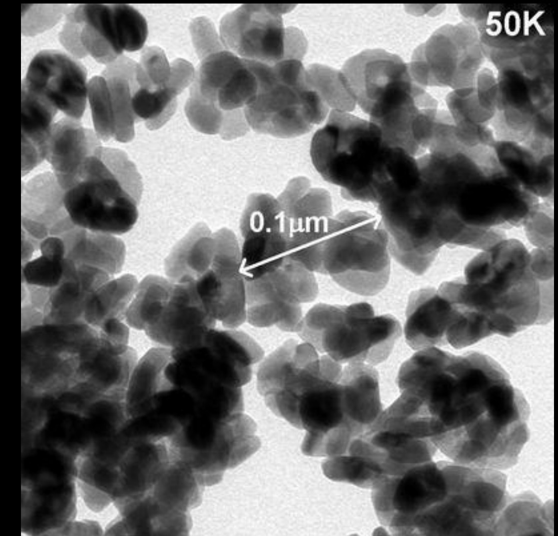
The influence of its electromagnetic polarization.

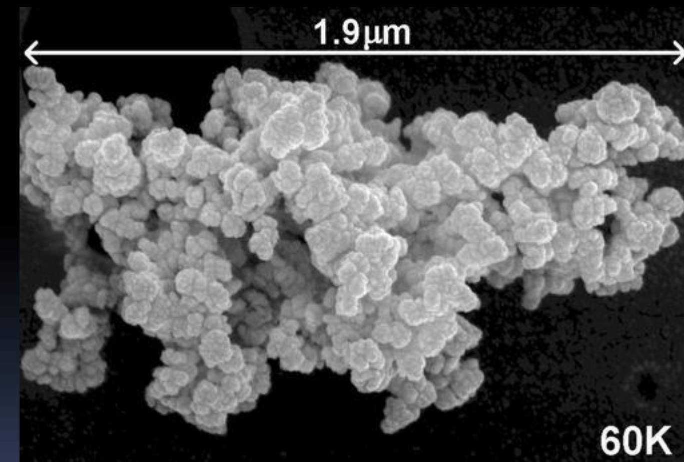
KBr :
(Potassium Bromide)
Mixing ratio 1:500
(sample:KBr)
d=13mm ; mass=0.2g

CsI :
(Cesium Iodine)
Mixing ratio 1:500
(sample:CsI)
d=13mm ; mass=0.22g

-- Disparity in spectra --







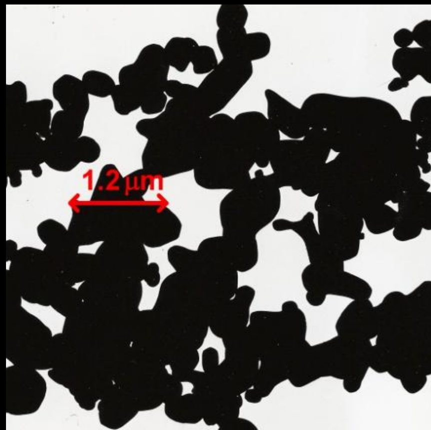
Tamanai et al. (2009)

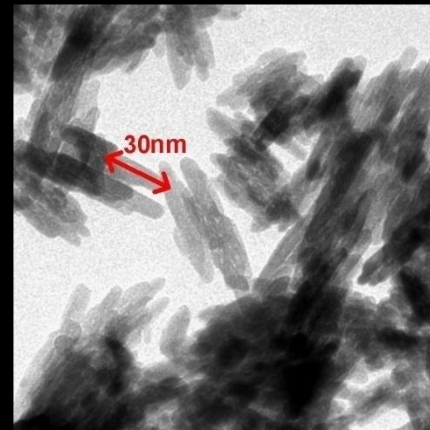
- Using different dispersion methods
- Particles may transform during the grinding procedure
- Sample structure deformation caused by the high pressurization required
- Particle orientation

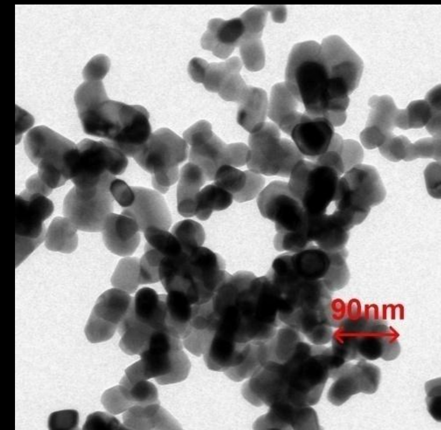
-- Morphological effects --

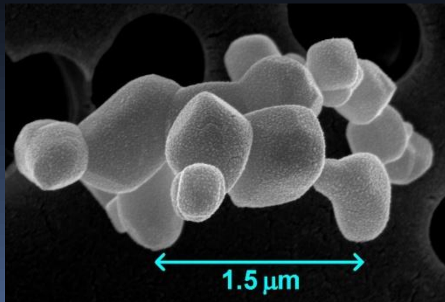
TiO_2 (Rutile)

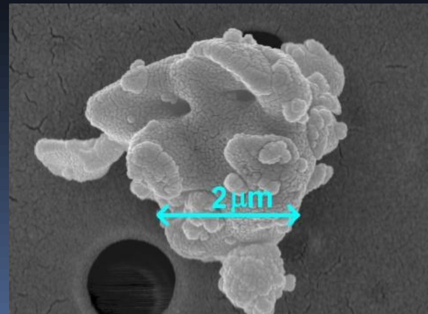
Irregular shape w/ rounded edges	Irregular shape with not rounded edges	Long and thin	Rounded
R1	R2	R3	R4

