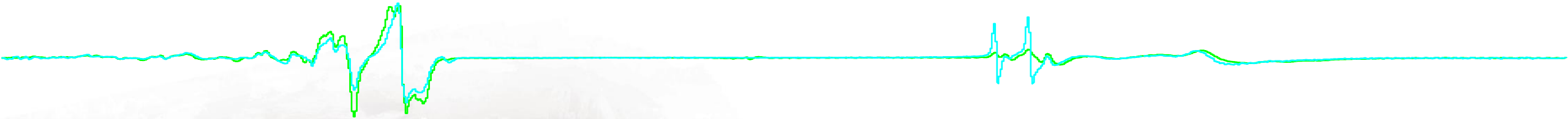


SYNCHROTRON INFRARED MICROSPECTROSCOPY

Christophe Sandt
SMIS beamline
Synchrotron SOLEIL

School on Synchrotron Light Sources and Their Applications
Smr 4205 January 13, 2026

PLAN

General introduction → Applications → Introduction to FTIR Spectroscopy

Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

PLAN

General introduction → Applications → Introduction to FTIR Spectroscopy

Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

WHY USE SYNCHROTRON FOR INFRARED MICROSPECTROSCOPY?

1) HIGH SPATIAL RESOLUTION

- Conventional μFTIR (thermal source): 20-25 μm best resolution (high flux, low brilliance)
- Synchrotron Radiation μFTIR: 3-20 μm resolution (low flux, high brilliance)

2) ULTRABROADBAND SOURCE

- The synchrotron source covers the whole IR domain:
  - Far-IR 25-900 μm
  - Mid-IR: 2.5-25 μm
  - Near-IR: 1-2.5 μm
- Thermal sources only cover part of the far-IR and near-IR
- IR lasers are narrow-band

3) BECAUSE IR SPECTROSCOPY CAN or MAY ANSWER YOUR SCIENTIFIC QUESTION

1) Chemical composition of the sample
2) Chemical phase of the sample
3) Spatial distribution of the molecules in the sample
4) Molecular conformation or orientation in the sample
5) Interaction of the sample and its environment
6) Measuring the sample under constraint (temp., press., stretch., irradiation, aging, reacting …) in real-time
7) Sample must be measured without contact or non-destructively

SAMPLE CONSTRAINTS

1) Sample must be **chemically heterogeneous**.
   - No gaz or liquid (unless there is a liquid phase separation)
   - Heterogeneity at the **micron scale** for **microspectroscopy**
   - Heterogeneity at the **nano-scale** for **nano-IR** techniques

2) **Small samples** that can not be measured at lower resolutions
   - Microparticles
   - Animal or plant cells
   - Microfibers…

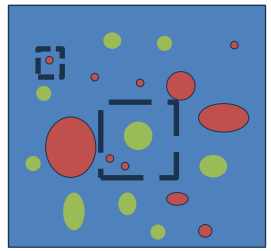
3) Sample must be in a suitable **form**:
   - **Thin** for transmission measurements
     (few µm to few tens of µm)
     - Can be naturally thin
     - Can be thin-sectioned
     - Can be compressed in a **Diamond Compression Cell** -► may induce loss of spatial organization
   - **Flat** and **reflective** for reflection measurements
   - **Flat**, **smooth** and **solid** for Attenuated Total Reflection (ATR) measurements

4) Sample **preparation** is paramount and must be specifically adapted to the technique
   1) Thin sections
   2) Polishing
   3) Embedding/no embedding
   4) Chemical fixation
   5) Flattening
   6) …

5) Experimental plan
   - IR spectroscopy is most often an indirect technique:
     - Need appropriate controls for comparison
     - Need the proper dynamic for the chemical changes expected
   - Slow measurements at high resolution:
     - Small sample sizes
     - Target specific regions
   - Number of samples (Statistical significance, statistical power)

What synchrotron IR source does **not** do

- Provide better sensitivity
  - Unless you can get better sensitivity from measuring at higher spatial resolution

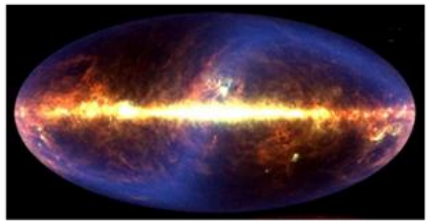


- Give narrower absorption bands
  - The absorption band width is caused by the conformational freedom of the molecules
  - Absorption bands measured with an IR or a synchrotron source will have the same width

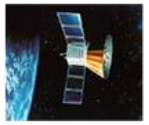
- Penetrate deeper in sample
  - The synchrotron source can not measure thicker samples than conventional sources
  - Absorption obeys the Beer-Lambert-Bouguer law for all sources
  - Near-IR radiations penetrate 10-100 times deeper than mid-IR in samples
    - But what is the point of having micrometer lateral resolution over millimeters in the axial direction?

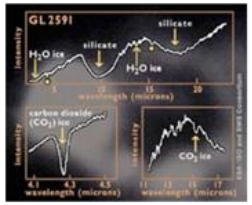
INFRARED SPECTROSCOPY IN SCIENCE & TECH

From parsec to nm



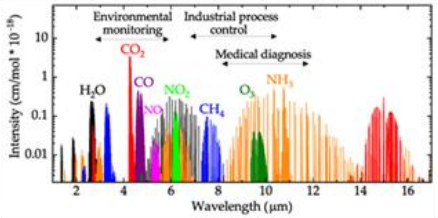
The Infrared Sky
January 28, 1998
DIRBE Team, COBE, NASA

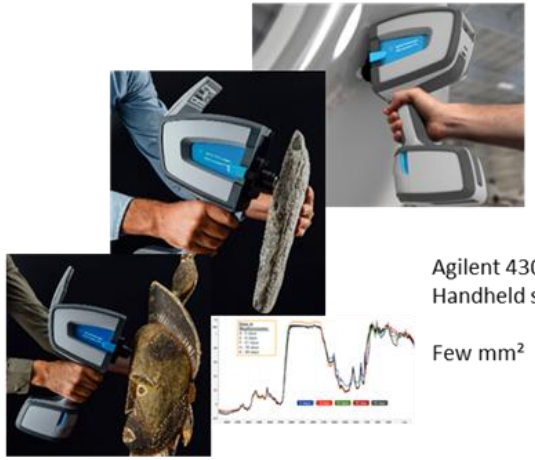




Warm dust ~100 µm
Cool stars energy peak ~ 1µm
Giant planets ~ 6-15µm
PAH 6 µm, silicates 10 µm
Dust re-radiation ~ 20-200µm

Atmospheric analysis
km²

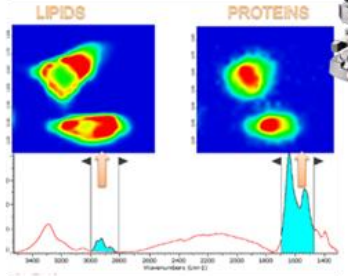




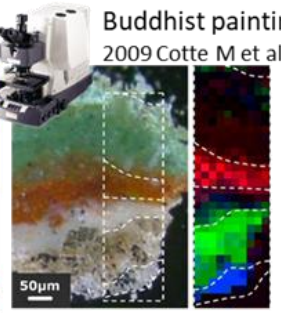
Agilent 4300
Handheld spectrometer

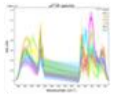
Few mm²

Single HeLa cell
2008 Chio-Srichan S et al.
Few µm²



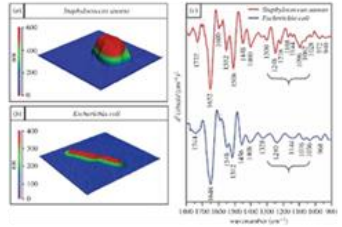
Buddhist painting
2009 Cotte M et al.

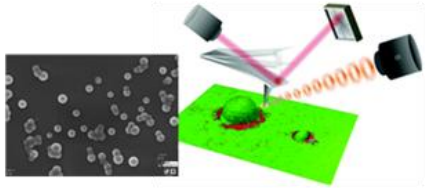




Single bacteria
2018 Kochan et al.
Interface

1000 m





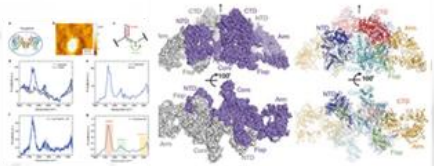
Single nanoparticle
2018 Mathurin et al.
Analyst

10-20 nm

Mid IR spectroscopy is used across multiple scales & sciences

Single protein
2020 Ruggieri et al.
Nature Comm, 11

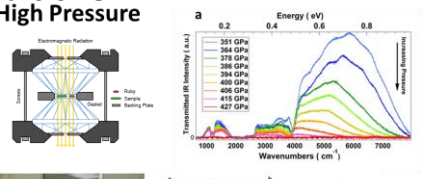
Few nm

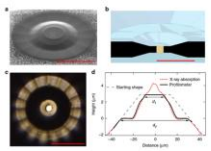


IR MICROSPECTROSCOPY @ SYNCHROTRONS

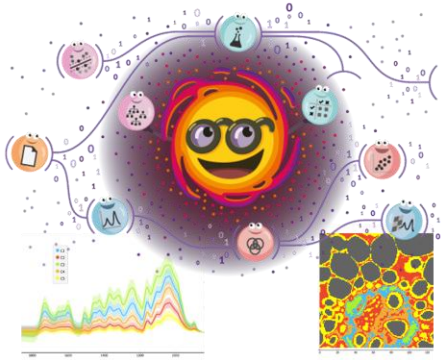
Materials in extreme conditions

High Pressure



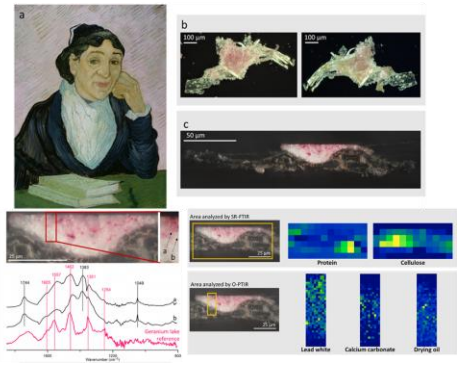


Data analysis

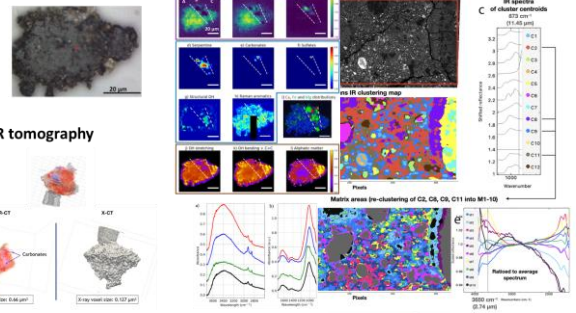


Quasar software
https://quasar.codes

Cultural heritage

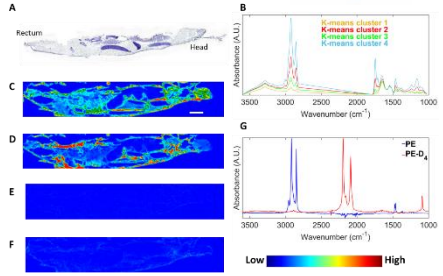


Astrophysics

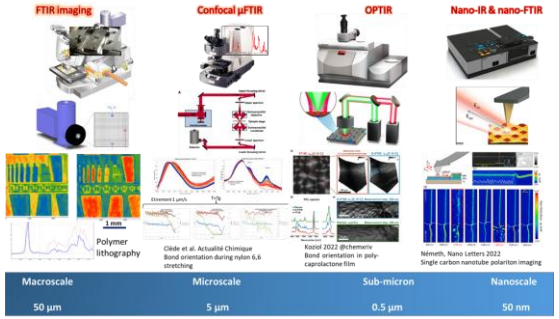


IR tomography

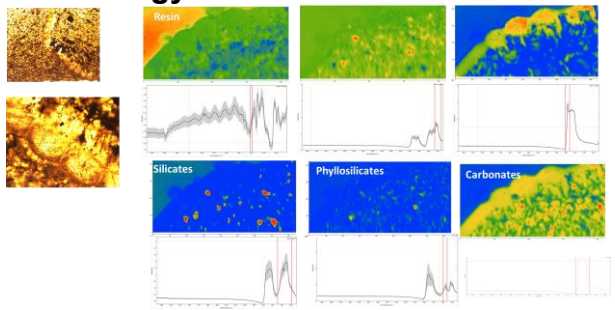
Environnement



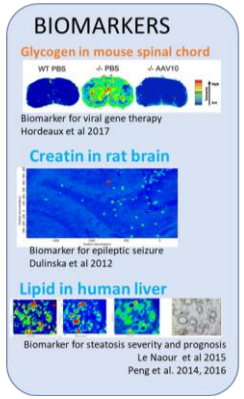
Polymer sciences

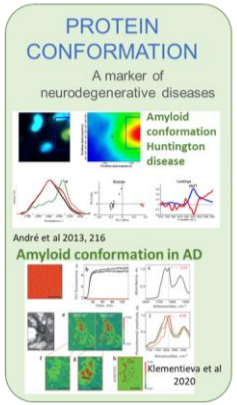


Paleontology



Biology and Biomedical





PLAN

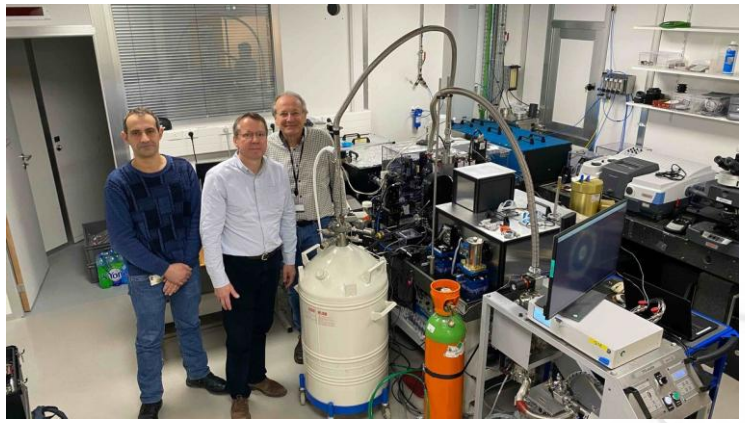
General introduction → **Applications** → Introduction to FTIR Spectroscopy

↓

Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

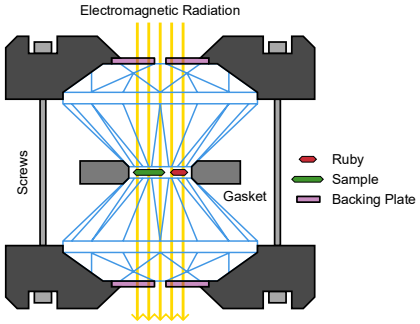
The quest for metallic hydrogen

- Most simple gaz can turn into metals in the correct Pressure/Temperature conditions
- Hydrogen was the last simple gaz that had not been metallized
  - Metal hydrogen predicted in 1935 Wigner, E. & Huntington, H. B. On the possibility of a metallic modification of hydrogen. *J.Chem. Phys*. 3, 764–770 (1935).
  - Five experimentally described phases of hydrogen
    - Phases I, III and IV: isostructural, hexagonal close-packed crystal lattice (300K, 254 Gpa)
    - Phases IV and V exist only above 200 K.
- Transition to metallic hydrogen predicted at 450 GPa (4.5 million atmospheres)



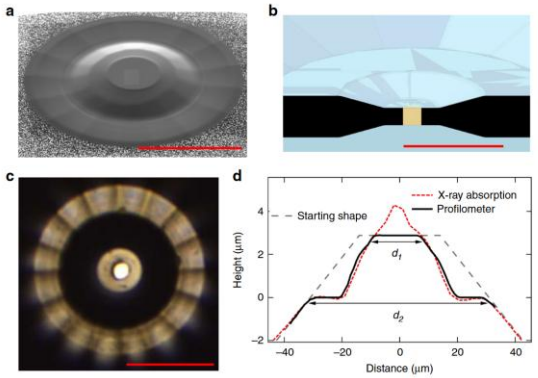
The quest for metalllic hydrogen

- The tools: Diamond Anvil Cell (DAC)



Pneumatic Drive System

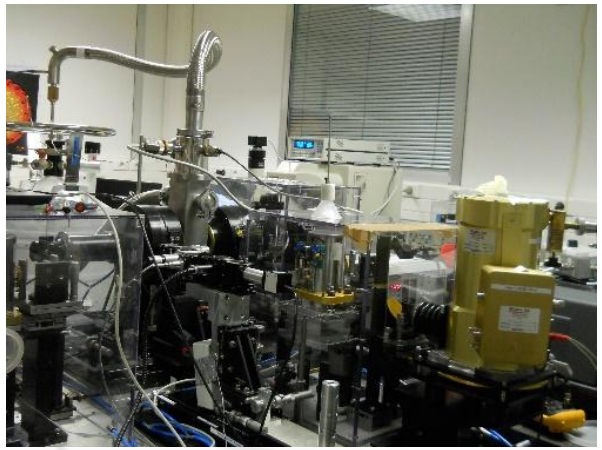
Loubeyre, Occelli, Dumas arXiv 2018
Loubeyre, Occelli, Dumas Nature 2020, 577,



Toroidal diamond culet
Pressures up to 600 GPa (6 Mbar)

  - horizontal microscope

Loubeyre, Occelli, Dumas arXhiv 2018
Loubeyre, Occelli, Dumas Nature 2020, 577,



Horizontal microscope
47 mm working distance to accomodate cryosta
15X magnification, 0.5NA
23 μm FWHM IR spot @ 10 μm wavelength