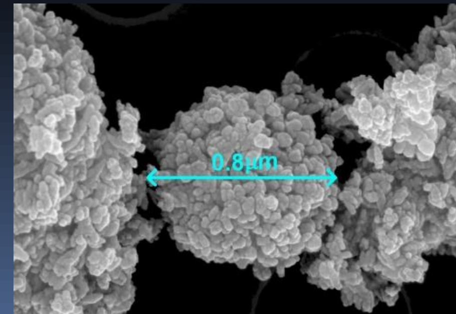


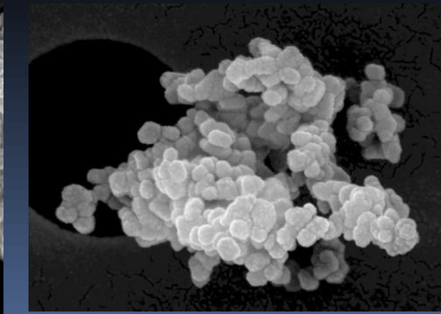




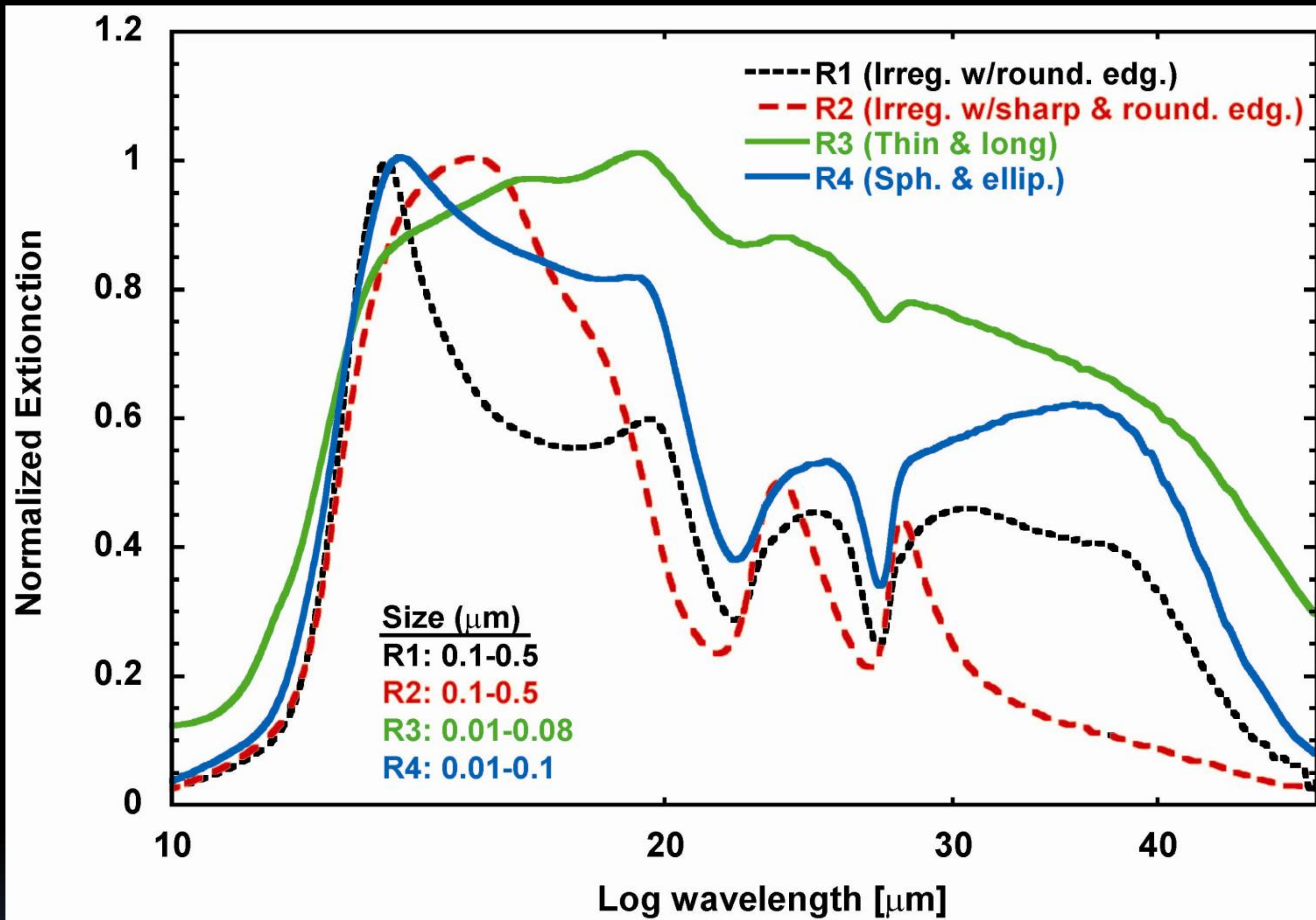








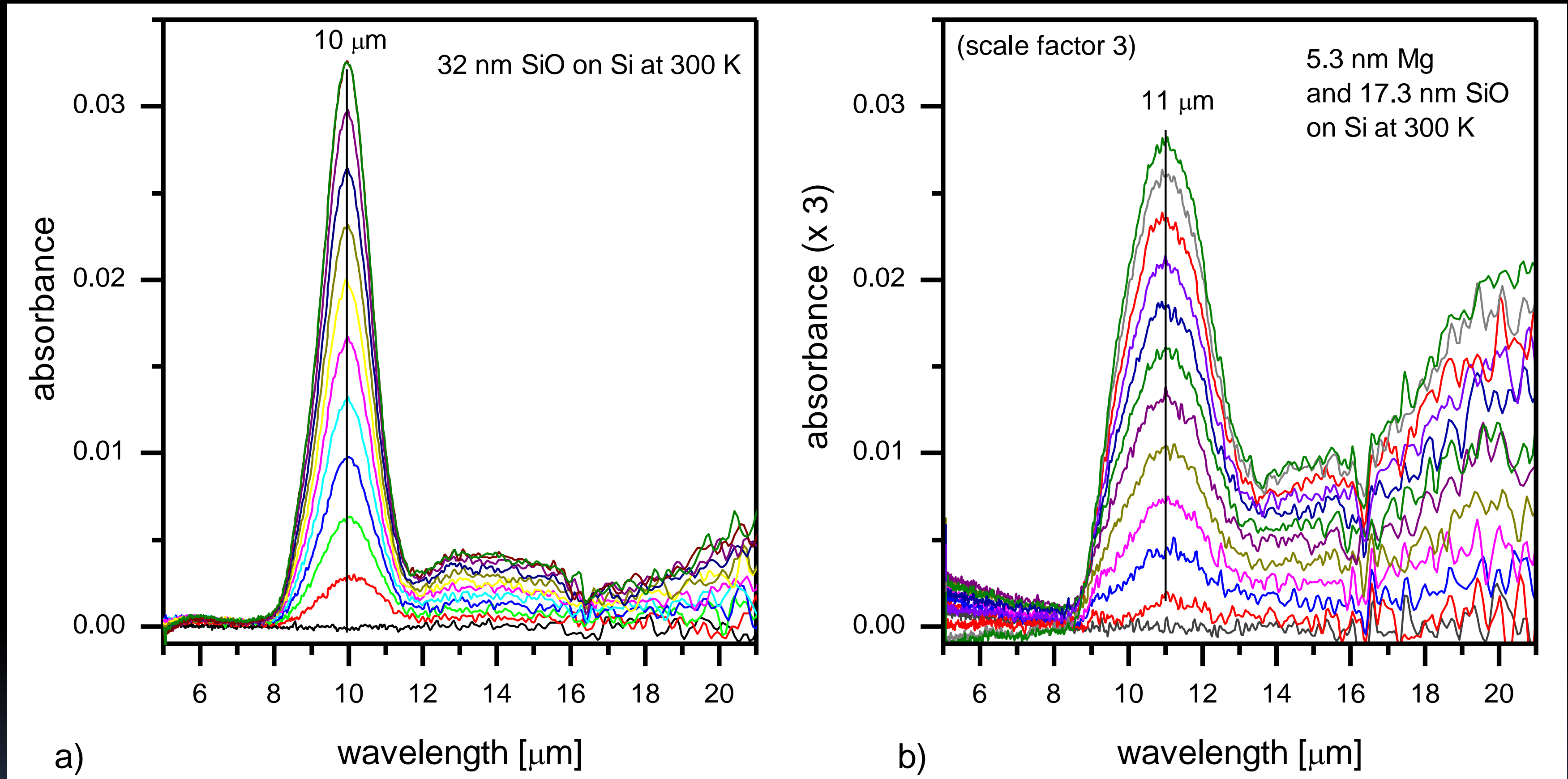
(TEM & SEM images: at Pathology w/ Dr. Nietzsche)



Peaks (microns)

R1	**13.53**	**19.56**	**24.70**	**30.30**	**35.80**
R2	**15.33**		**23.51**	**27.95**	
R3	**16.47**	**19.25**	**23.39**	**28.27**	
R4	**13.85**	**19.27**	**25.15**	**35.87**	