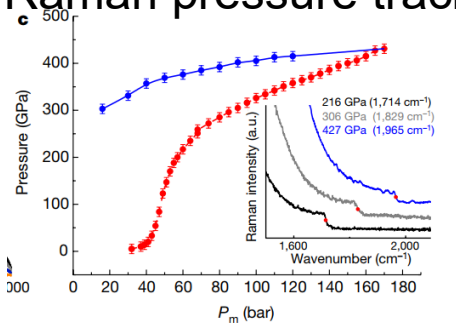
Raman accessory to measure diamond pressu

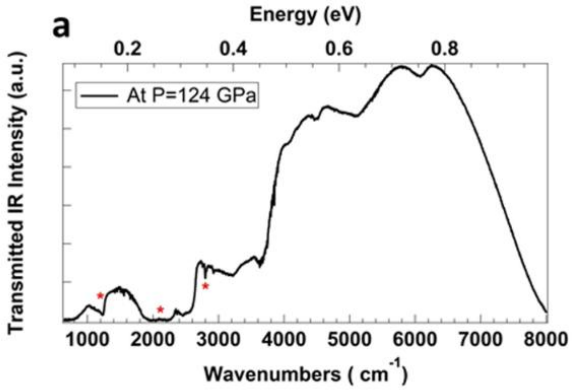
Measurements in a DAC inside a cryostat (at 80K) through a micrometric pinhole in a metallic gasket.
Initial pinhole size 10 μm; final 3-5 μm

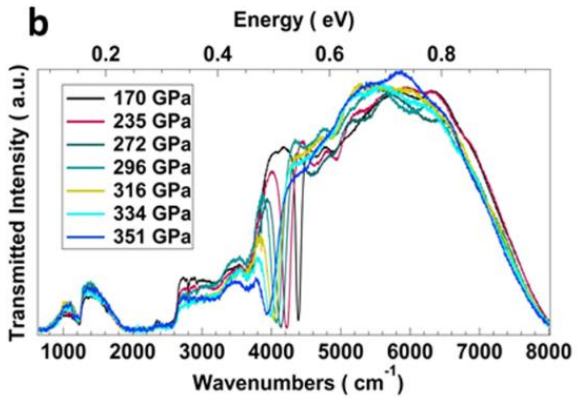
The quest for metallic hydrogen

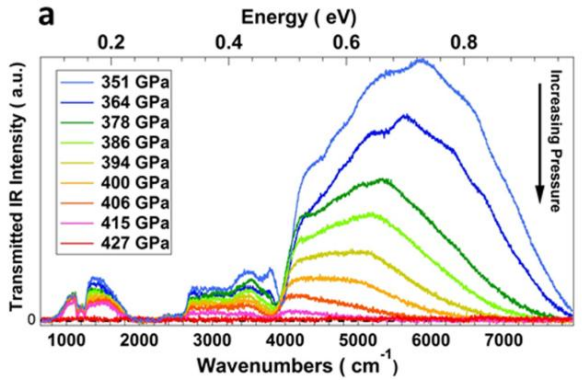
- Closure of the Fermi bandgap from the visible to the infrared domain

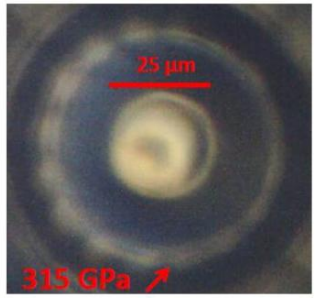
Raman pressure tracking

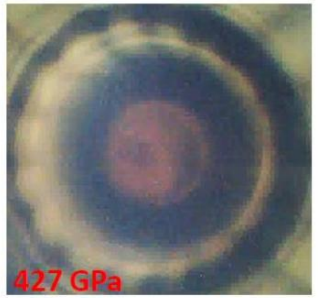


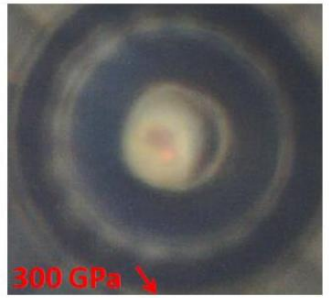




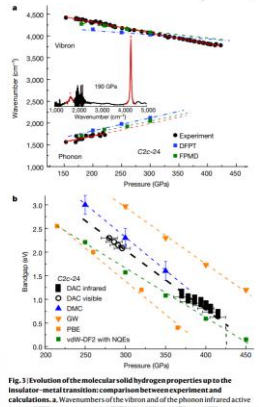








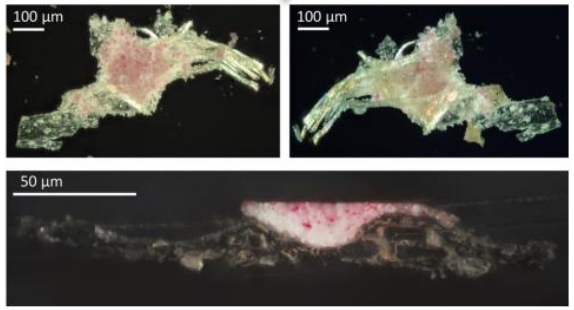
- Continuous vibron frequency shift
- First order phase transition near **425 GPa/80K** from insulator molecular solid hydrogen to metal hydrogen (4.25Gpa = 4.25 million atmospheres)
- Electronic band gap closure down to 0.5 eV
- Reversible phase transition, back to C2/c-24 phase



A new pigment in Van Gogh palette

- Multiscale characterization of multilayerd historical paintings
  - Layers < 10µm
- Non destructive analysis needed
- Ability to identify pigments, binders, support material…
- Characterization of material aging and degradation pathways
- Combination of OPTIR and SR-µFTIR
- Thin sections

L'Arlésienne
Portrait de madame Ginoux,
Van Gogh, 1888
Kröller-Müller Museum,
Netherland

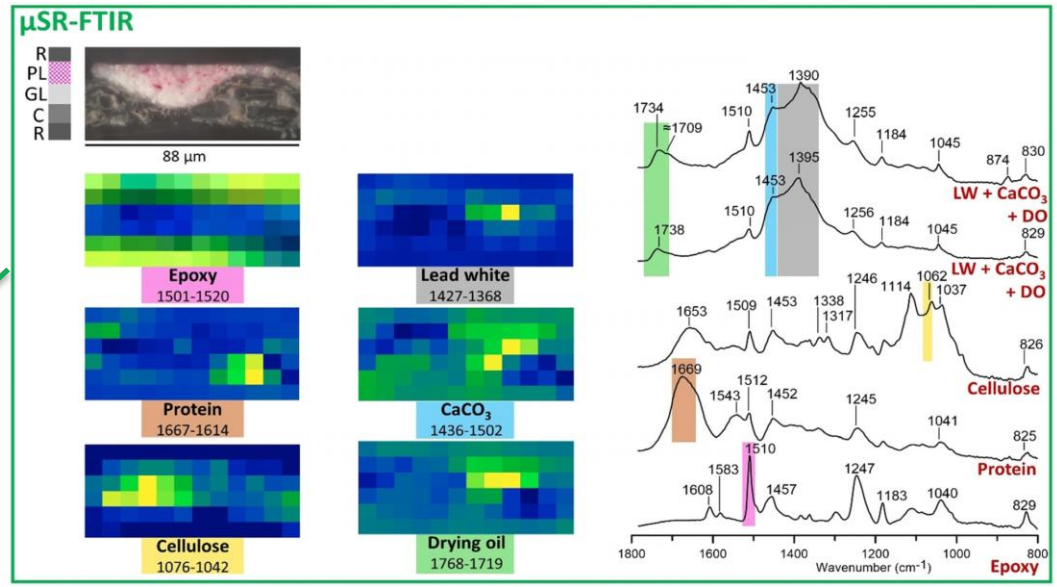


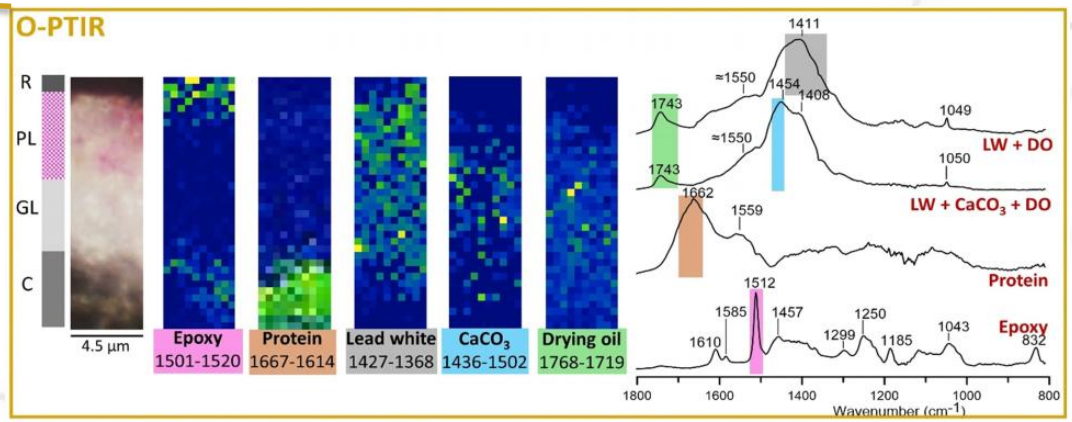
Beltran V. et al. 2021
Angewandte Chemie

Multiple spectroscopic methods

- SR-µFTIR characterization of:
  - Proteins , Calcium carbonate
  - Lead white, oil
  - Cellulose (canva)
  - Epoxy resin

- OPTIR:
  - Lead white, oil, CaCO3
  - Proteins and epoxy resin





Measuring the pink pigment in microparticles

- Small pink particles of 2 µm diameter
- Identification of a pink pigment in Raman
  - But possible confusion with other pink pigments
  - Several peaks missing in the Raman spectra
- Confirmation with OPTIR
  - Carboxylates 1550 and 1460 cm^{-1}
  - Xanthene and ketones 1605, 1351, 1254 cm-1
  - Resolved from the oil binder! 1719 cm^{-1}
  - Geranium lake characteristic peaks: 1560, 1465, 1355, 1240 cm^{-1}

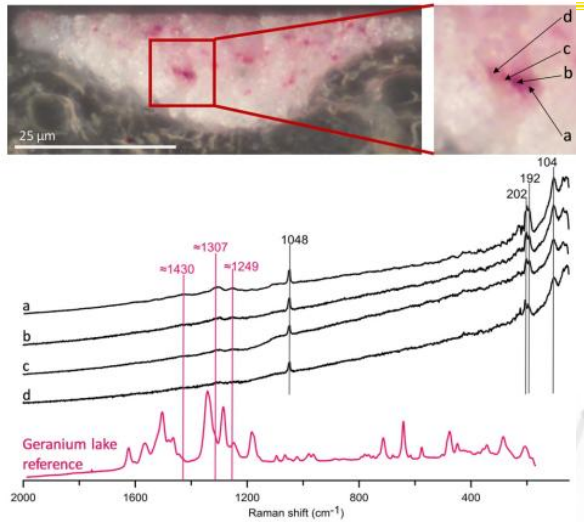


Figure 4. Characterization of a pink particle by µRaman spectroscopy.

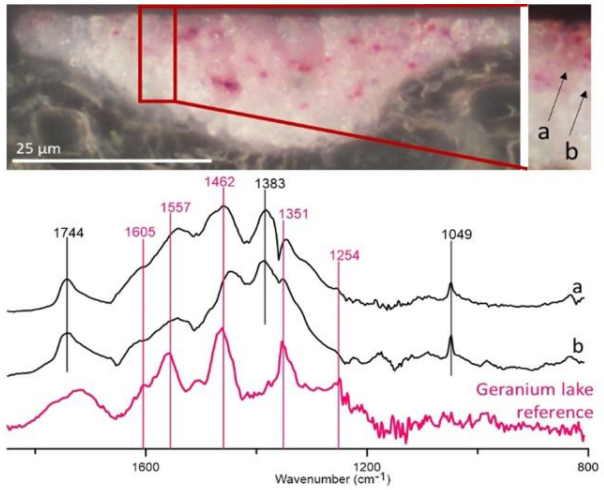
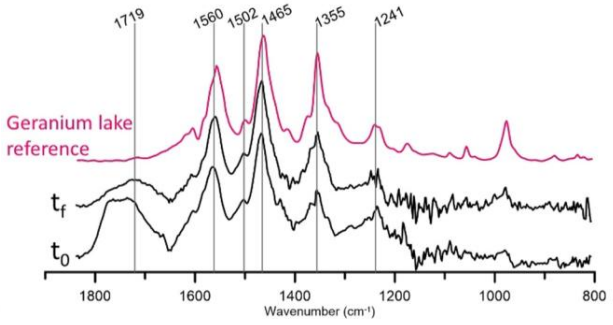


Figure 5. Characterization of the pink particles by O-PTIR spectrosco-



Identification of geranium lake

- First observation of Geranium lake in this painting

Beltran et al. 2021
Angewandte Chemie

- Geranium lakes have been previously observed in other paintings by Van Gogh
  - Normally detected by the presence of Br
  - Br not detected by SEM-EDX here

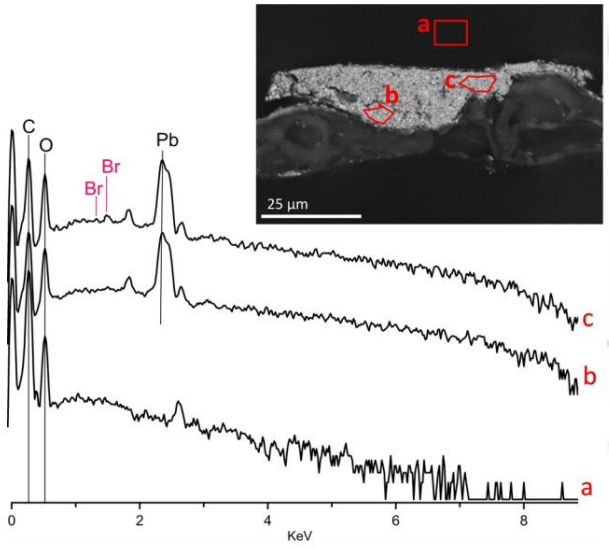
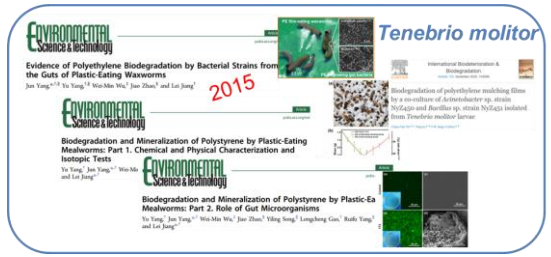


Figure 6. Characterization of the paint layer by SEM-EDX. BSE image

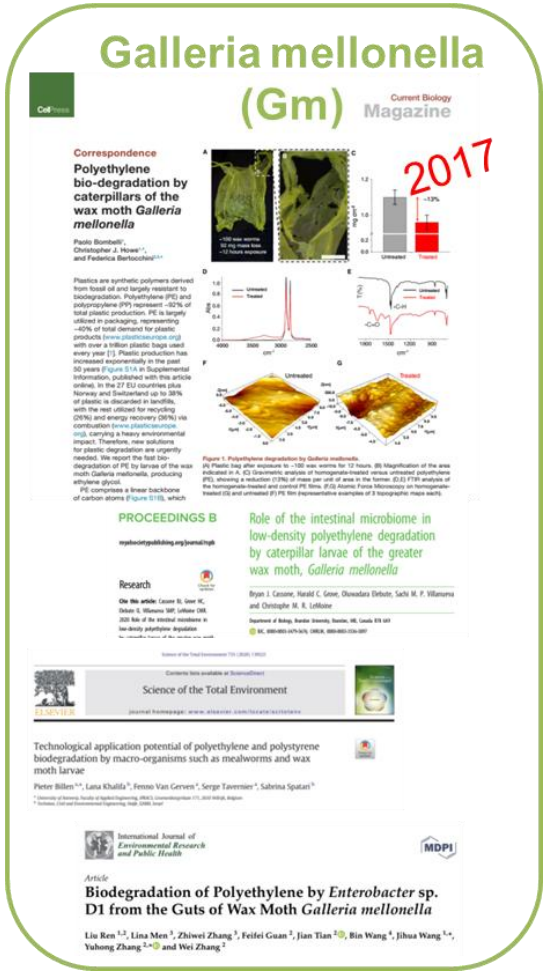
- GL is potosensitive
  - No photodegradation observed with OPTIR

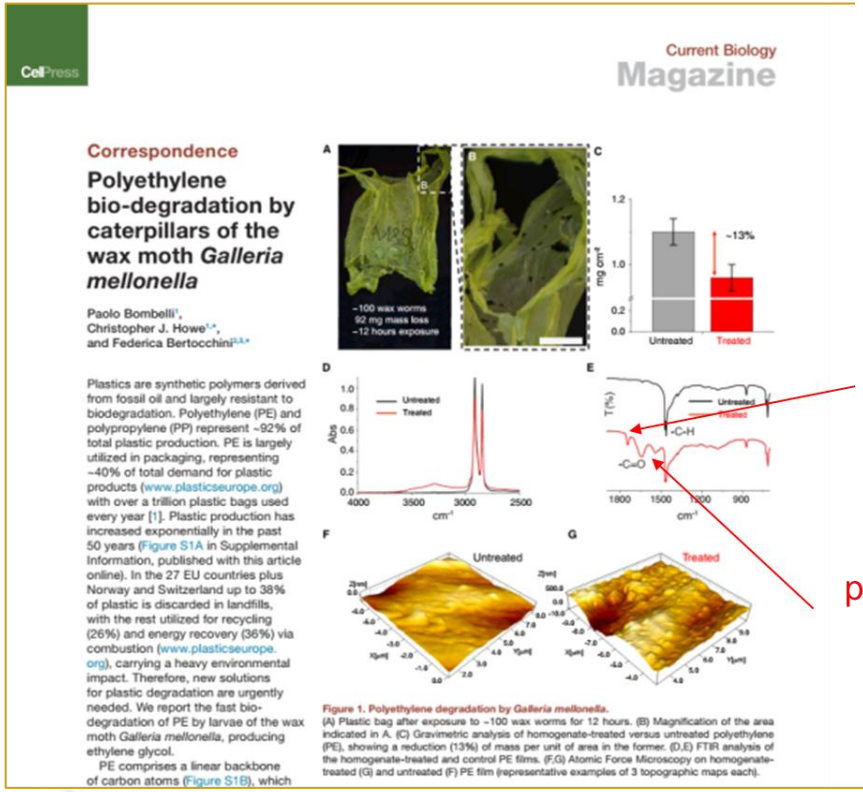
- OPTIR positively confirmed the presence of geranium lake in this Van Gogh painting

Do *G mellonella* larvae really bioassimilate PE?



T. molitor larvae eating polystyrene
Yang et al, ES&T 2015





Correspondence

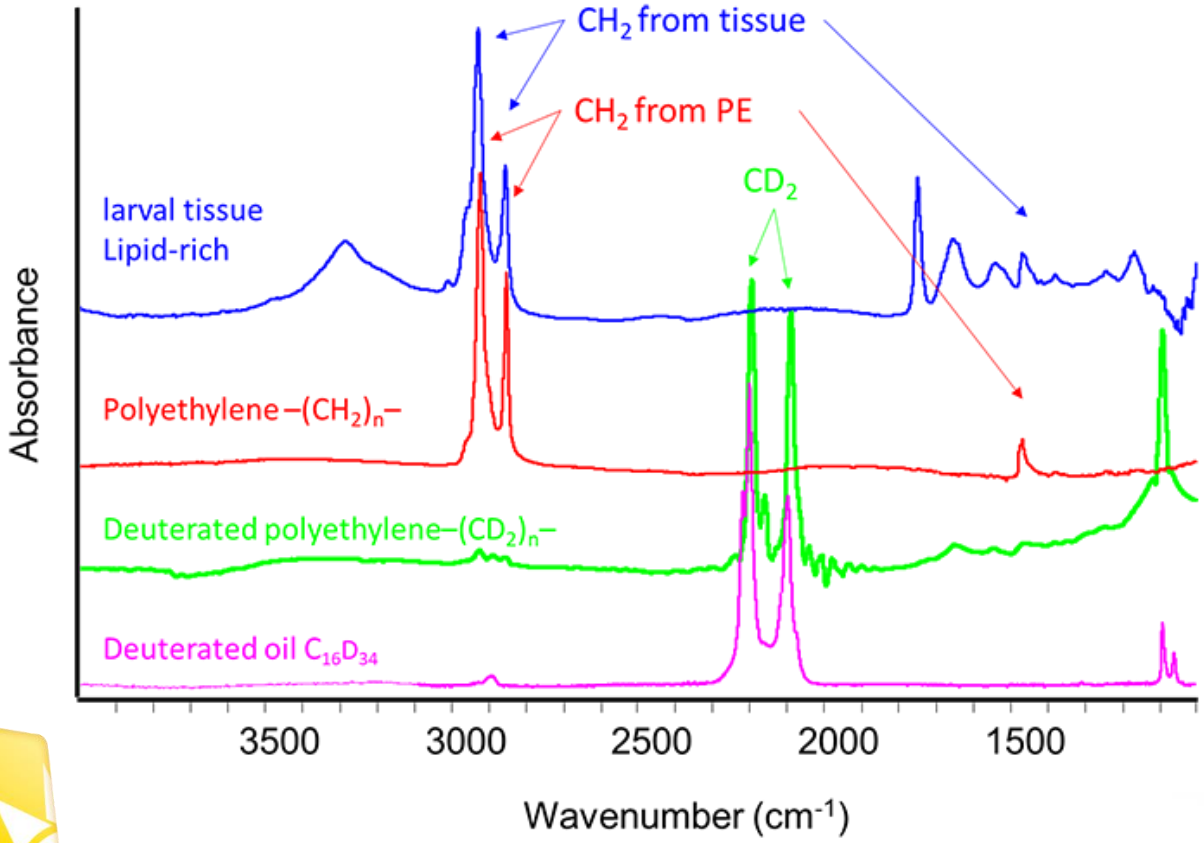
Polyethylene bio-degradation by caterpillars?

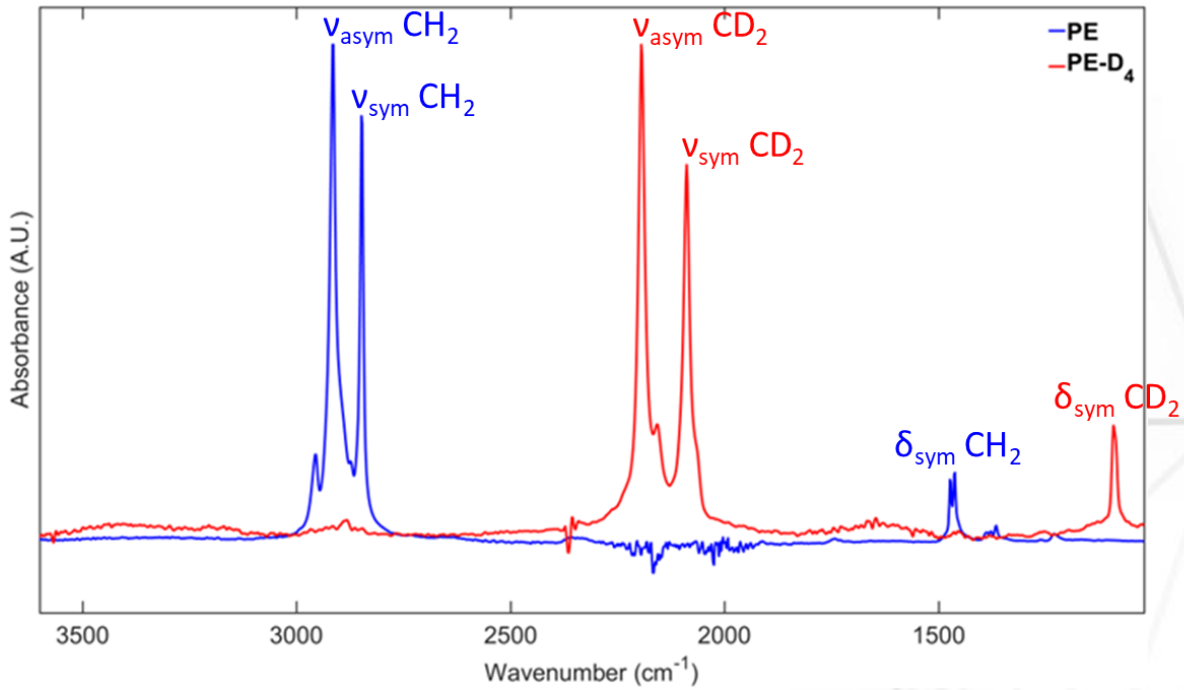
Carina Weber, Stefan Pusch, and Till Opatz*

CO from lipid esters. Not from PE oxidation

C=O from protein peptide bonds. Not from PE oxidation

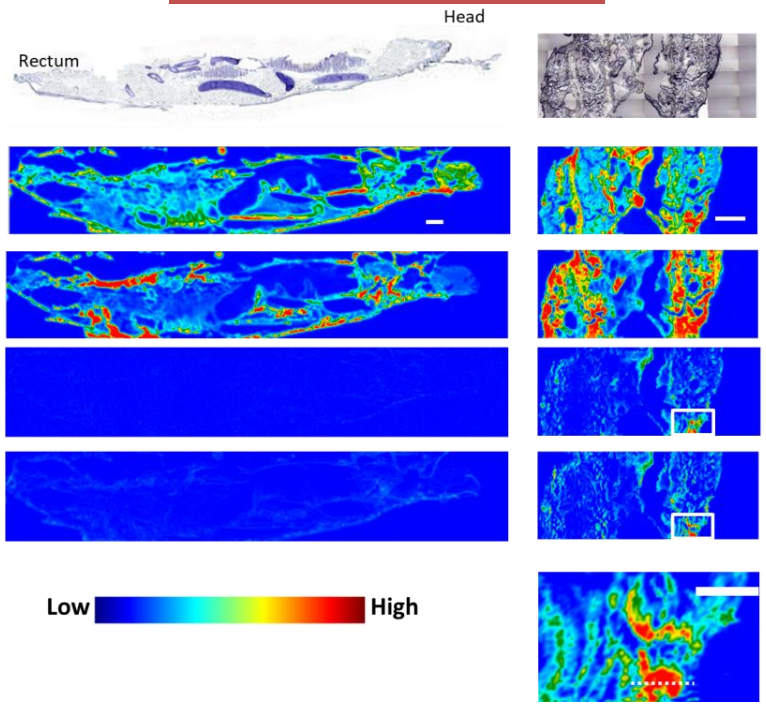
Do *G mellonella* larvae bioassimilate PE?



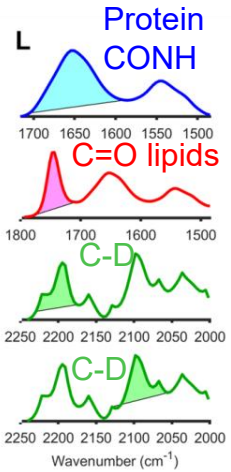


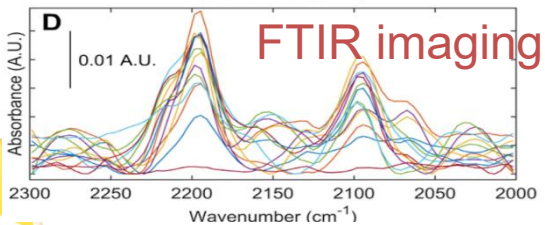
Do *G mellonella* larvae bioassimilate PE?

Deuterated oil diet

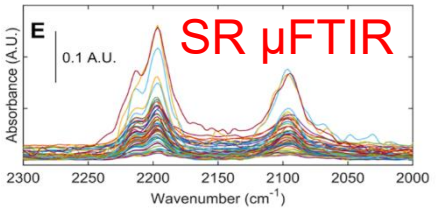


Réjasse et al. ES&T 2022



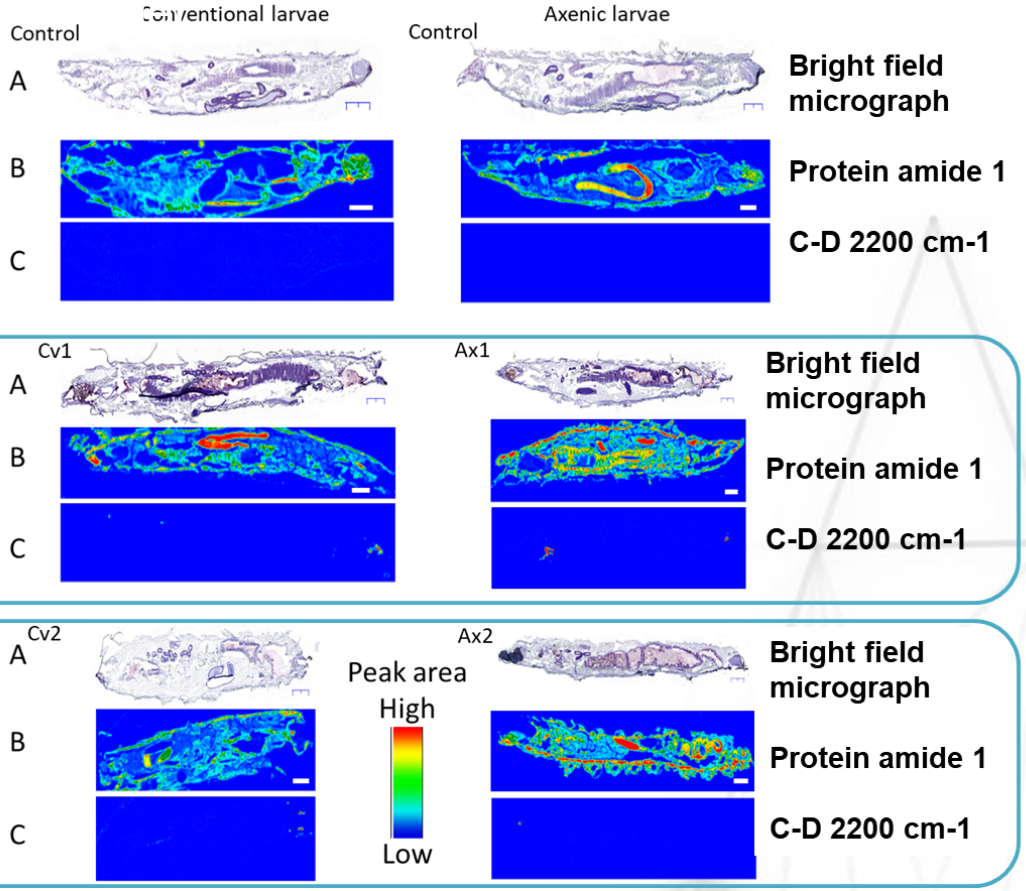


FTIR imaging



SR µFTIR

Deuterated PE



Do *G mellonella* larvae bioassimilate PE?

- Deuterium can be detected in larvae fed with deuterated oil
  - Discrete location after 24h
  - In all fat tissues after 72h

Isotopic labelling food with deuterium can be used to follow bioassimilation of 1-2 mg of food

- G mellonella larvae do not assimilate PE
  - Young larvae (L3 stage) die after 3 days on a PE diet
  - Old larvae (L6 stage) survive but stop gaining weight
  - No deuterium is found in larvae after a deuterated PE diet

PE is not transformed into biomass by the larvae

- G mellonella chew PE
  - PE is fragmented in micro/nanoplastics
  - PE fragments travel in the larvae gut
  - PE fragments are excreted in the frass
  - PE is weakly oxidised in the process

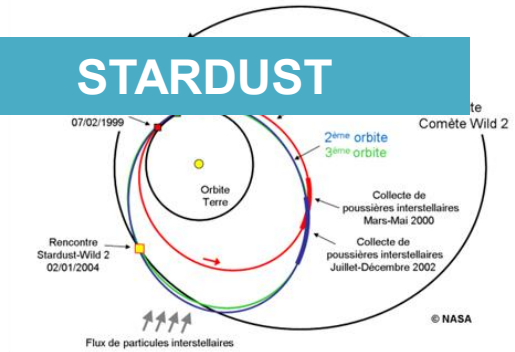
Larvae create minuscule fragments that are more difficult to collect and eliminate

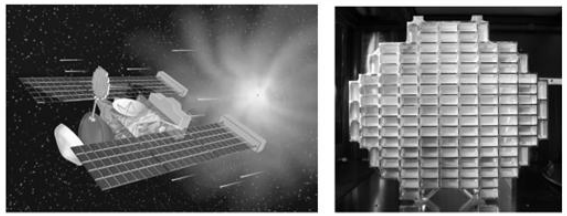
FTIR applications in astrochemistry

- Everything we know about the solar system and other galaxies is from telescopic spectroscopy observations
  - IR observatories, satellites (IRAS, COBE, Spitzer, HERSCHEL)
- Laboratory analyses are necessary to understand these observations
  - IR microspectroscopy is widely used for organic and inorganic matter characterization
  - Laboratory Analogs and Sample return mission
- Results answers questions about:
  - The composition of planets, asteroids, stars, dust, clouds and nebula…
  - The evolution of the solar system
  - The origin of water, inorganic and organic molecules on earth

Space sample return misssions

STARDUST





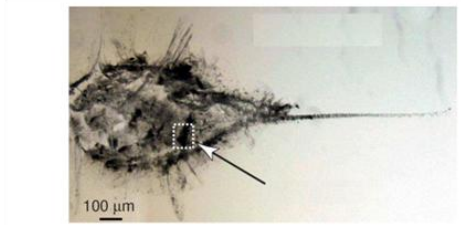
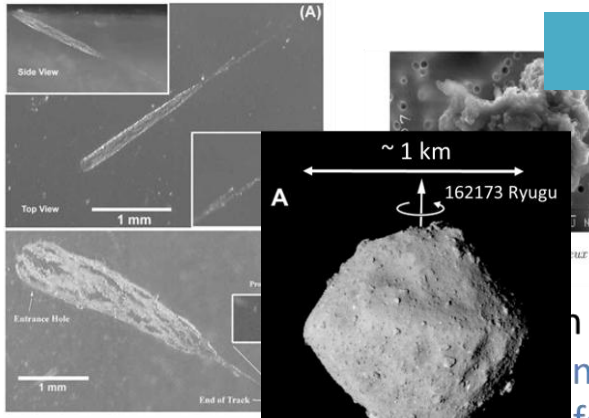


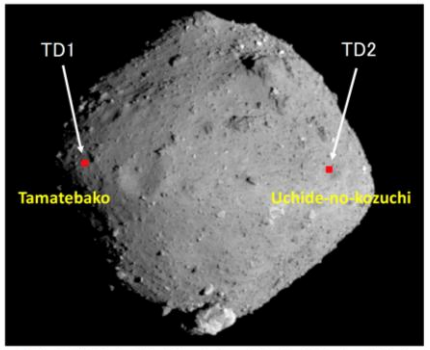
Figure 1.1 – *Image optique de la trace 35 extraite de la cellule C2054. La flèche indique la région où ont été prélevées les particules 35,21 et 35,26.* ©NASA.