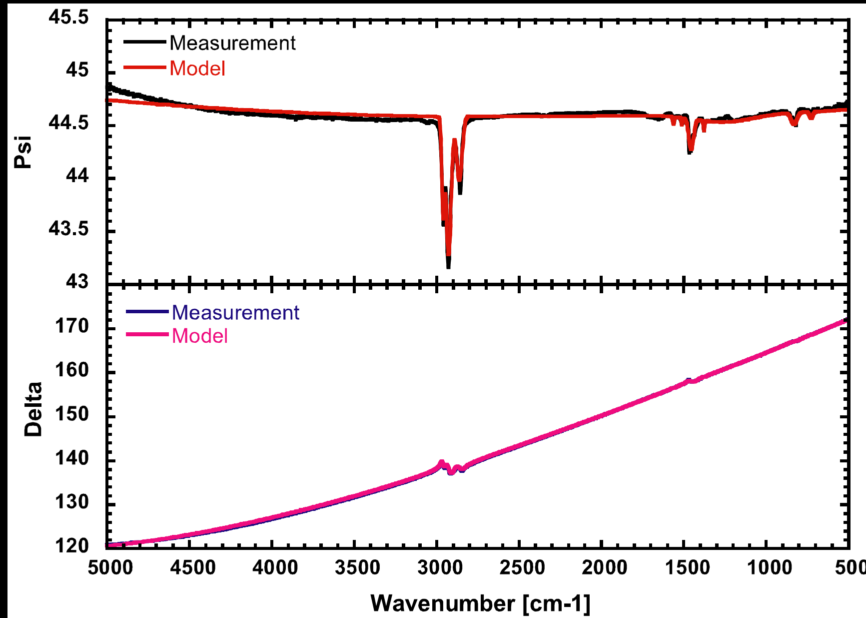
In situ IR Measurements

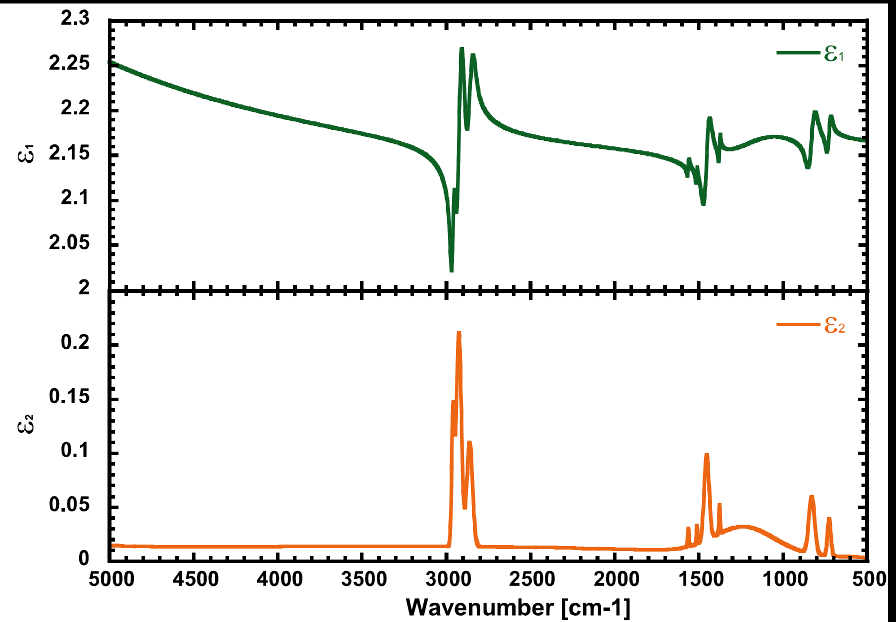


- Redshift of the Si-O stretching vibration bands (from 10 μm to 11 μm) and broadening are confirmed. Metal itself seems to be "invisible".

Ellipsometry Measurements

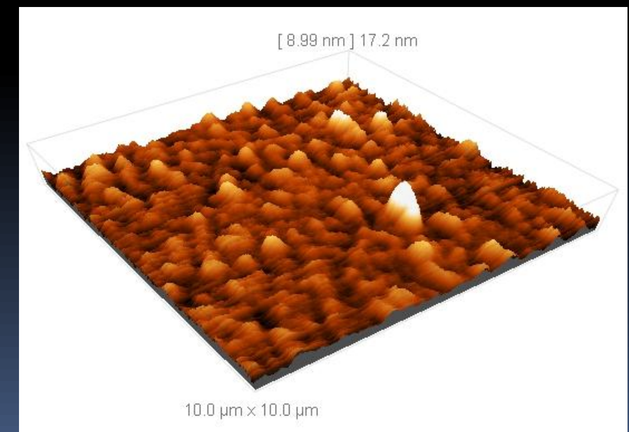
Spin coating (P3HT on Au substrate)





- The thickness of P3HT thin film deposited on Au substrate is 218.6 nm.
- The average surface roughness is approximately 15 nm obtained by AFM analysis 10x10 μm).
- All of the dielectric functions here is derived by means of Gaussian oscillators for model fittings.

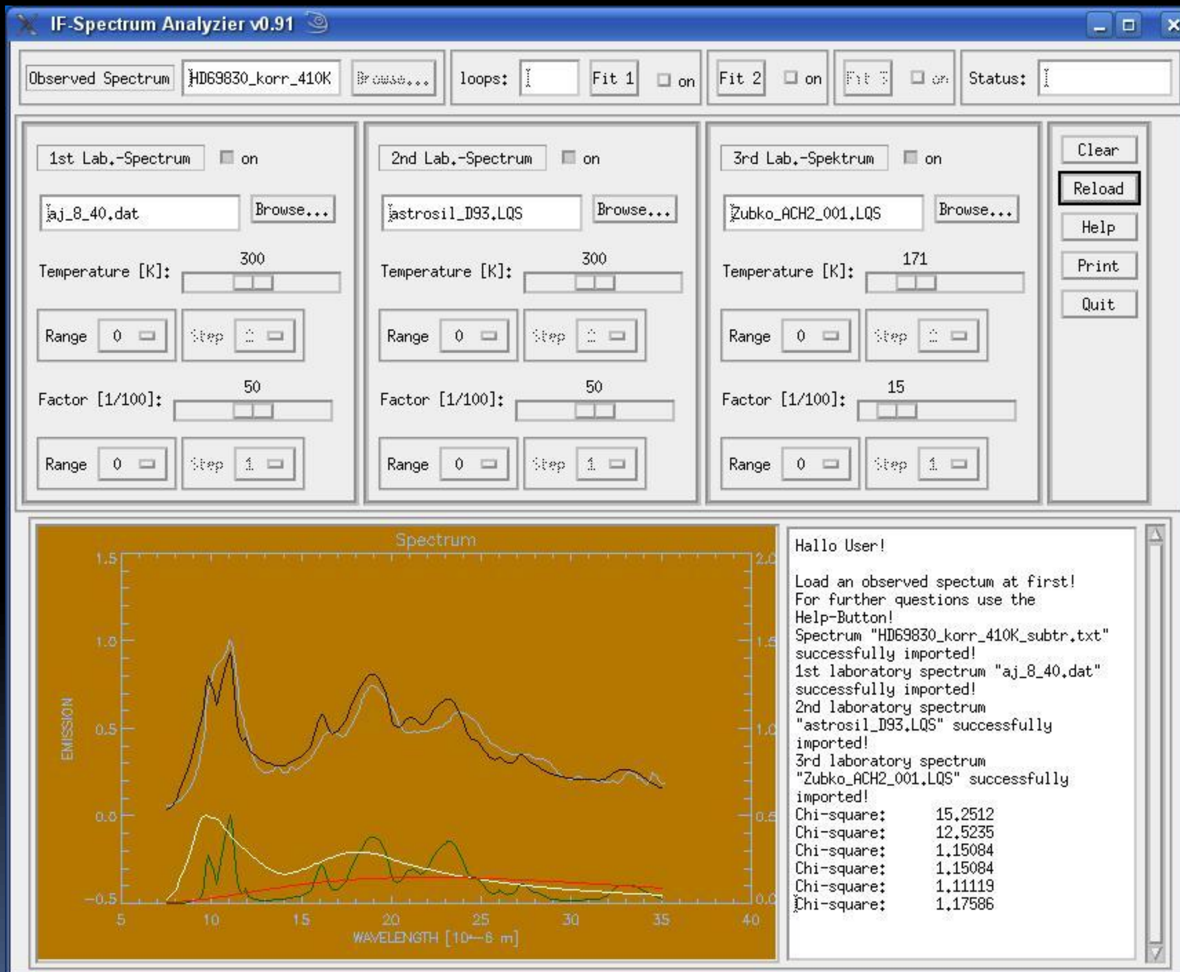
Tamanai et al. 2010 (conf.Tessaloniki, Greece)