Hayabusa 2

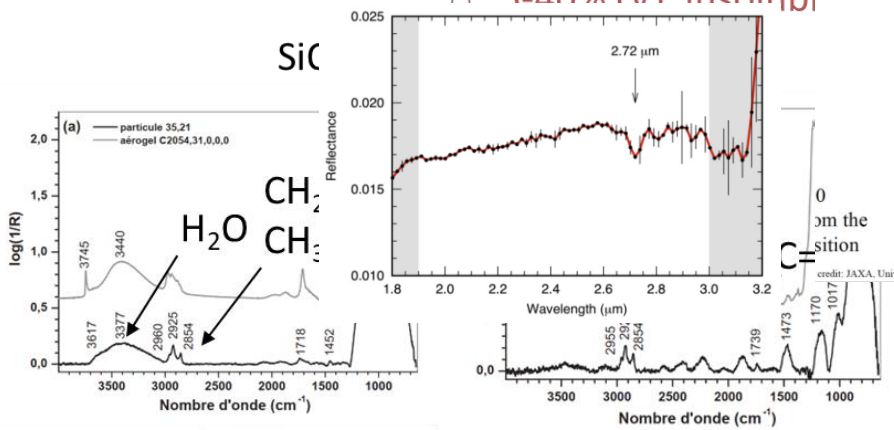


Albedo	0.045 +/- 0.002	0.044 +/- 0.002
Spectral Type (Tholen taxonomy)	C	B
Density	~1.19 g/cm^3	~1.26 g/cm^3

Locations for the 1st (TD1) and 2nd (TD2) touchdown



credit: JAXA, University of Tokyo, Kochi University, Rikkyo University, Nagoya University, Chiba Institute of Technology, Meiji University, Univer



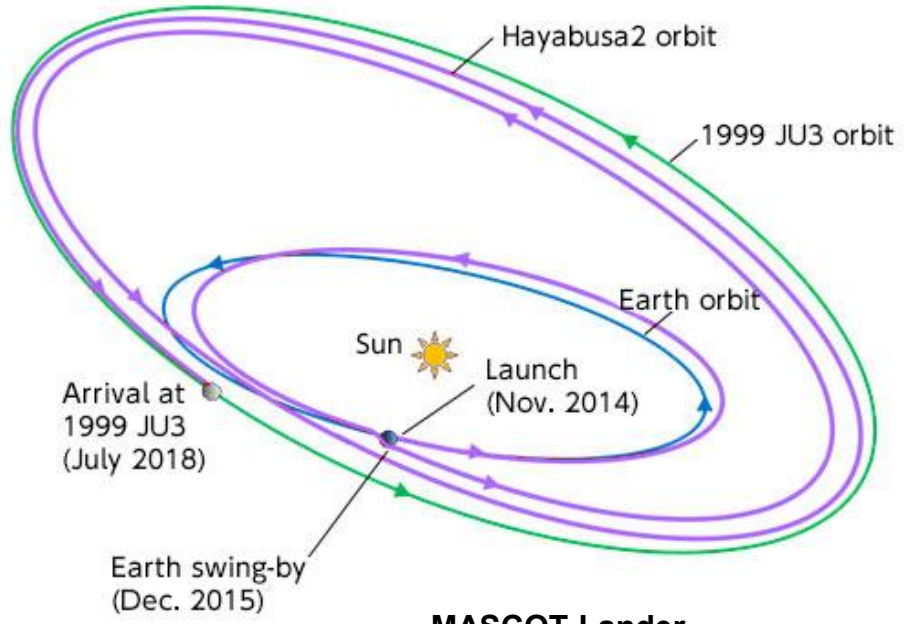
F Grossemy, PhD thesis 2008

OSIRIS REX

Hayabusa 2 schedule

- **November 30, 2014: Launch**
- **End of 2015: Earth swing-by**
- **Summer 2018: Arrival at the asteroid**
  - Stay there for about 18 months
  - IR observation: Near InfraRed Spectrometer (NIR and the Thermal Infrared Imager (TIR)
  - Separating the small rover “MINERVA”
  - Separating the small lander “MASCOT”
  - Sample collection
  - Launching the Small Carry on Impact
- **End of 2020: Return to Earth**

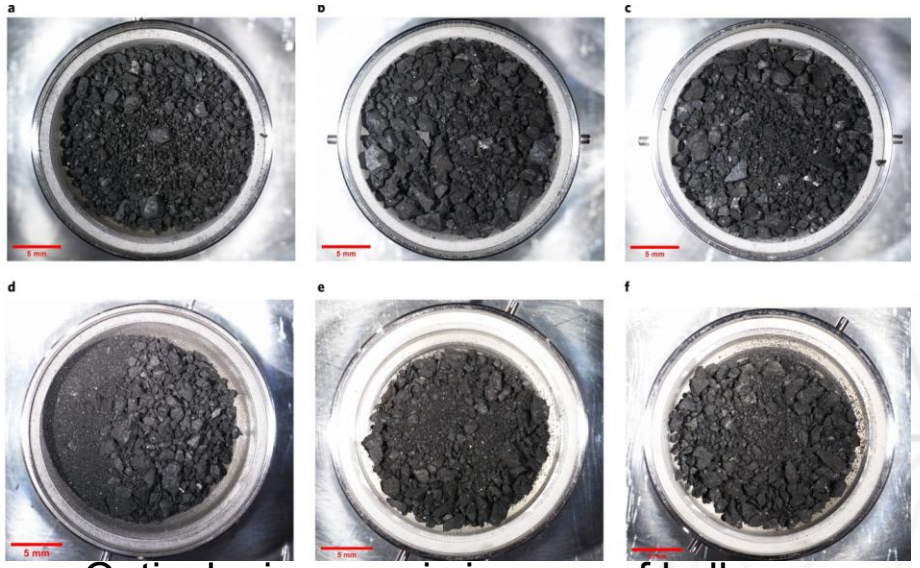
Earth -Ryugu distance : 299,947,616 km
16 minutes 40 sec light travel



MASCOT Lander
1. MicrOmega infrared microscope
2. Magnetometer (MAG)
3. Radiometer (MARA)
4. Wide-angle camera (CAM)

Hayabusa 2

- Several grams of asteroid matter brought back to earth
- Stored at curation facility in Japan
- Dissiminated to research groups abroad:
  - IAS: Institut d'Astrophysique Spatiale, Orsay
  - ISMO: Institut des Sciences Moléculaires d'Orsay



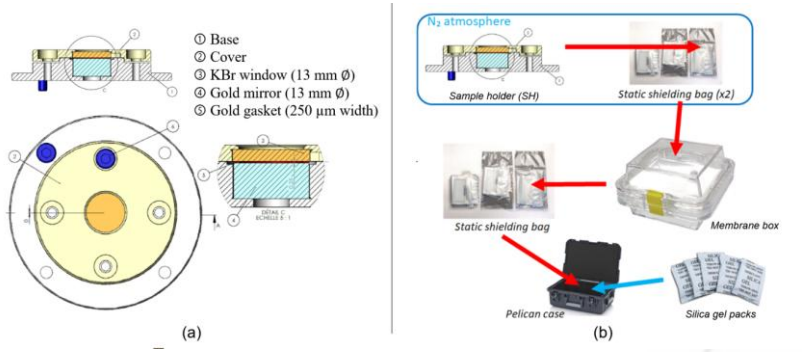
Optical microscopic images of bulk samples from Chambers A and C

Hayabusa 2

2 radically different strategies

IAS : try to preserve the grains from atmospheric alterations

- Synchrotron µFTIR and µRaman of whole grains
- IR tomography
- MicrOmega instrument on board the lander and at curation facility

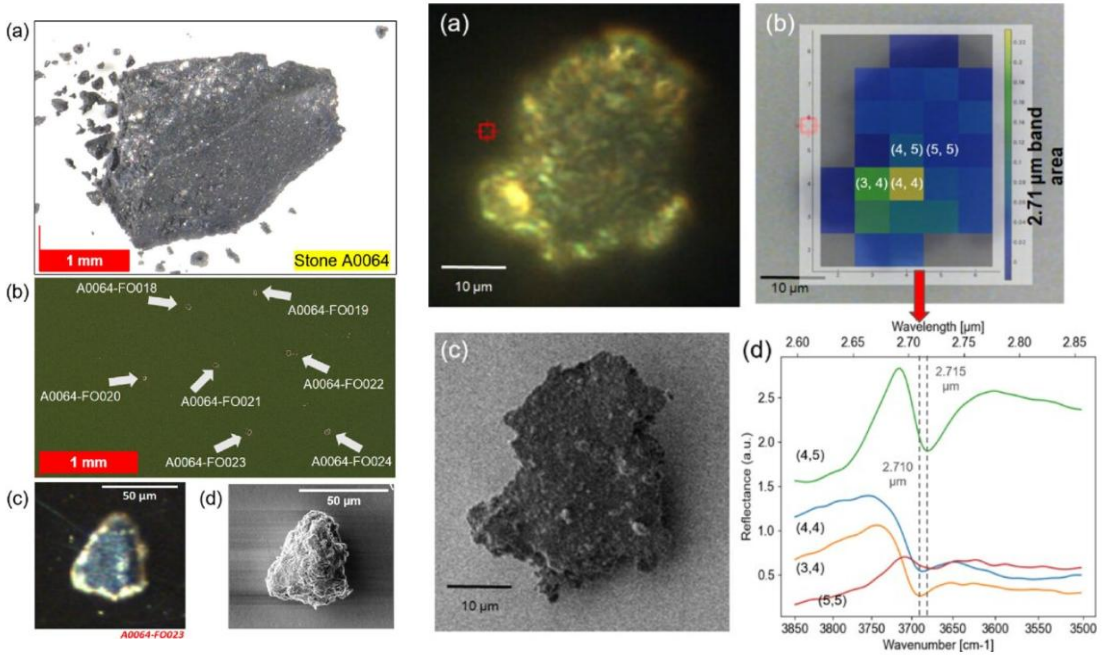


ISMO: flatten the grains in Diamond Compression cells

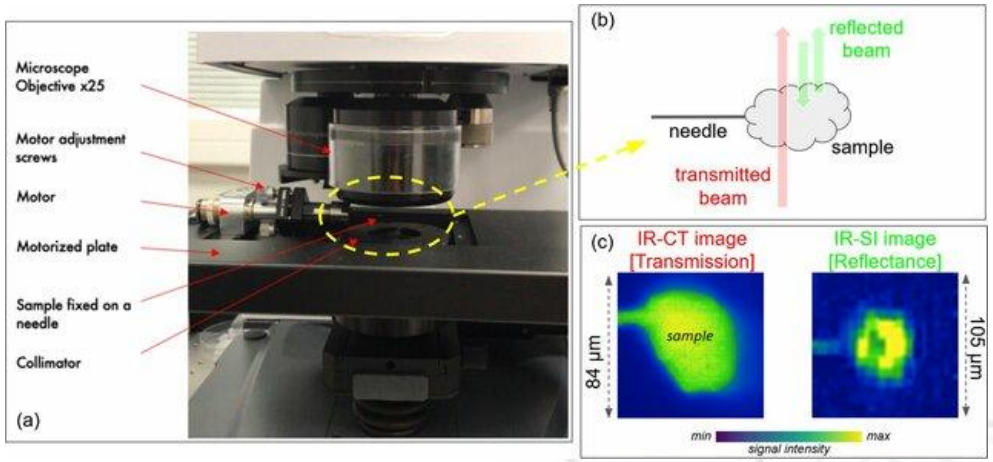
- Synchrotron µFTIR: mid-IR and far-IR
- AFM-IR

Hayabusa 2 IAS team

- Trace of aqueous alterations

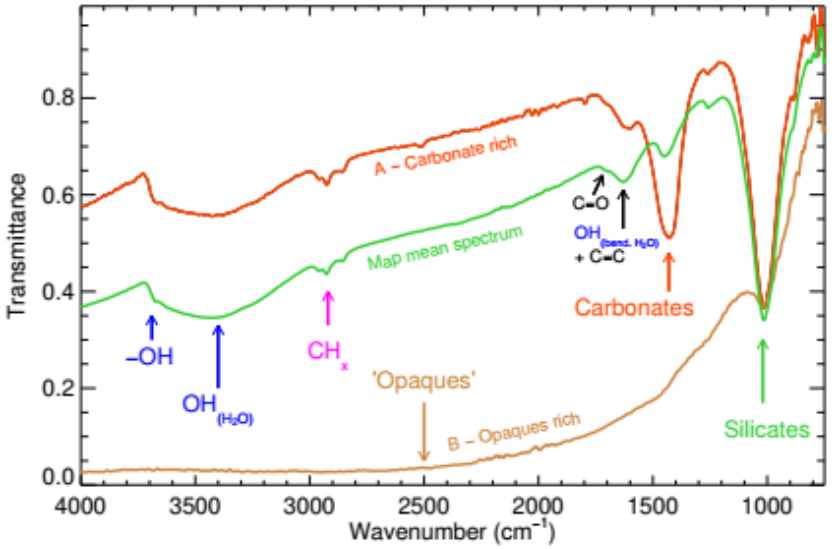


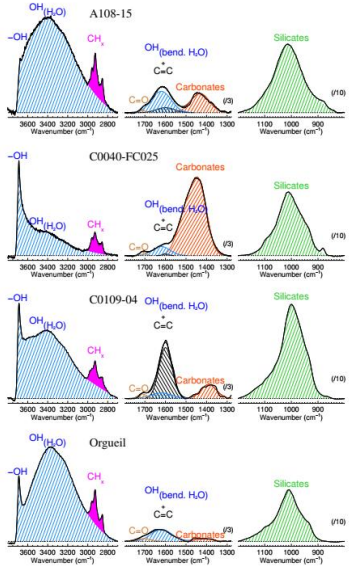
- IR tomography



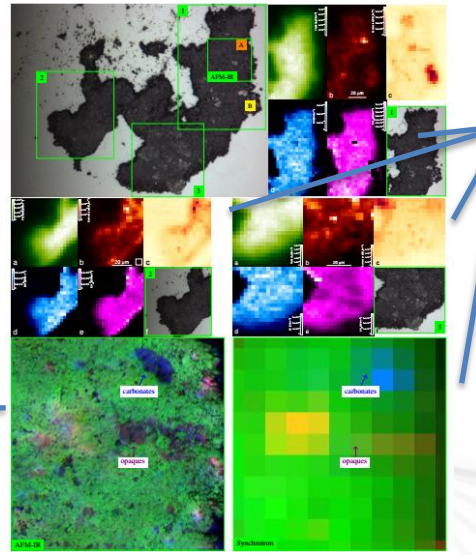
Hayabusa 2 ismo team

- SR-µFTIR
  - Phyllosilicate matrix
  - Organic component dominated by aliphatic CH_x, high CH_2/CH_3ratio
  - C=C ubiquituous
  - Carbonates : dominated by dolomite and saponite (far-IR)
  - Very similar composition to other carbone rich meteorites
- AFM-IR





150 µm

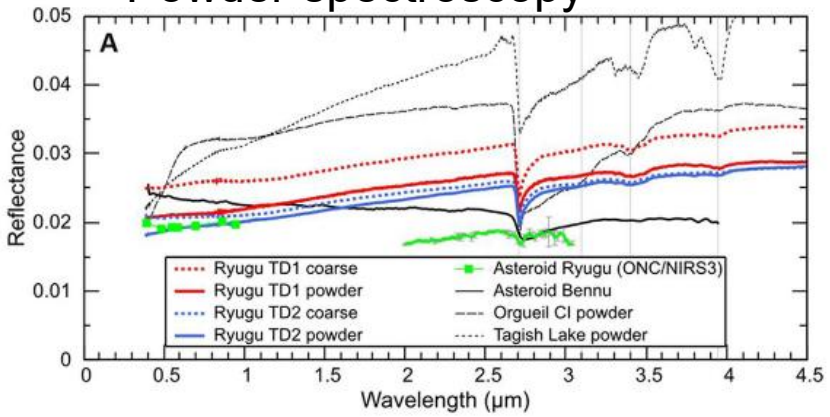


AFM-IR map
Silicate
Carbonates
"Opaques"

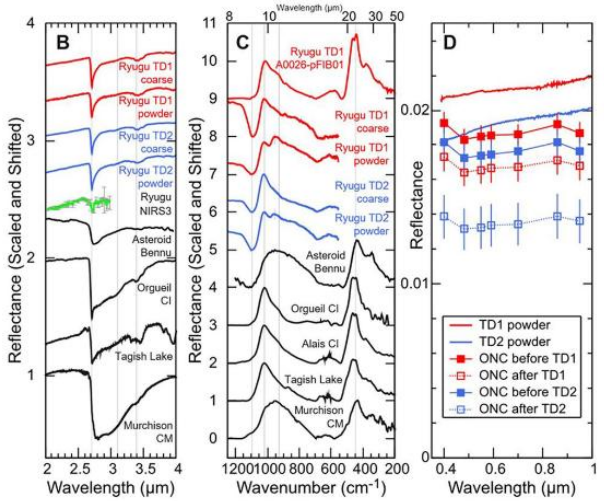
SR-µFTIR maps
Silicate
Carbonates
"Opaques"

Main findings

Powder spectroscopy



Single grain **micro**spectroscopy



- Ryugu is similar to known CIs with important differences
- Ryugu is very close to Orgueil meteorite
  Existing meteorite collection is biased!
- Ryugu is the new standard for CI

- Ryugu has formed in the far outer system after 2 My and then migrated closer to the sun
- Rich in silicates and carbonates
- 3 My at 50°C: aqueous alterations
- Traces of olivine, pyroxene, amorphous silicates, calcite, and phosphide

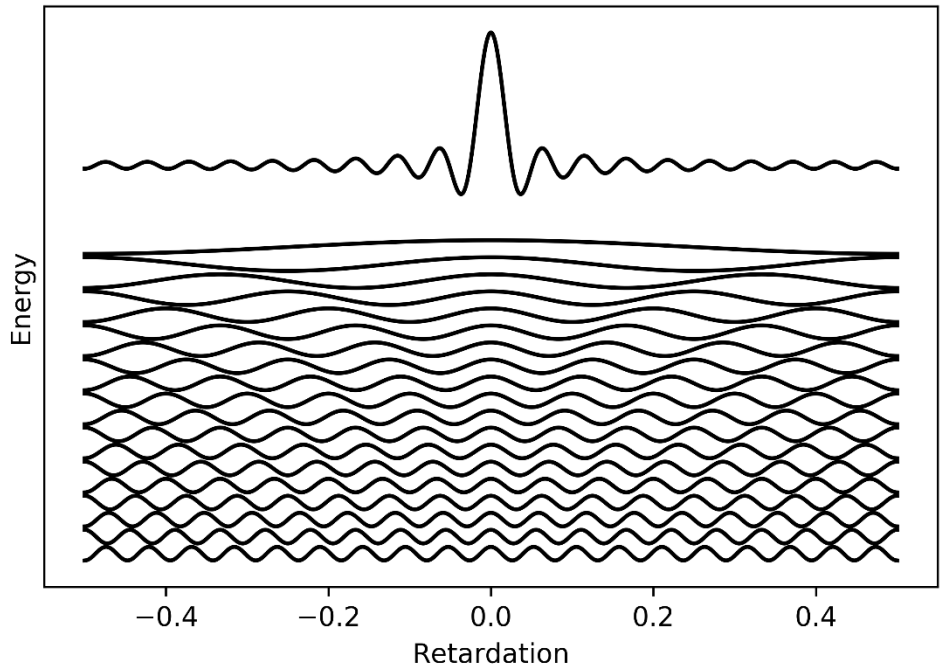
T. Nakamura et **[215]**, Science 2022 DOI: 10.1126/science.abn8671.