Morphological feature of lateral dimensions

Astronomical Application

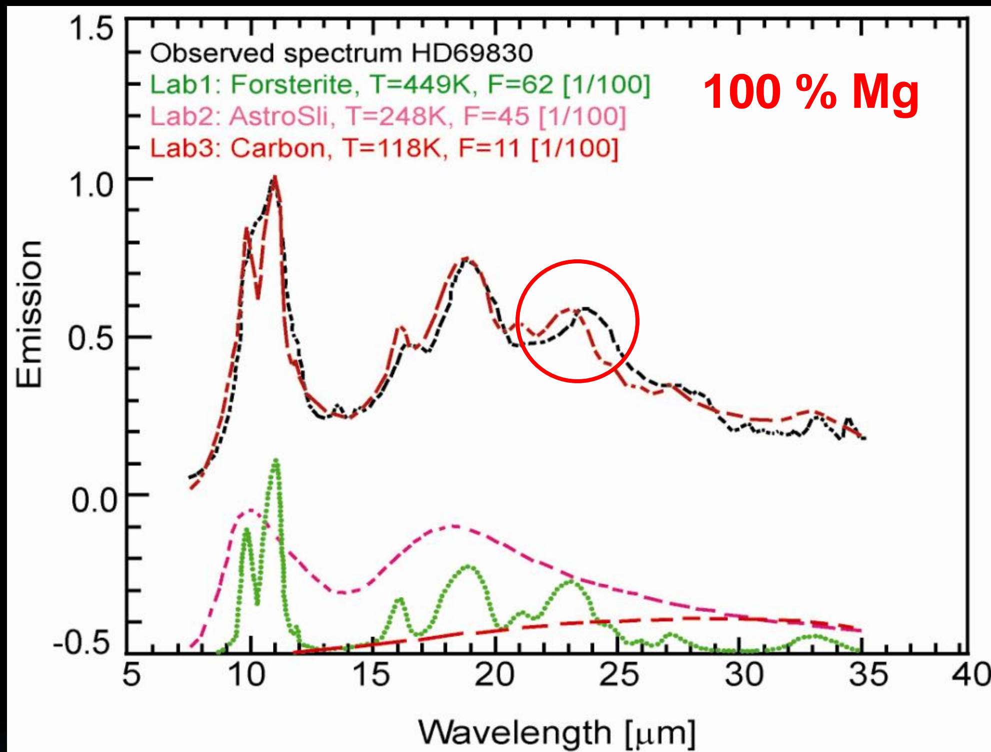
First steps: Some own fitting tests for HD 69830



- The spectrum → the product of the emission cross section of the dust with a Planck function given by the equilibrium T of the dust

– IDL programme IRSA by Lutz Bornschein

Some own fitting tests for HD 69830



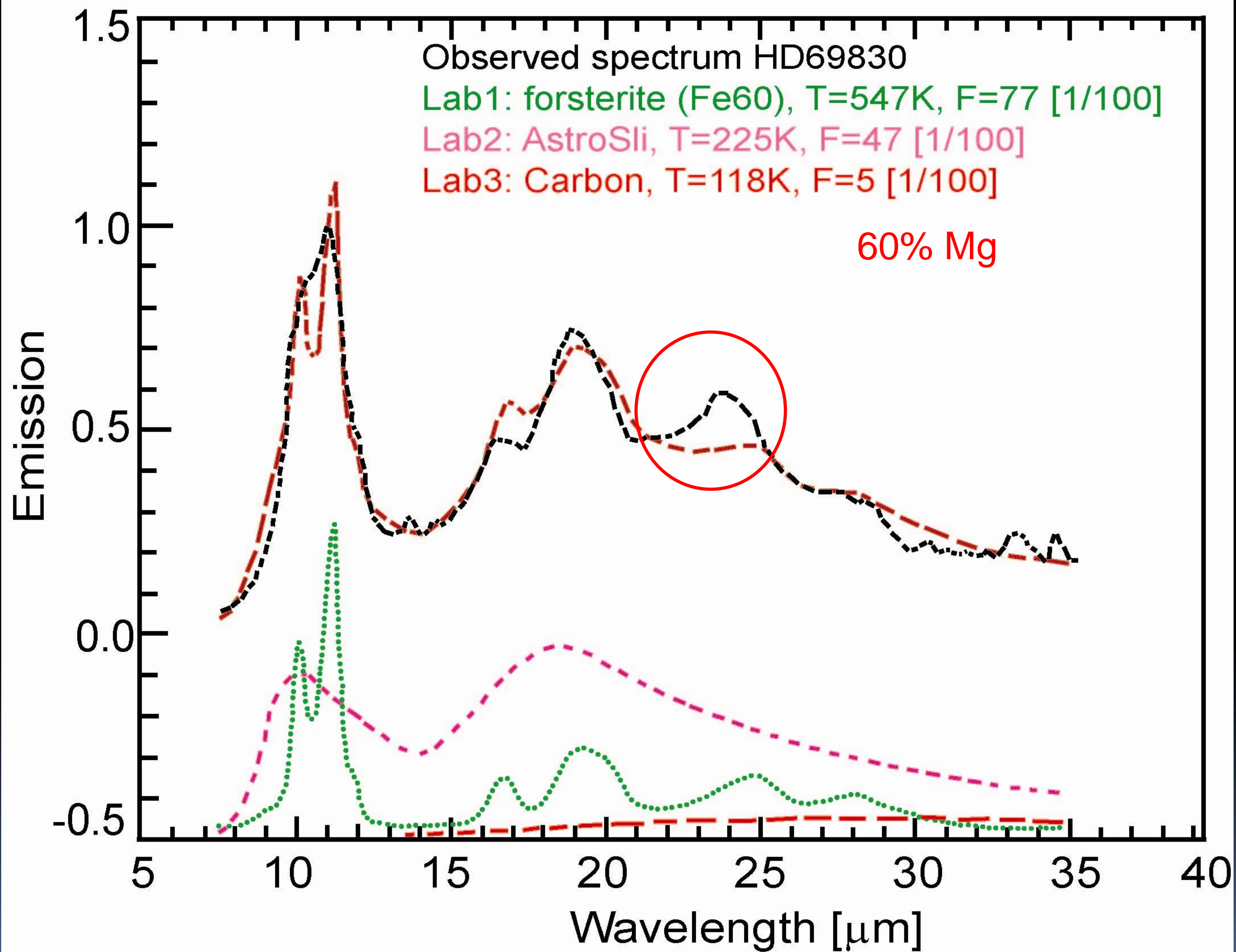
Intention: simplification, search for real „hard facts“ (constraints on dust mixture)

Used dust spectra:
- olivines and pyroxenes from aerosol measurements
- Koike et al. (2003) olivines
- amorphous silicates
- „carbon“ for grey emission (may also mimic colder dust component)

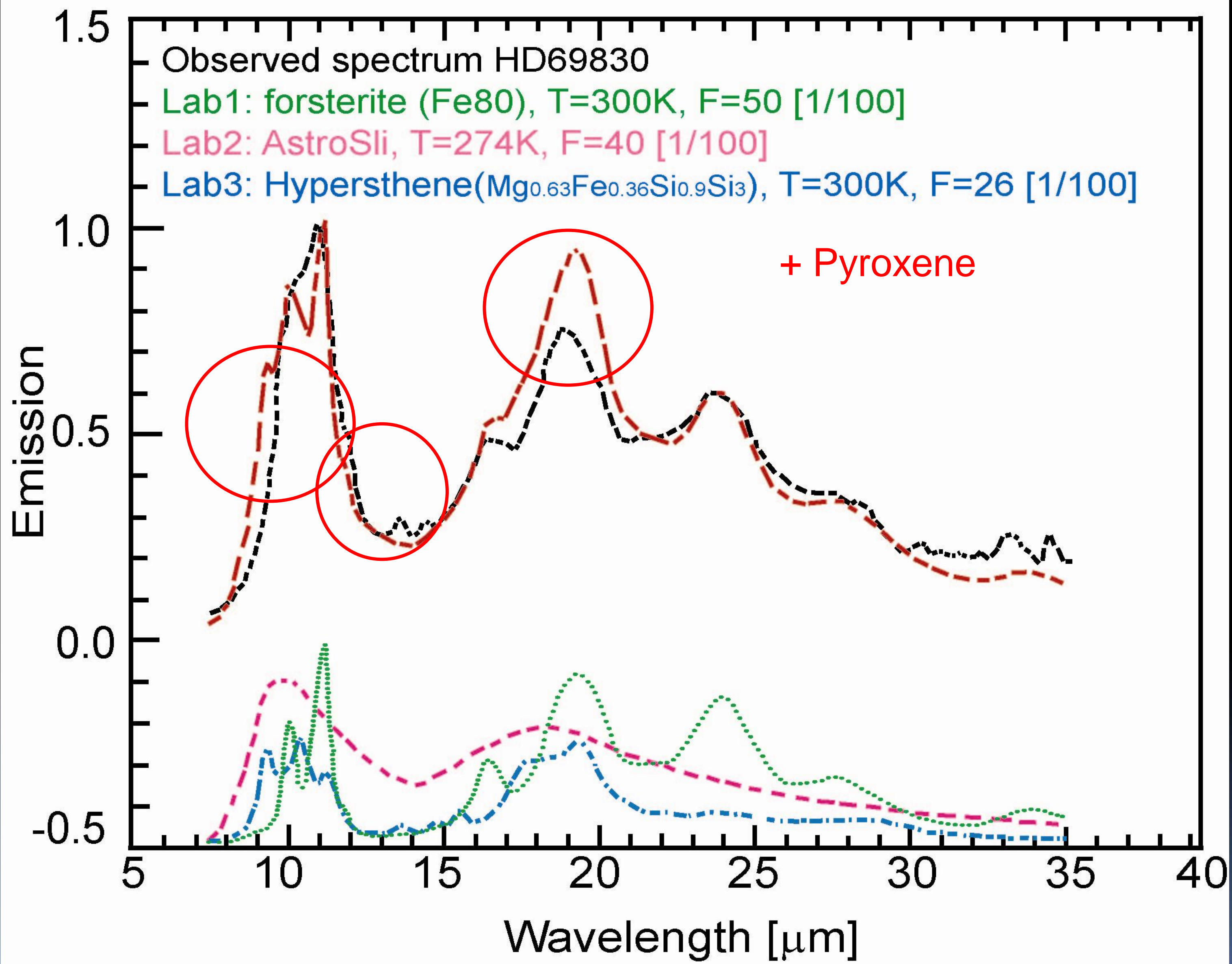
Three-component model:
- Fo60+ olivine (synthetic, Koike)
- Astronom. Silicate (amorphous, D&L93)
- „carbon“ cold dust

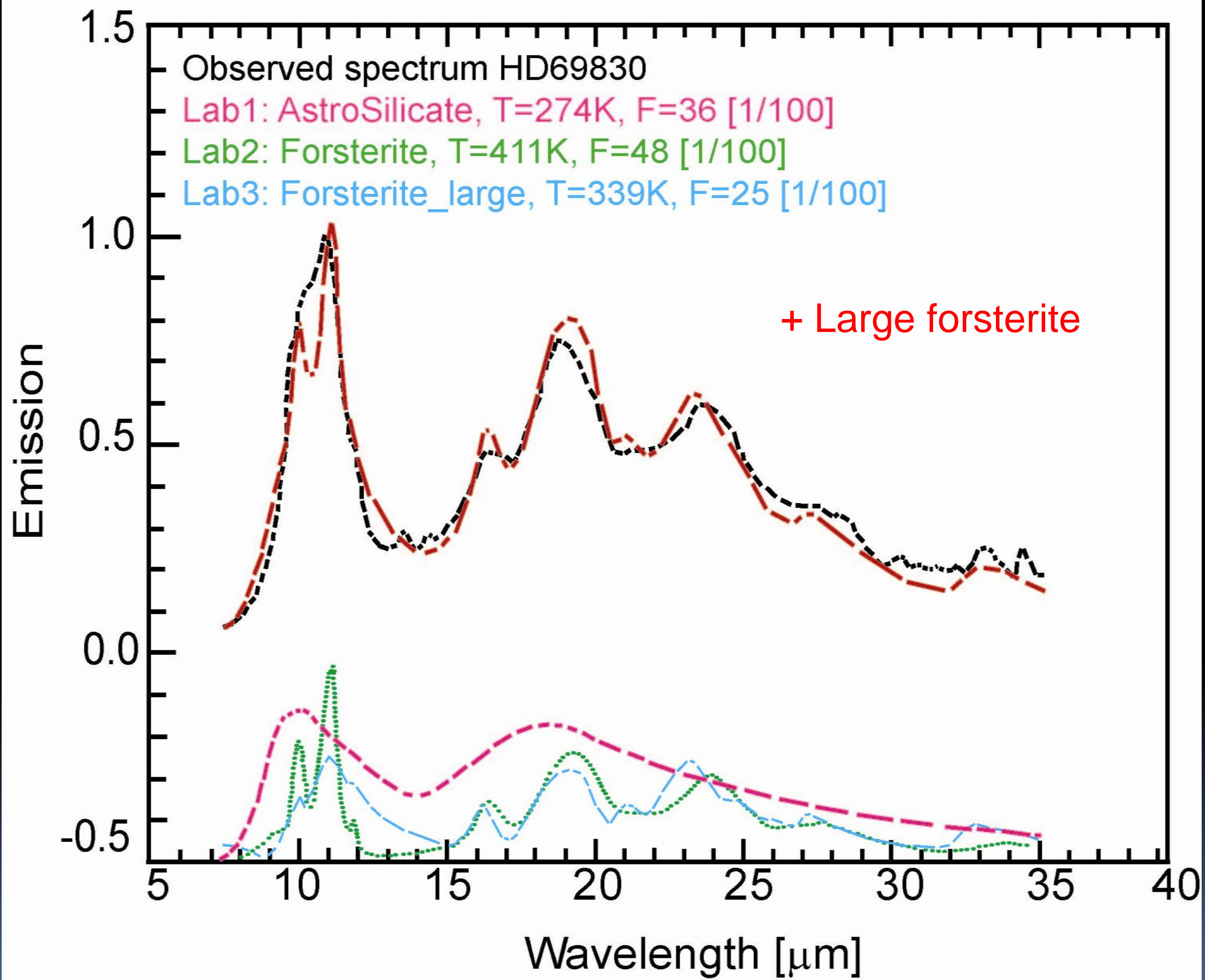
- Beichman et al. (2005): Spitzer IRS
- T(dust) ~ 400K
- M(dust) ~ 1000 zodi