PLAN

General introduction → Applications → Introduction to FTIR Spectroscopy

Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

FT-IR SPECTROSCOPY

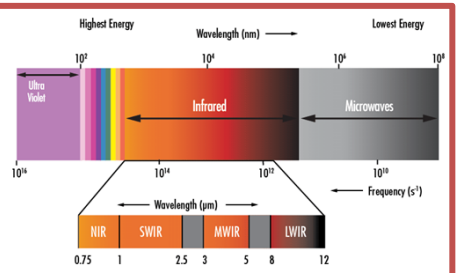


IR SPECTROSCOPY

Optical method in the IR range

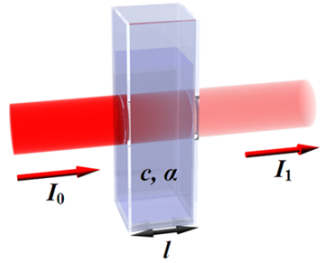
- ”Light*”- matter interaction
- Near, mid, far IR:

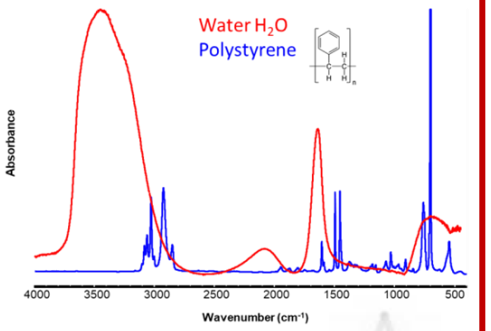
* actually IR radiation, not light



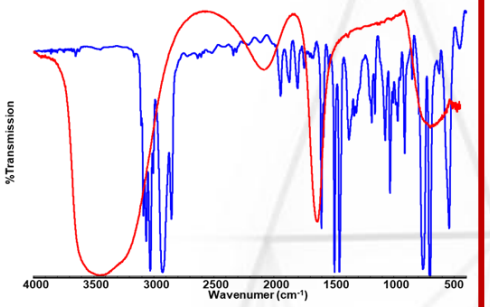
Domain	Wavelengths	Wavenumbers
Near IR	0.8-2.5 µm	1250 – 4000 cm^{-1}
Mid IR:	2.5-25 µm	4000 – 400 cm^{-1}
Far IR	25-1000 µm	400-10 cm^{-1} .

Absorption spectroscopy



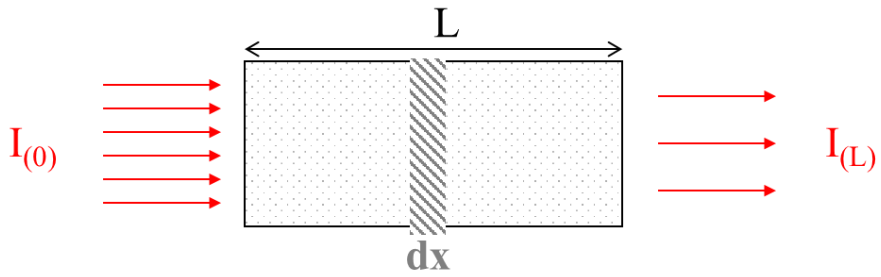


$$A = -log\frac{I}{I_0} = \varepsilon_\lambda cl$$



Beer Lambert Bouguer law
A= Absorbance
I, I_0 : Intensity of the transmitted and incident beam
ε= molar absorptivity ($cm^{-1}·L·mol^{-1}$)
C= concentration ($mol.L^{-1}$)
l= pathlength (cm)

DERIVATION OF THE BLB LAW



$$-dI_{(x)} = KI_{(x)}cdx$$

$$-\left[\ln I_{(x)}\right]_{I_{(o)}}^{I_{(L)}} = \left[Kcx\right]_0^L$$

$$\ln\left(\frac{I_{(0)}}{I_{(L)}}\right) = KcL$$

$$\frac{I_{(L)}}{I_{(0)}} = e^{-KcL}$$

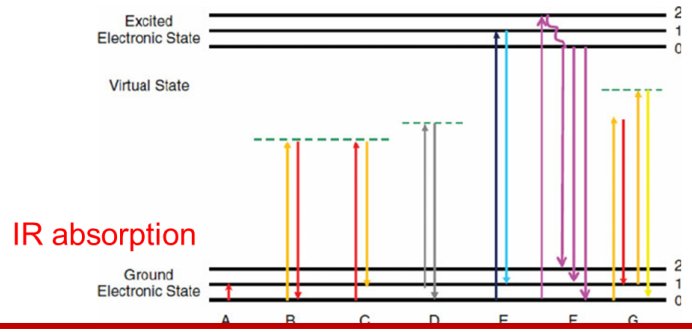
$$A = \log\left(\frac{I_{(0)}}{I_{(L)}}\right)$$

K: absorptivity coefficient
c: concentration
x: distance
I_0: incident beam Intensity
I_L: transmitted beam Intensity

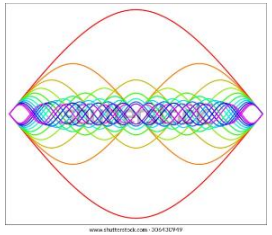
IR SPECTROSCOPY

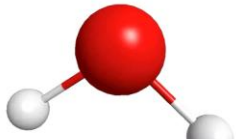
VIBRATIONAL SPECTROSCOPY

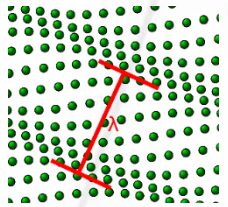
- Probes vibrations of molecular bonds
  - Actually **Ro**vibrational: probes **vibrations and rotations**
  - **Rotational** energy levels can only be measured in diluted gas



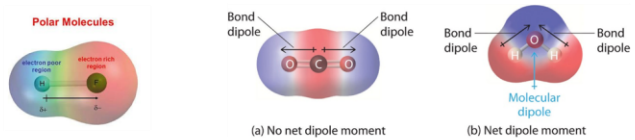
- Different energy ranges probe different vibration types:
  - Near IR: 0.8-2.5 µm or 12500 – 4000 cm^{-1}: overtones of fundamental vibrations .
    - Low absorptivity, low sensitivity long penetration pathlength.
  - Mid IR: 2.5-25 µm or 4000 – 400 cm^{-1}: fundamental vibrations and combinations.
    - High molar absorptivities, high sensitivity, low penetration.
  - Far IR: 25-1000 µm or 400-10 cm^{-1} : low-energy modes, skeletal vibrations, phonons.







- IR active vibrations: molecualr bond with **permanent** dipolar moment



- IR absorption is proportional to the stength of the dipolar moment
- Symmetric bonds/molecules are not active
  - IR spectroscopy is linked to molecular symmetry
  - C-C and C=C bonds are almost inactive
    - Small distortions of the molecule symmetry can make these bonds sligthly active

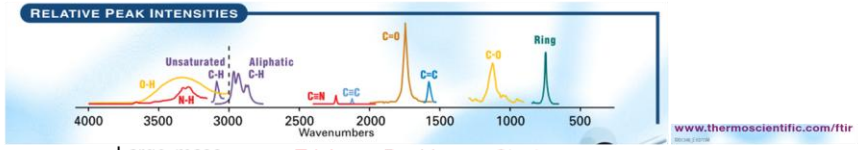
IR SPECTROSCOPY

DEPENDENCE ON BOND STRENGTH

- Peak position depends on bond strength
  - Atom masses and bond conformation
  - Single/double/triple bond

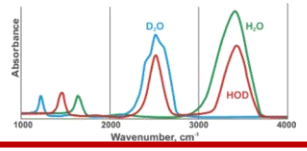
$$\sigma = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

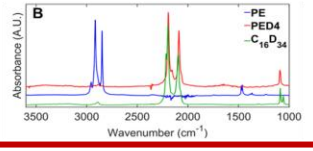
In the harmonic approximation



Large mass differences O-H N-H C-H | Triple bonds | Double bonds | Single bonds

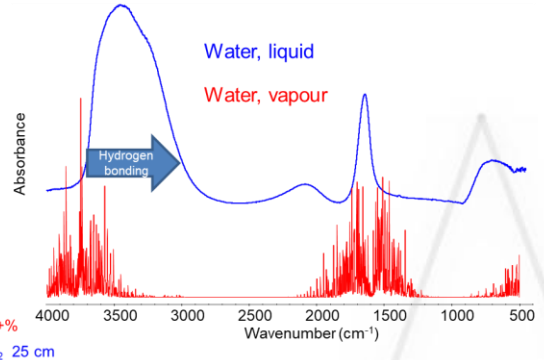
- Isotopic labelling can be used to shift peaks



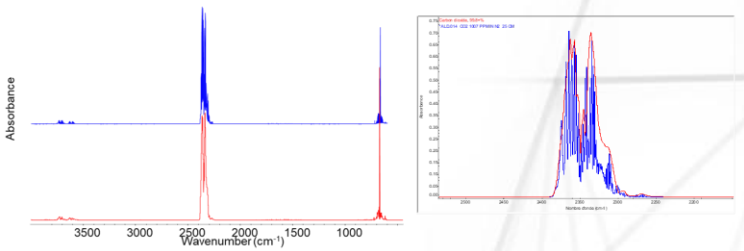


PHASE SENSITIVITY

- Peak width depends on the organisation/phase:
  - Gaz: narrow peaks
- Conformational entropy
  - Crystalline samples: narrow peaks
  - Amorphous samples : large peaks
- Hydrogen - bonding
  - Shift peaks to lower frequency
  - Increases peak width
- Interaction between molecules
  - Affect peak position and peak width



Carbon dioxide, 99.8+%
CO2 1007 PPM IN N_2 25 cm



DERIVATION OF THE PEAK POSITION IN THE HARMONIC APROXIMATION

Vibration frequency f

Displacement around the center of mass: x

Force constant k

There is two ways of calculating f:

- Solve the derivative of E_0 versus time which is equal to zero since E_0 is conserved
- Or solve ma=-kx

$$\vec{F} = -kx$$

$$\vec{F} = m\vec{a}$$

a: acceleration

Total Energy: $E_0 = E_c + E_P$

E_0: total energy

E_c=1/2mv²

E_p=kx

E_c: kinetic energy

E_P: potential energy

E_0=1/2mv²+kx

E_0 is conserved: $\frac{\partial E_0}{\partial t} = 0$

$$m\vec{a} = -kx$$

$$m\frac{\partial^2 x}{\partial t^2} + kx = 0$$

Solution of the differential equation:

x(t)=Acos(ωt)

with ω the angular frequency: ω=2πf with f the oscillation frequency

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

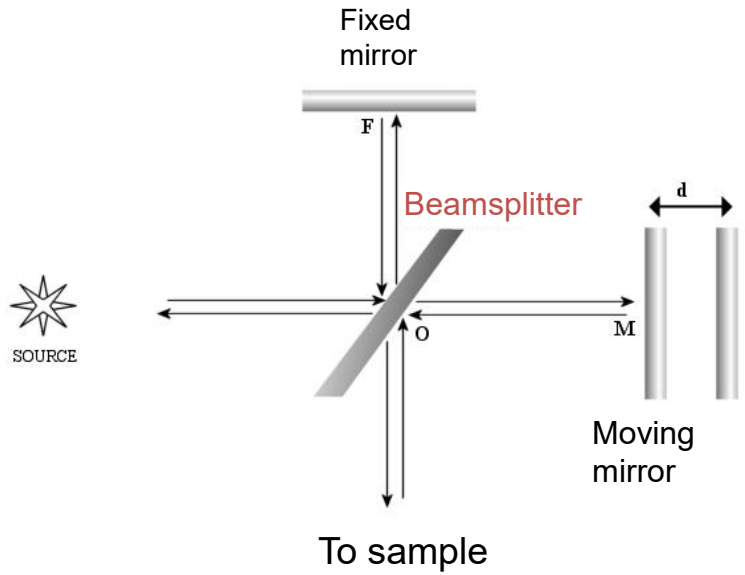
K: force constant

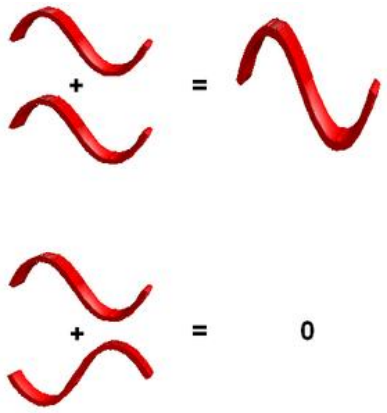
μ: reduced mass

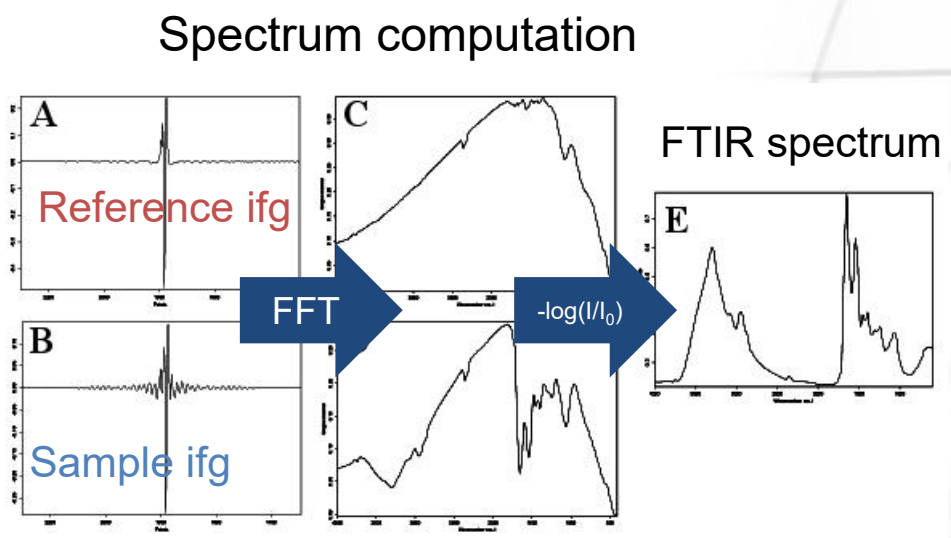
$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

FOURIER-TRANSFORM IR SPECTROSCOPY

- Most modern IR spectrometers are Fourier-Transform spectrometers
- They use an interferometer to create interferences in the beam
  - The interferometer produces an interferogram (ifg)
- Fast Fourier-Transform (FFT) is the mathematical operation used to retrieve the wavelengths and compute the single beam spectra
  - Single beam spectra are ratioed to get the final transmittance/absorbance spectrum