K0 V
13 pc
2000 Myr ?
3 planets



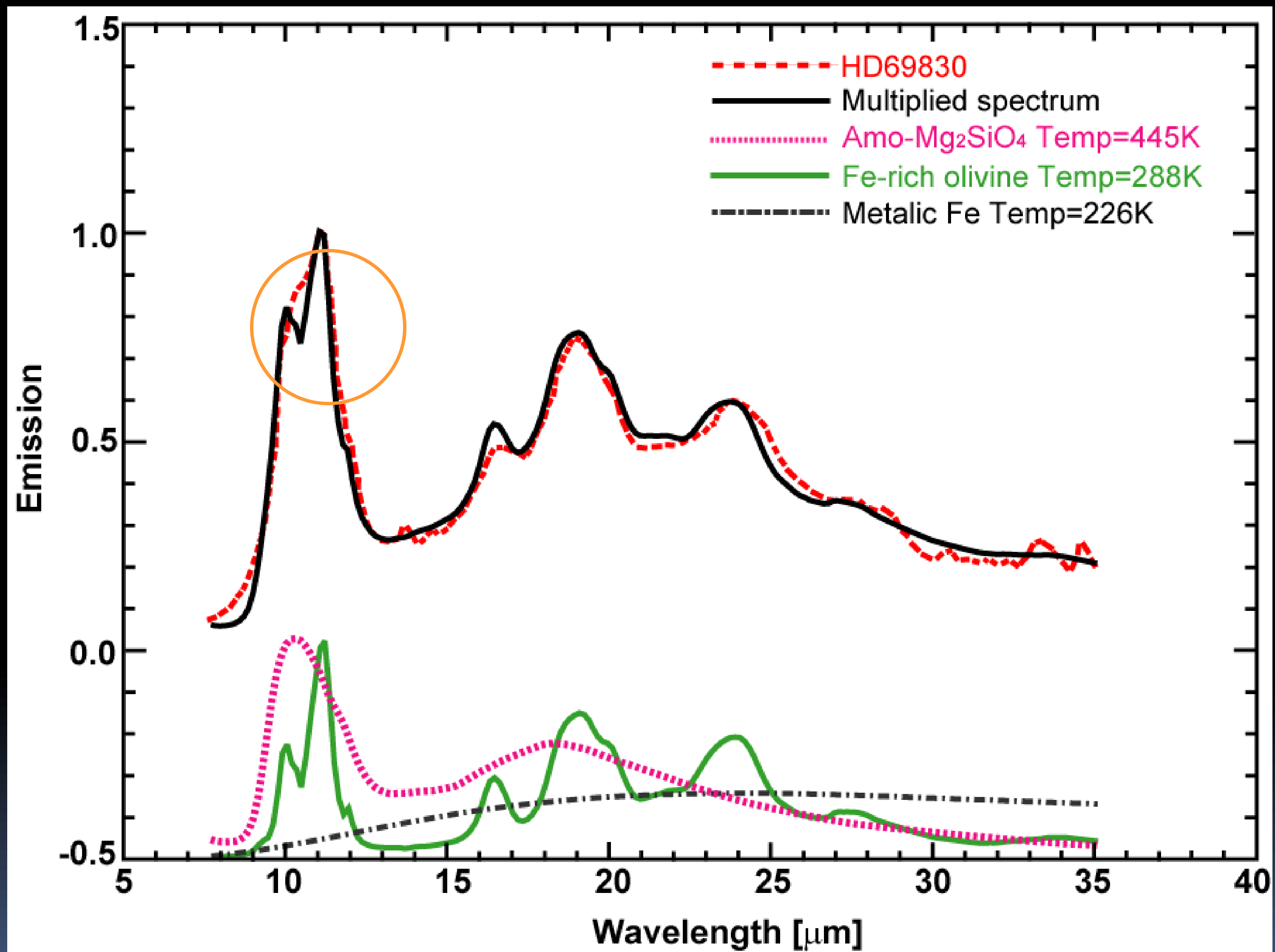
Observed spectrum HD69830
Lab1: forsterite (Fe60), T=547K, F=77 [1/100]
Lab2: AstroSli, T=225K, F=47 [1/100]
Lab3: Carbon, T=118K, F=5 [1/100]
60% Mg
Emission
1.5
1.0
0.5
0.0
-0.5
5
10
15
20
25
30
35
40
Wavelength [μm]


Observed spectrum HD69830
Lab1: forsterite (Fe80), T=300K, F=50 [1/100]
Lab2: AstroSli, T=274K, F=40 [1/100]
Lab3: Hypersthene(Mg0.63Fe0.36Si0.9Si3), T=300K, F=26 [1/100]
+ Pyroxene
Emission
Wavelength [μm]
1.5
1.0
0.5
0.0
-0.5
5
10
15
20
25
30
35
40



Observed spectrum HD69830
Lab1: AstroSilicate, T=274K, F=36 [1/100]
Lab2: Forsterite, T=411K, F=48 [1/100]
Lab3: Forsterite_large, T=339K, F=25 [1/100]
+ Large forsterite
Emission
Wavelength [μm]
1.5
1.0
0.5
0.0
-0.5
5
10
15
20
25
30
35
40

Best fit for HD69830



Tamanai & Mutschke 2010

Database

Peak Search: to search for your desired spectra via inputting a peak position.

Basic information: Chemical formula, density, particle size, product info., etc…

Plot: Aerosol and CsI pellet measurements. Numerical data sets are downloadable.

Images: obtained by scanning and transmission electron microscopes (SEM & TEM)

Database of aerosol spectra for cosmic dust

Laboratory Astrophysics Group of the AIU Jena

Created by David Schmitz

http://elbe.astro.uni-jena.de

Possibilities for Future

Current project

Investigation for electro organics

Infrared spectroscopic measurements for organic thin films in ultra high vacuum (UHV) condition

Verify:

- Effects through the surface metallization and interface intermixing
- Degradation of IR and VIS spectra by light, adsorbates, heating

  --- Detect weak points & physical origin

  --- Role of morphology and interfaces

IR-Setup at Clustertool

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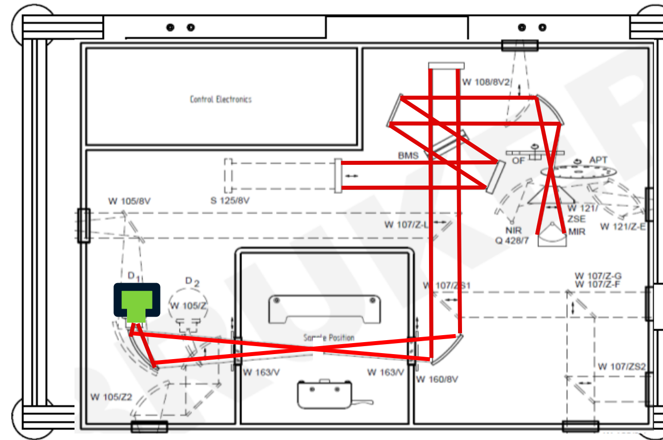
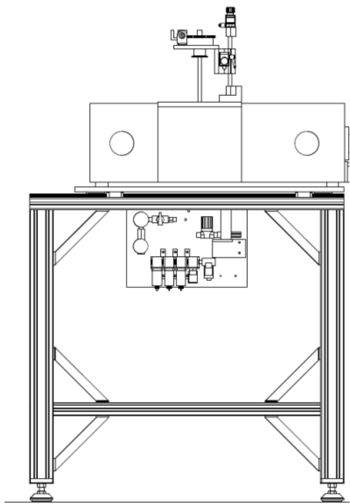
BRUKER Vertex 80v
FTIR spectrometer

Top view



Side view



Diagrams by Glaser (KIP)

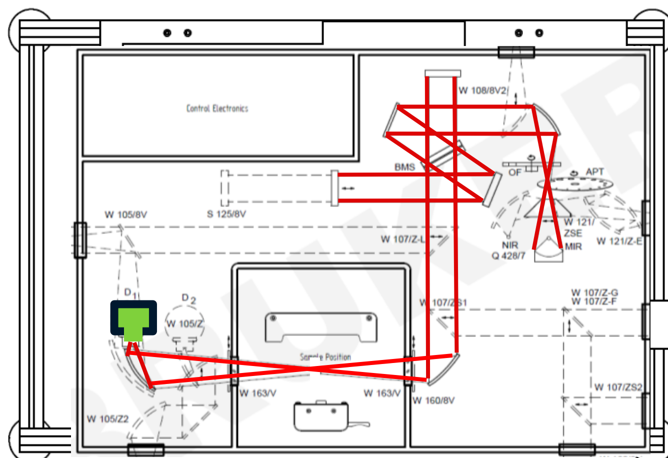
IR-Setup at Clustertool

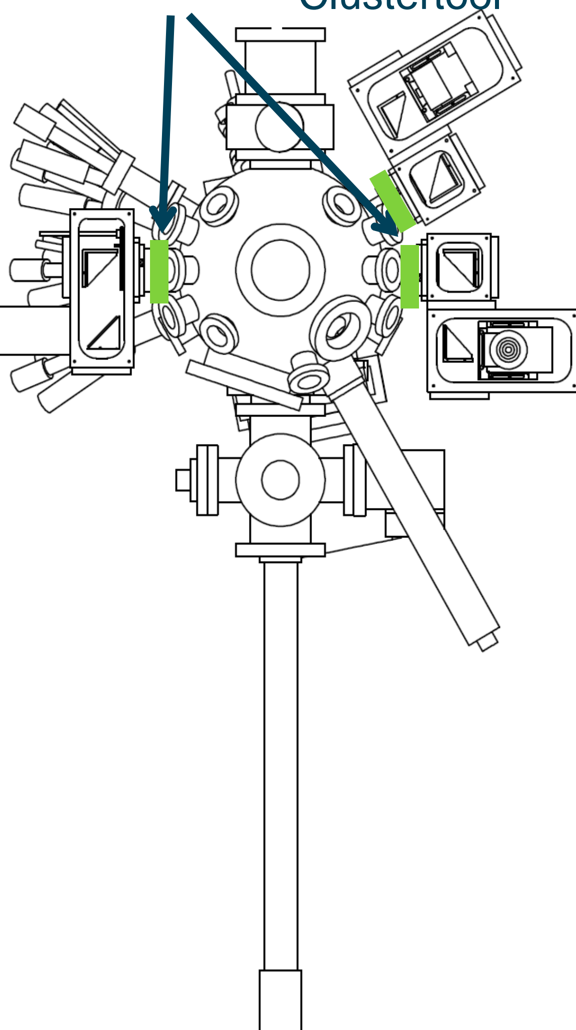
BRUKER Vertex 80v FTIR spectrometer

Top view

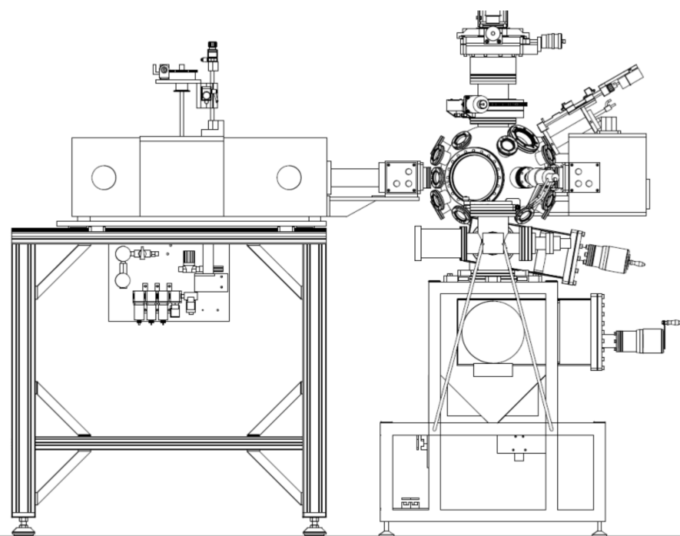
KBr window

Connection to Clustertool





Side view



IR-Setup at Clustertool

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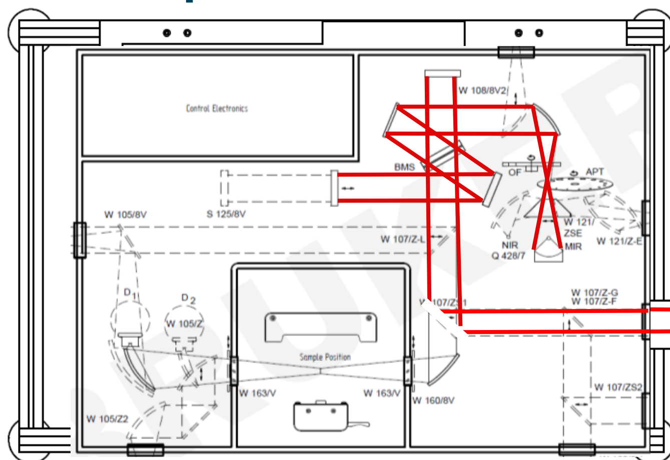
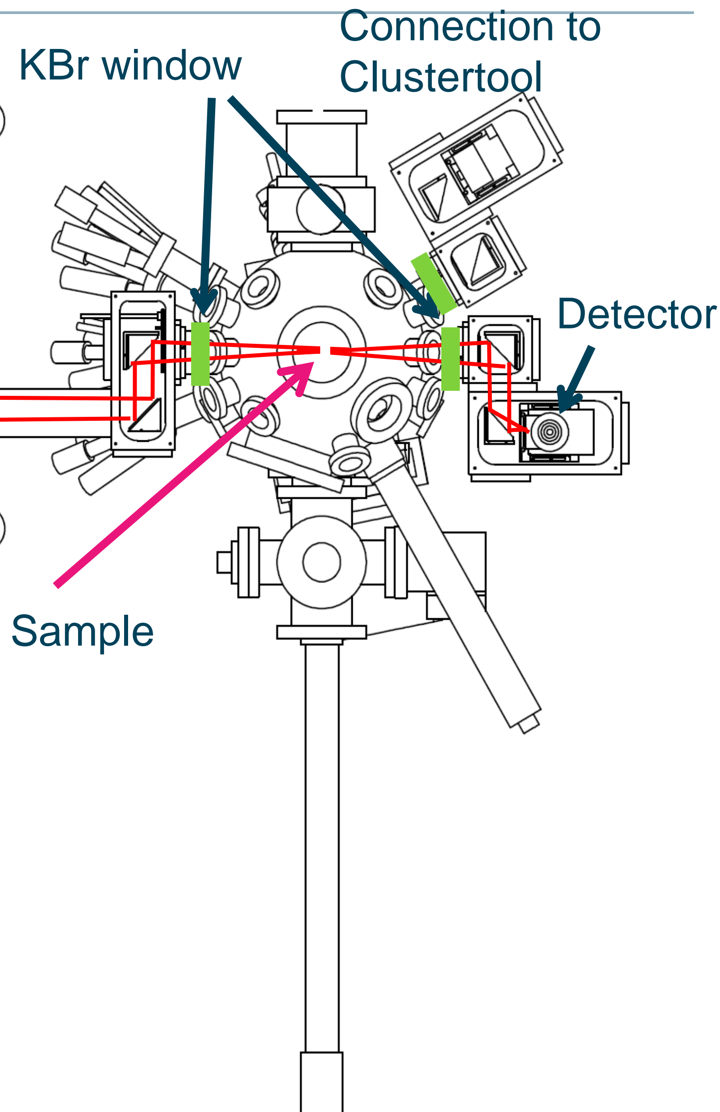
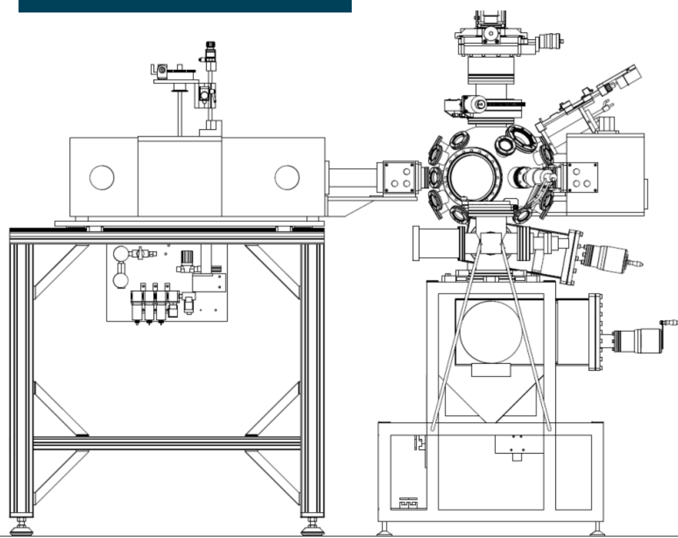
Top view