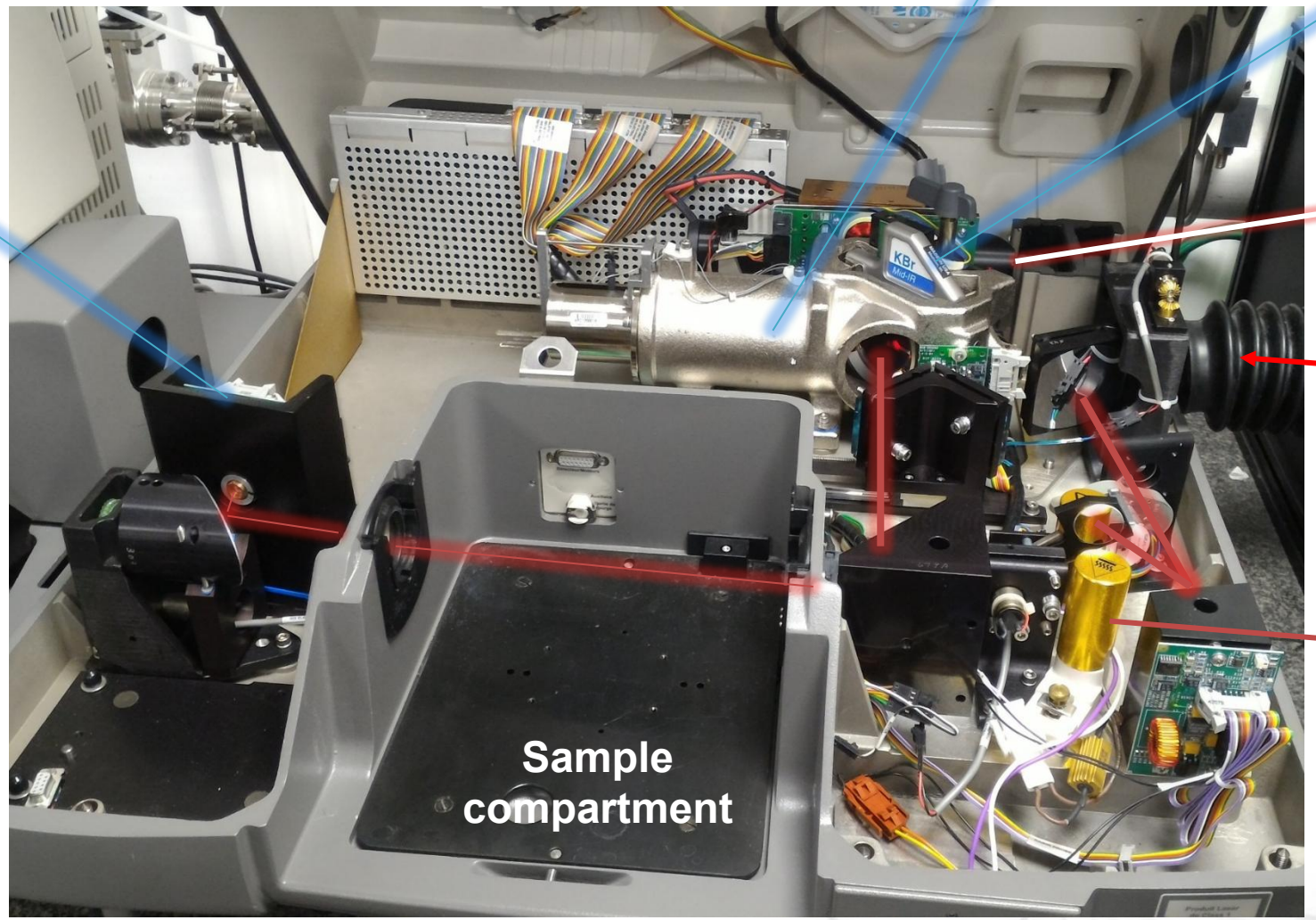




ADVANTAGES OF FTIR

- FREQUENCY ACCURACY (CONNE'S ADVANTAGE)
  - Internal laser measuring the mirror position
  - Internal frequency calibration (10^{-4} cm^{-1})
  - Permanent autoalignment: no need for frequency calibration
- MULTIPLEX ADVANTAGE (FELGETT'S ADVANTAGE)
  - Improvement in signal to noise ratio coming from measuring ALL wavelengths simultaneously (no detector slit or pupils)
- SPEED ADVANTAGE
  - All wavelengths are mesured simultaneously: faster measurement
- SIGNAL to NOISE (SNR) advantage
  - Since measurement is faster and accurate it is possible to **average** multiple measurements
  - SNR increases like $\sqrt{N}$ where N= number of scans

ANATOMY OF THE SPECTROMETER



PLAN

General introduction → Applications → Introduction to FTIR Spectroscopy

↓

Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

μFTIR results from coupling an FTIR spectrometer and an IR microscope

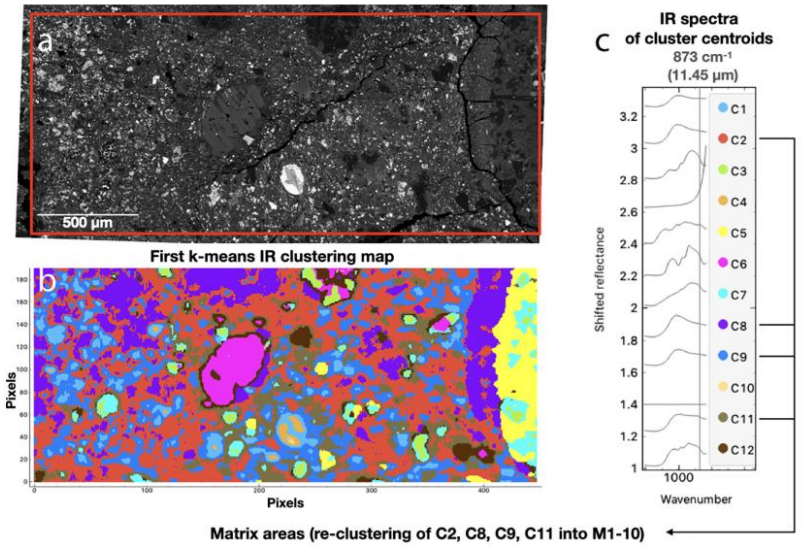
- Designed to analyze ‘small’ samples
- Multiple commercial solution exist (~60-300 k€)
- Can be used with multiple IR sources
  - Thermal sources (“globar”)
  - Synchrotron sources
  - Laser sources
    - QCL, SC, OPO…






PRINCIPLE OF µFTIR

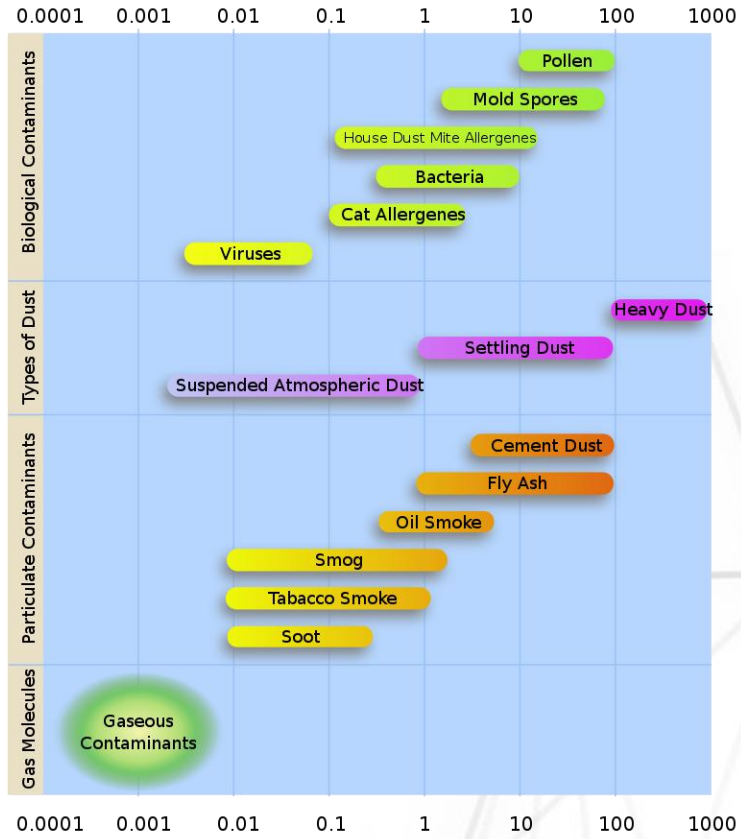
- Measure **small** & **heterogeneous** samples
- Combine **chemical** & **spatial** information
- Chemical mapping
  - Point by point acquisition of spectra
- Chemical imaging
  - Hyperspectral wide field acquisition on large array detectors
  - Single wavelength images

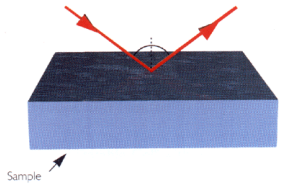


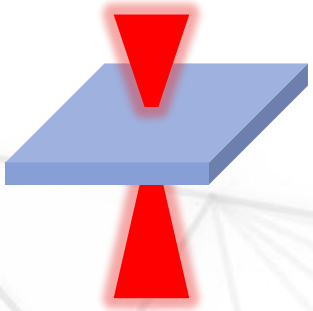
Hyperspectral FTIR imaging of an asteroid thin section
From Hewins et al. 2021

HOW SMALL IS SMALL ?

- FTIR spectrometer: measures samples 1-10 mm in size
  - Small samples are < 1mm
- Typical microspectroscopy samples:
  - < 1 mm
  - few µm to few cm
- The third dimension
  - Reflective samples: surface state (‘skin depth’ 1/α)
  - Transmission: thin samples, thickness: ~0.1-30 µm

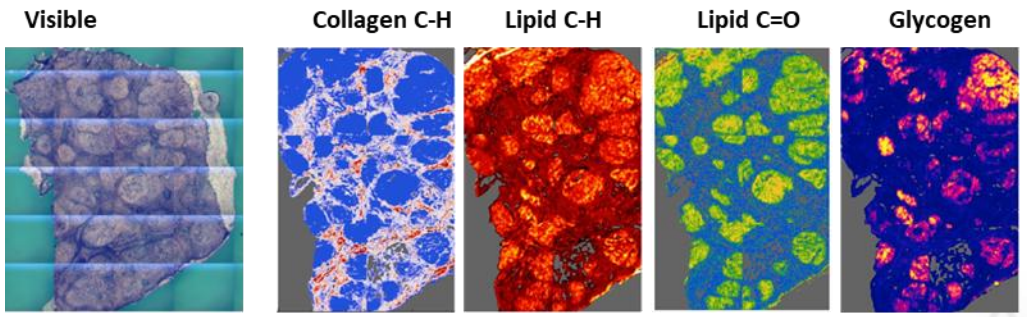


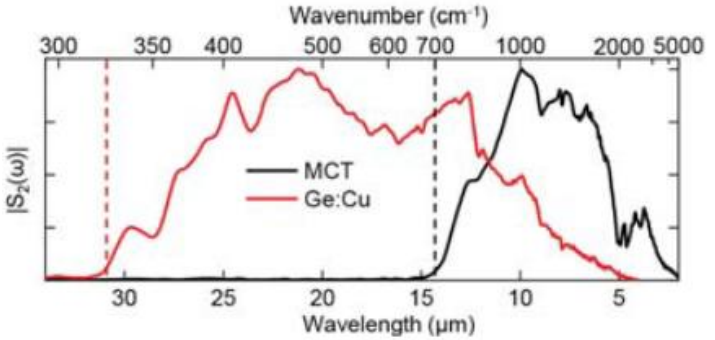


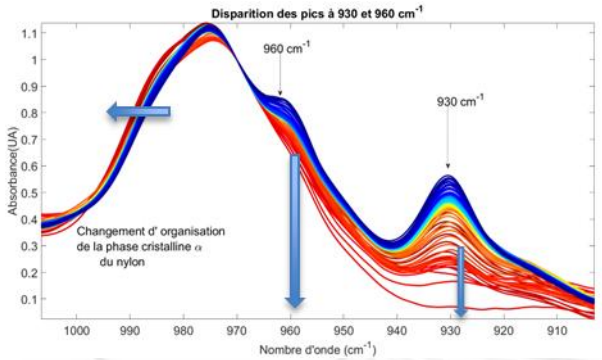


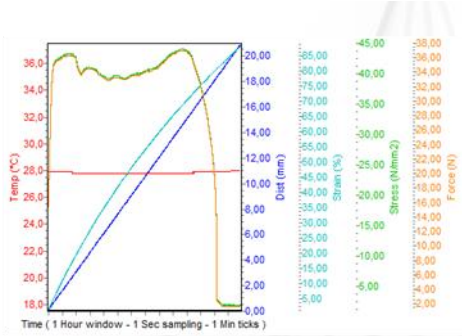
µFTIR ACROSS MULTIPLE DIMENSIONS

- Spatial dimensions
  - X,Y,(Z)
  - Polarization: orientation sensitive
- Spectral dimensions
  - Coupling with UV and Visible observation
  - Near-IR (0.8-2.5 µm)
  - Mid-IR (2.5-25 µm or 2.5-50 µm (ISO 20473:2007))
  - Far-IR (25-250 µm)
- Time dimensions
  - Non-destructive
  - Evolution/aging
  - Phase transitions
  - Kinetics (µs – hours)



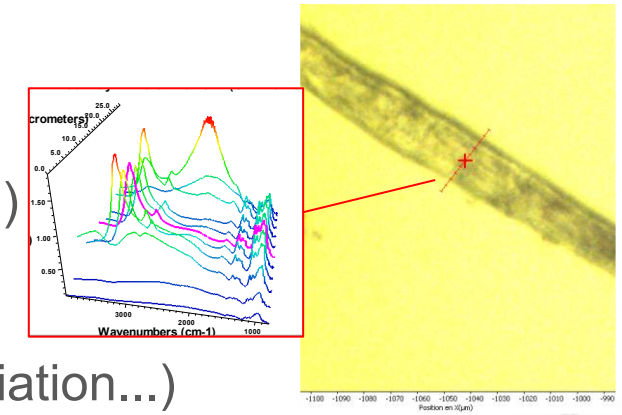




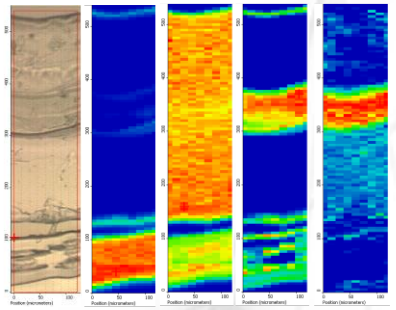


UTILIZATION

- Small samples
  - Isolated individual particles (micro and nanoplastics, dust, grains…)
  - Isolated fibres (polymers, hair, wool…)
  - Single biological cells
  - Material under constraints (temperature, pressure, stretching, irradiation...)
  - Materials in extreme conditions (pressure, temperature…) Diamond Anvil Cells (DAC)
  - …



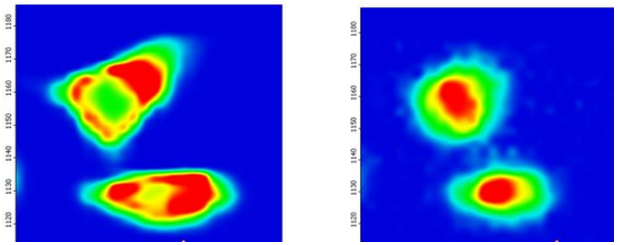
- Mapping heterogeneous samples:
  - Individual particles **within** matrices (colorants in binder, grains in minerals, contaminants in polymers or on silicon wafers…)
  - Multilayers (paintings, laminates …)
  - Interfaces, thin films
  - Biological tissues
  - Single cells



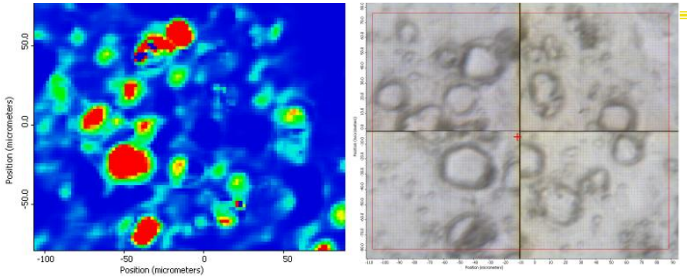
- …

SAMPLES

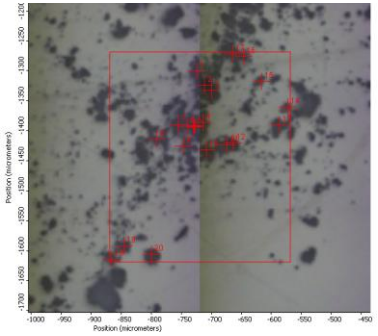
Single cells



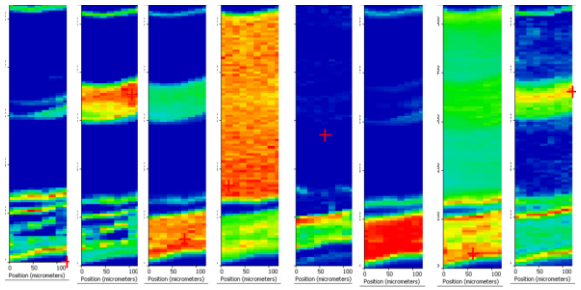
Inclusions



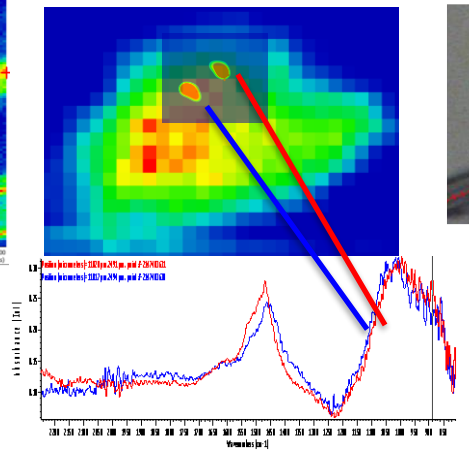
Particles



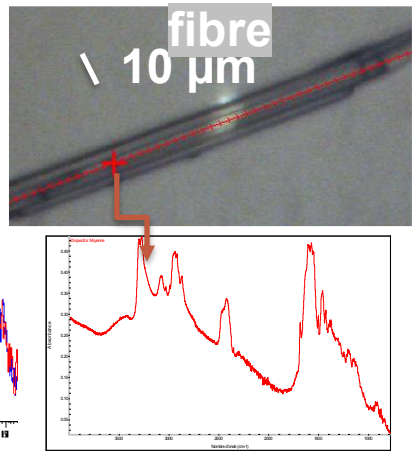
Polymer laminate



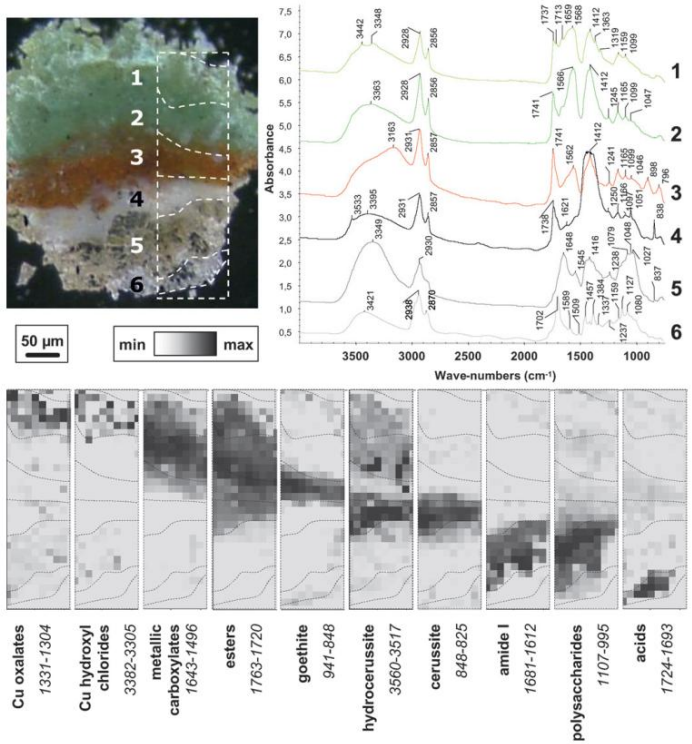
Asteroid grain



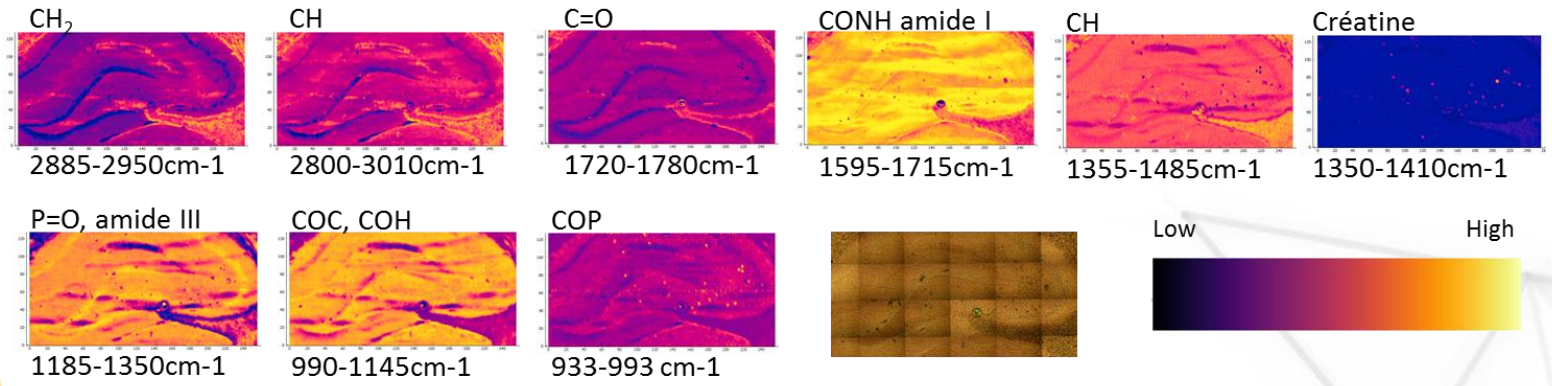
Protein fibre



Mural Paintings



Biological tissues



Cotte et al. J. Anal. At. Spectrom., 2008, 23, 820–828

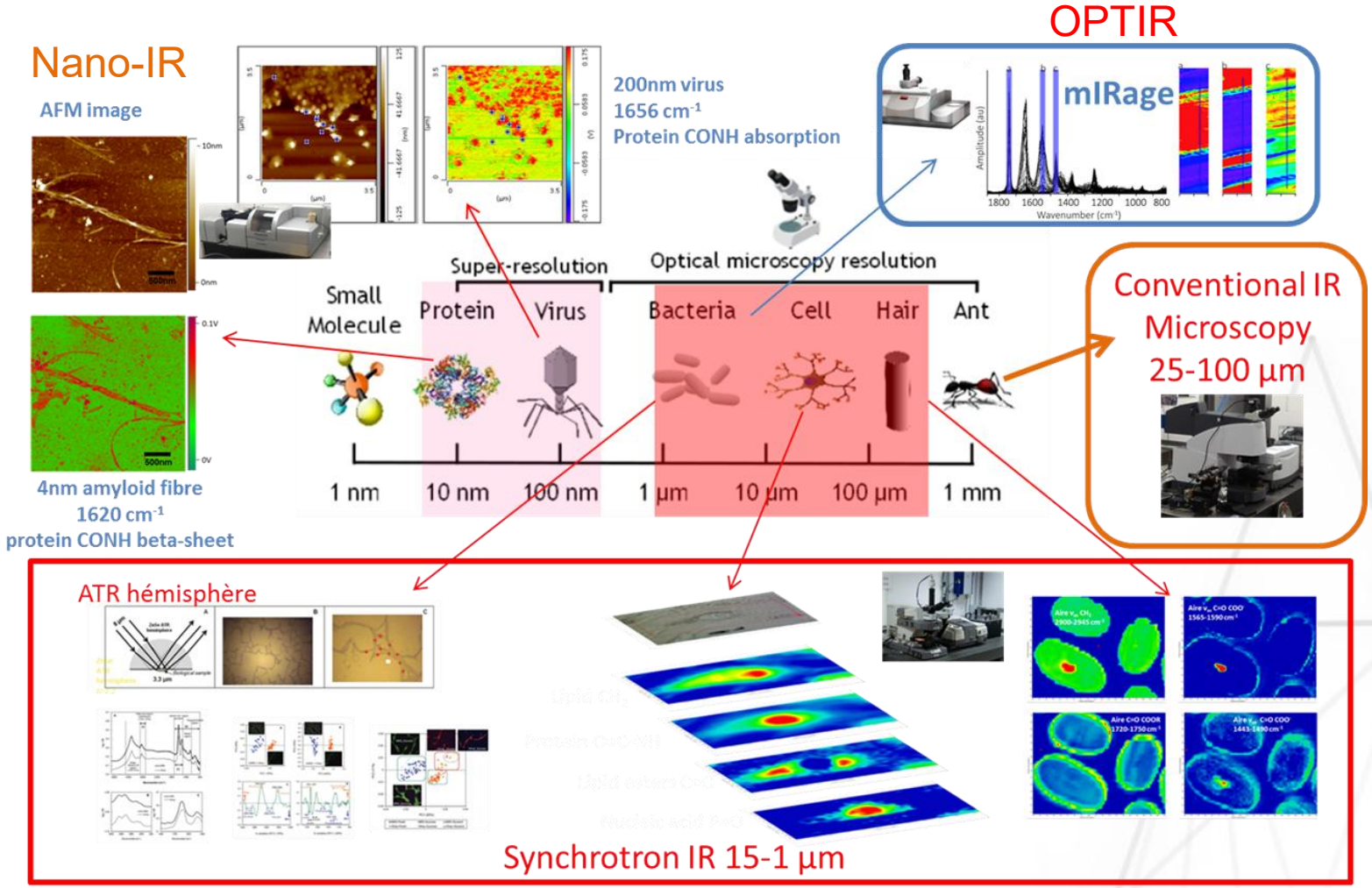
UTILIZATION

- PHYSICS
  - MATERIAL IN EXTREME CONDITIONS
  - ELECTRONICS, BAND GAP, CHARGE CARRIER DENSITY
  - HIGH PRESSURES, HIGH TEMPERATURES
- CHEMISTRY
  - POLYMERS
  - CATALYSIS
  - SURFACES
  - ELECTROCHEMISTRY
- BIOLOGY
  - TISSUE SECTIONS
  - HARD TISSUES (bone, dentin, cartilage)
  - 2D/3D CELL CULTURES,
  - LIVING CELLS
  - BIOMATERIALS
  - DIAGNOSIS
  - COSMETICS (hair, skin, nails)
- ENVIRONMENT
  - PLANTS, PLANT CELL WALLS
  - SOILS
  - AEROSOLS
  - MINERALOGY & GEOLOGY
  - MICROPLASTICS
- CULTURAL HERITAGE SCIENCES
  - POLYCHROMY, PAINTINGS
  - RESINS, VARNISHES
  - MATERIALS woods, bones, ceramics…
- ASTROCHEMISTRY
  - METEORITES, MICROMETEORITES, UCAMM Ultra Carboneceous Antartic Micro-Meteorites
  - IDP Interplanetary Dust Particles
  - SPACE RETURN SAMPLES (Hayabusa 1/2, Stardust…)
- FORENSICS
- PHARMACEUTICS

IR MICROSPECTROSCOPY METHODS

- Confocal Fourier Transform IR microspectroscopy (µFTIR)
  - Conventional
  - **Synchrotron**
- Hyperspectral FTIR Imaging
- Direct Laser IR imaging
- Optical Photothermal IR
- Nano-IR
  - Photothermal (AFM-IR)
  - Scattering (sSNOM)

- Differ in:
  - Measurement principle
  - Spatial resolution
  - Spectral range
  - Samples and sample preparation
  - Abilities (sensitivity, quantification, speed)



PLAN

General introduction → Applications → Introduction to FTIR Spectroscopy

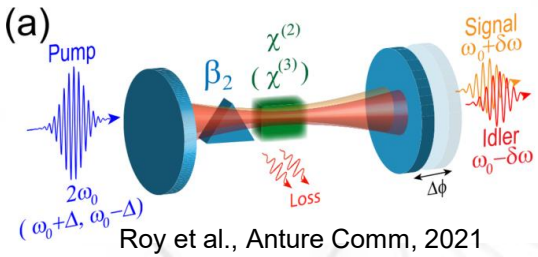
Introduction ot FTIR Microspectroscopy → **Instrumentation** → Beyond the diffraction limit

SOURCES FOR IR MICROSCOPY

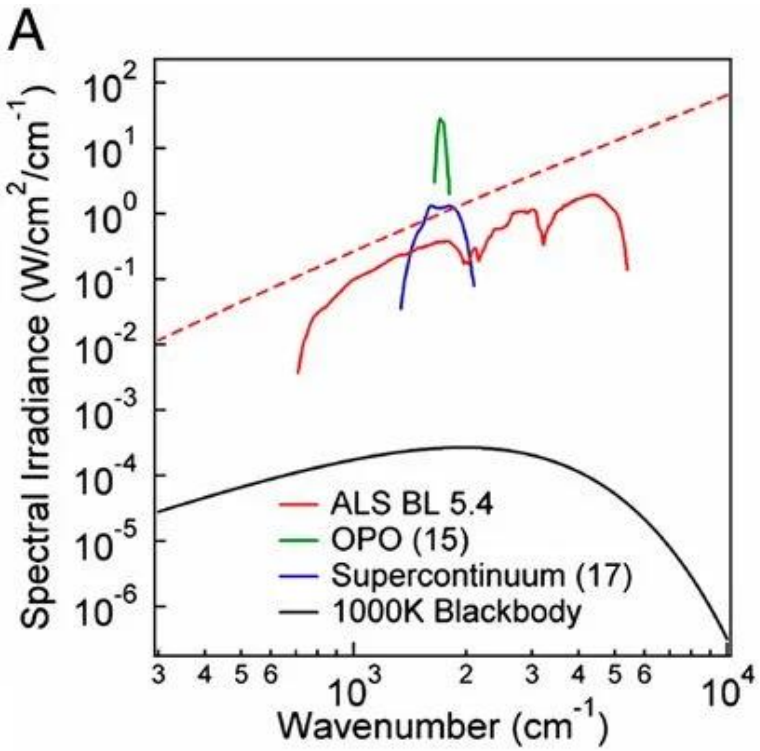
- Conventionnal source: globars
  - SiC bar heated at 1200-1300K: black body radiation
  - Stable, broadband (mid-IR)
  - Cheap (500€)

- Synchrotrons
  - Electrons accelerated at the speed of light
  - **Ultrabroadband** (THz, far IR, mid IR, near IR … hard X-rays)
  - High brilliance
  - Very expensive 500 M€, rare, **user facilities**

- IR lasers
  - Quantum Cascade Lasers (accordable)
  - Supercontinuum lasers
  - Optical Parametric Oscillators (OPO)
    - Expansive (100 k€), rare
    - Aggressive for sample
    - Unstable



Roy et al., Anture Comm, 2021



Bechtel PNAS 2014

IR @ SYNCHROTRONS











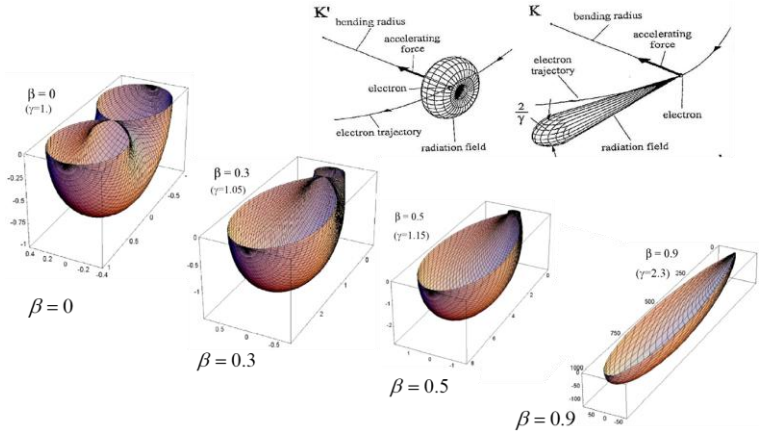




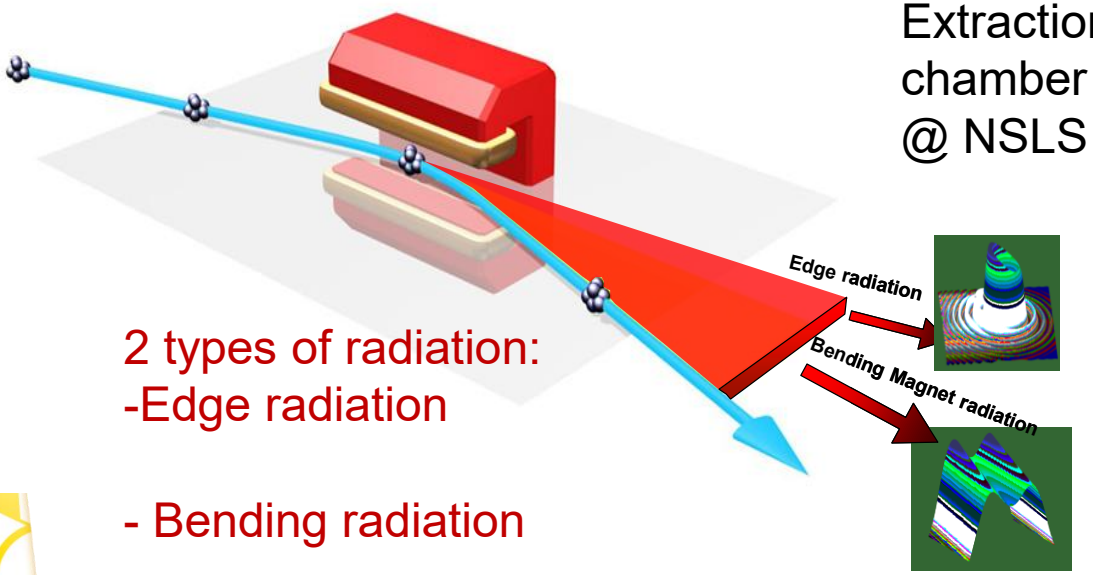
µFTIR @ synchrotron

Synchrotron	Beamline name
ALBA	MIRAS
ALS	BL1.4, BL2.4
Australian Sync	IR microspectroscopy
BESSY	IRIS
DIAMOND	MIRIAM
DAφNE	SINBAD IR
ELETTRA	SISSI
ESRF	ID21
MAX IV	??
NSLS II	FIS
SESAME	EMIRA
SLRI	BL4.1IR
SOLARIS	CIRI
SOLEIL	SMIS
SPRING-8	BL43-IR

IR GENERATION AT SYNCHROTRON SOURCES



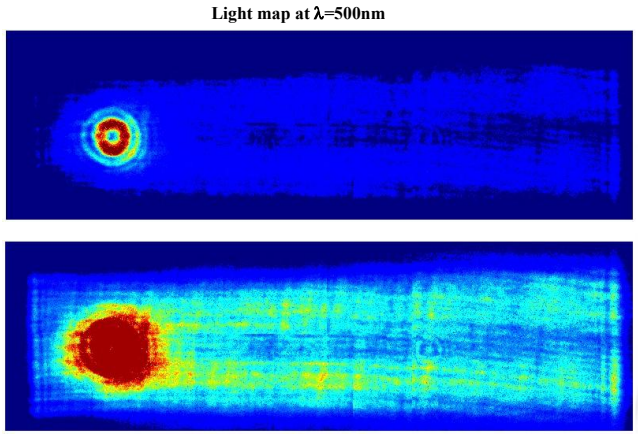
IR is generally collected with a slotted mirror from a **bending magnet** source:



2 types of radiation:
-Edge radiation

- Bending radiation

Extraction chamber @ NSLS I



Polarization
Edge radiation: circular
Bending radiation: straight

IR flux is proportional to synchrotron current intensity

SYNCHROTRON µFTIR

- COUPLING A SYNCHROTRON SOURCE TO AN IR MICROSCOPE

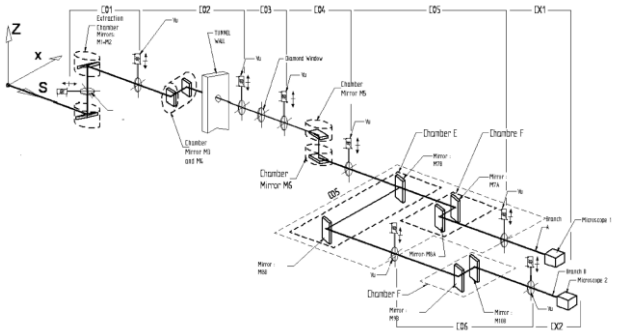
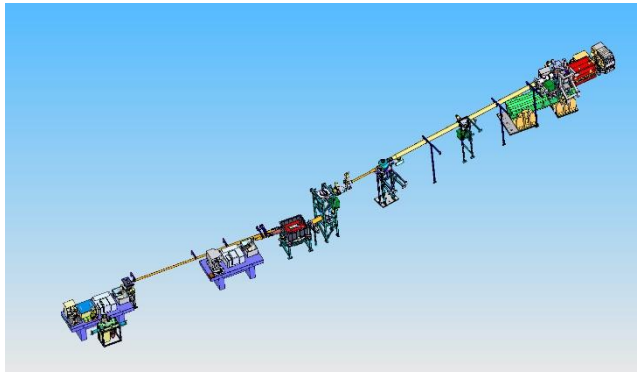
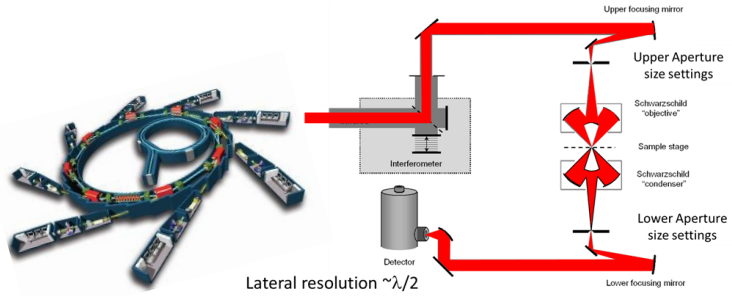


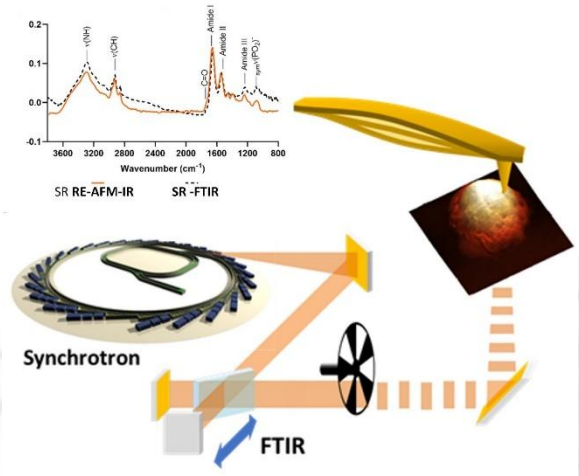
Fig. 7. The layout of the SMIS beamline at SOLEIL.