BRUKER Vertex 80v FTIR spectrometer





Side view



IR-setup at Clustertool

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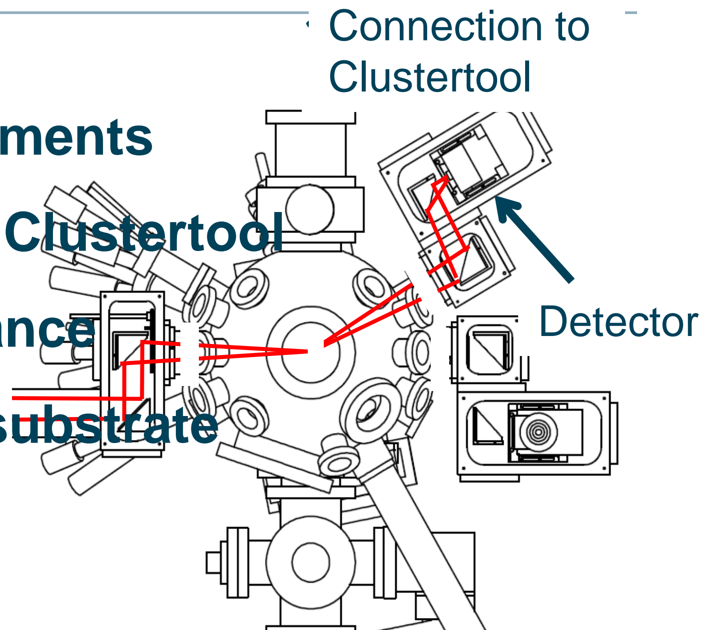

- Transmission and Reflection (75°) measurements
- Transfer from/to the other chambers of the Clustertool
- 2-crucible evaporator and quartz microbalance
- Resistive heating and cooling (LN_2) of the substrate
- Mass spectrometer
- Separate transfer system
- Spectral range extension for the FIR and NIR-range

Spectral range in spectrometer: ~ 20 – 10 000 cm^{-1} (500 - 1µm)

spectral range in UHV: ~ 330 – 10 000 cm^{-1} (30 - 1µm)

- UV-VIS-spectrometer

IR-setup at Clustertool

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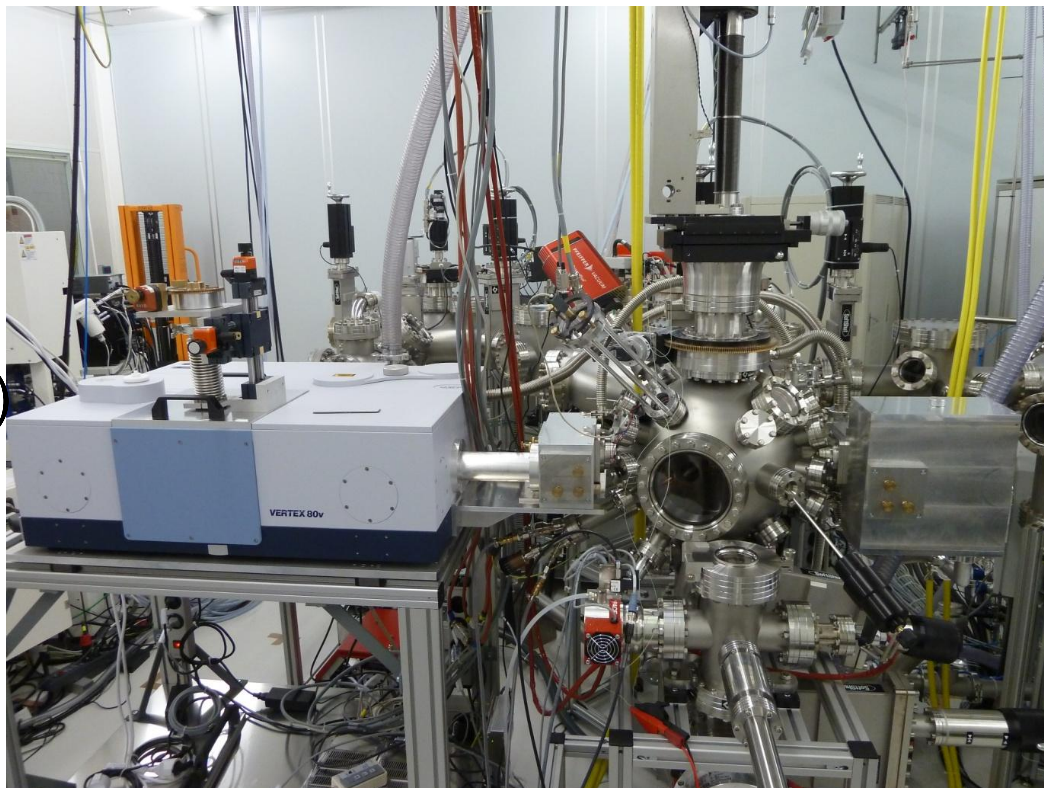
Devices:

- FTIR Spectrometer
- XPS (X-ray photoelectron spectroscopy)
- UPS (ultraviolet photoelectron spectroscopy)
- IPES (Inverse photoemission spectroscopy)
- AFM (Atomic force microscope)
- SEM w/ FIB (Scanning electron microscope with focused iron beam)



iL at Heidelberg, Germany

Summary

FTIR spectroscopy
- Aerosol spectroscopy
- In-situ FTIR spectroscopy
- IR ellipsometry

Sample preparation
- Pellet technique
- Aerosol technique
- On substrate

Current to future
- The growth of organic layers under physical vapor deposition
- Optical properties
- Interface effects

e.g.
Deriving optical constants of deposited film by means of IR ellipsometry
→ Derived optical constants can be used for theoretical calculations

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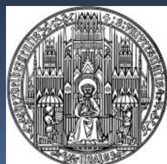

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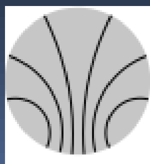

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