- CONFOCAL MICROSCOPY



NANO-IR

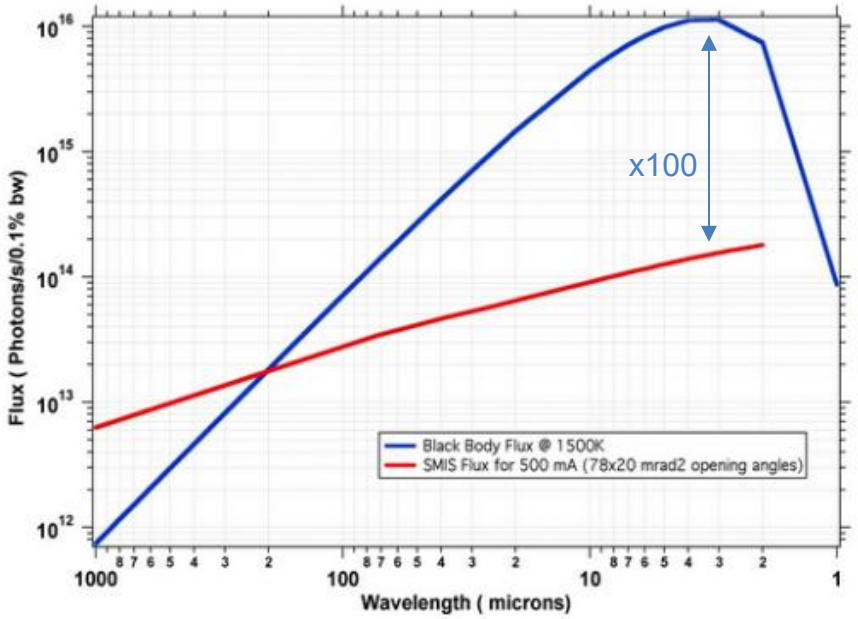


WHY USE SYNCHROTRON?

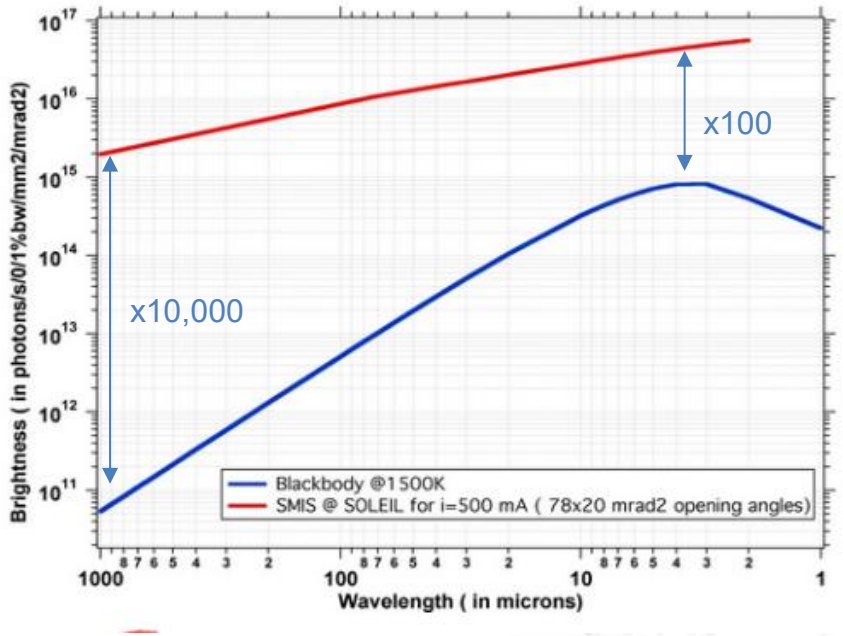
- Brilliance:

Black body thermal source (globar)
SOLEIL Synchrotron

FLUX



BRILLIANCE

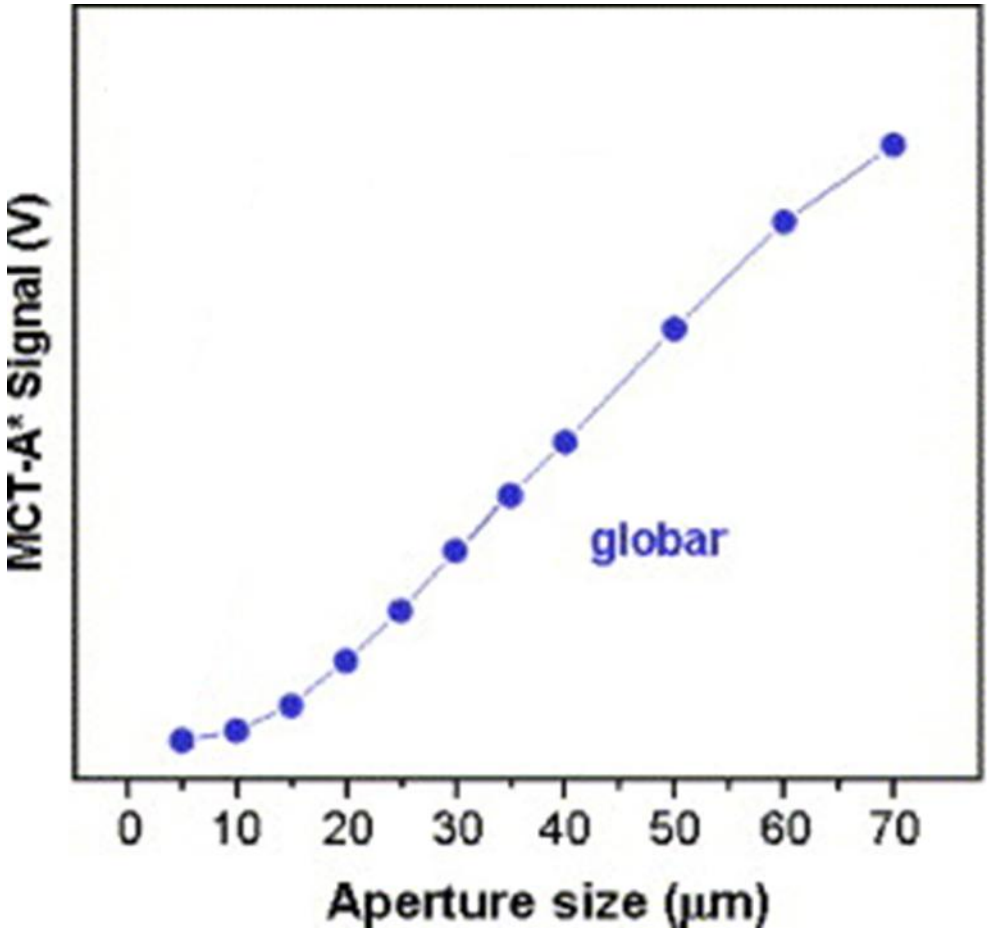


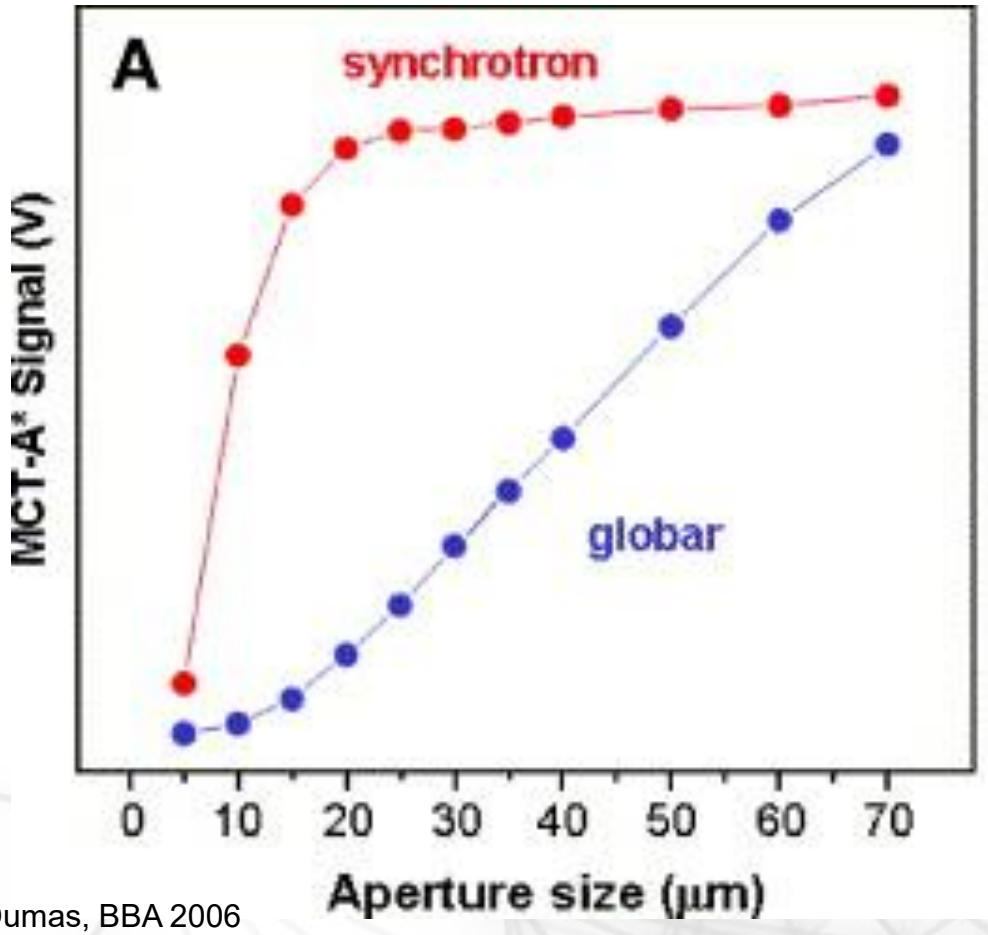
- Ultrabroadband:
  - From the THz
  - To the X-ray

WHY USE SYNCHROTRON?

- Effect of the microscope aperture size on the IR signal

Signal versus confocal aperture size

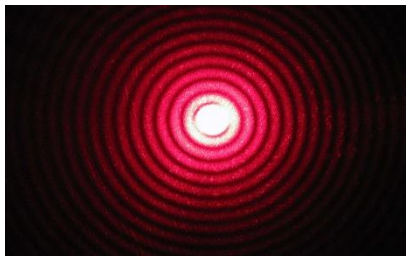




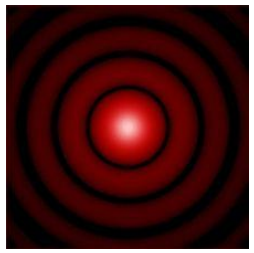
From Miller & Dumas, BBA 2006

INSIDE THE MICROSCOPE

- GENERATING A MICRO SPOT IN AN IR MICROSCOPE: **PINHOLES**



Diffraction pattern by a single pinhole

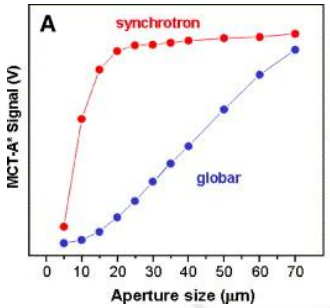


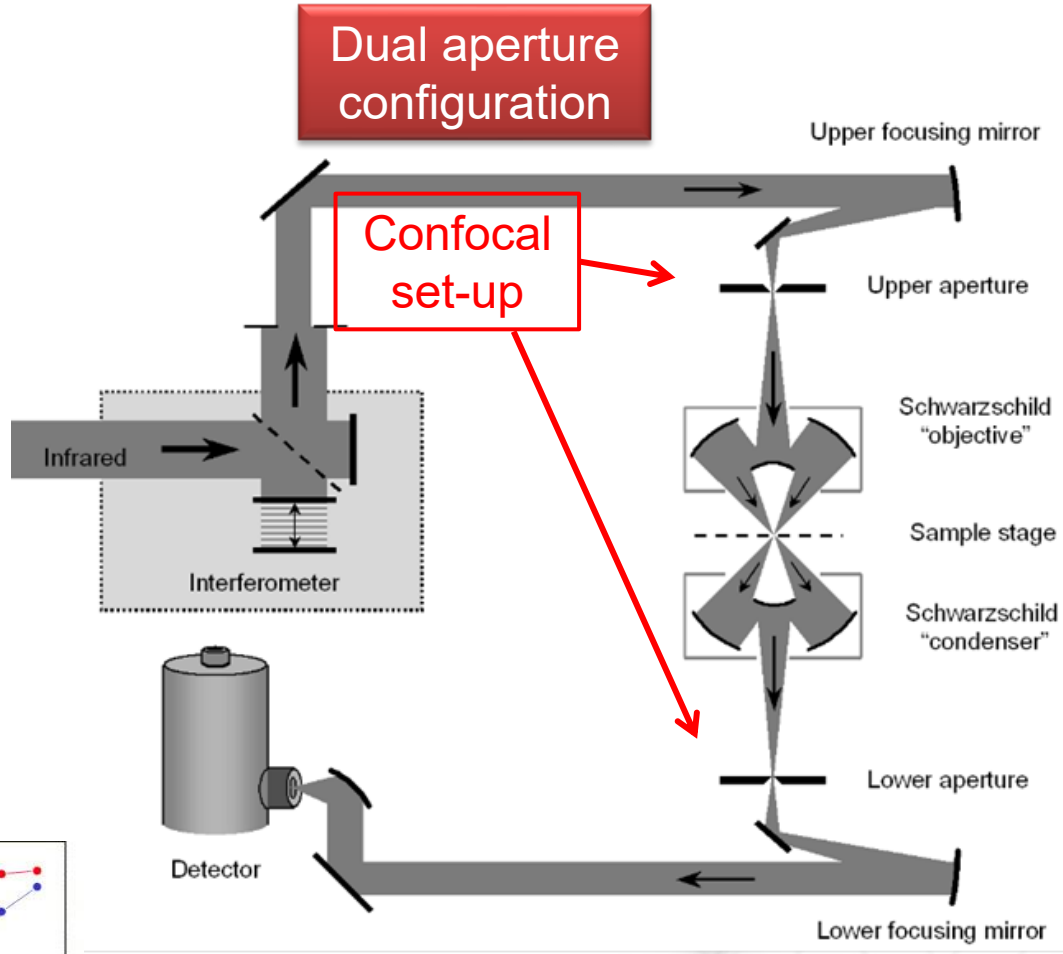
Diffraction pattern in a confocal system

Lateral resolution: ~λ/2

Diffraction limits spatial resolution

Confocal apertures reduce diffraction
Confocal apertures induce huge signal losses

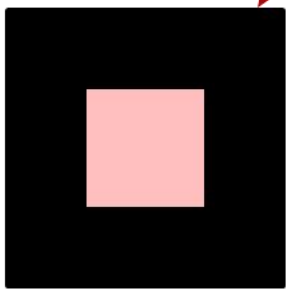




WHY USE SYNCHROTRON?

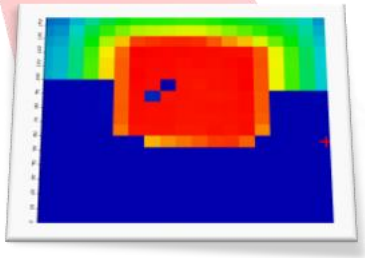
The **Confocal** FTIR microscope has been the staple of synchrotron IR beamlines for over 30 years

Thermal SOURCE



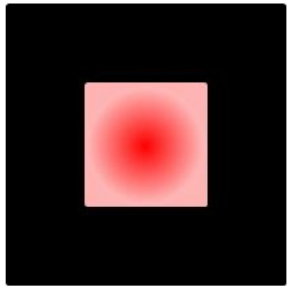
SPATIAL RESOLUTION
25-50 µm
LIMITED BY THE SOURCE BRILLIANCE

SPECTRAL RANGE
400-7500 cm^{-1}

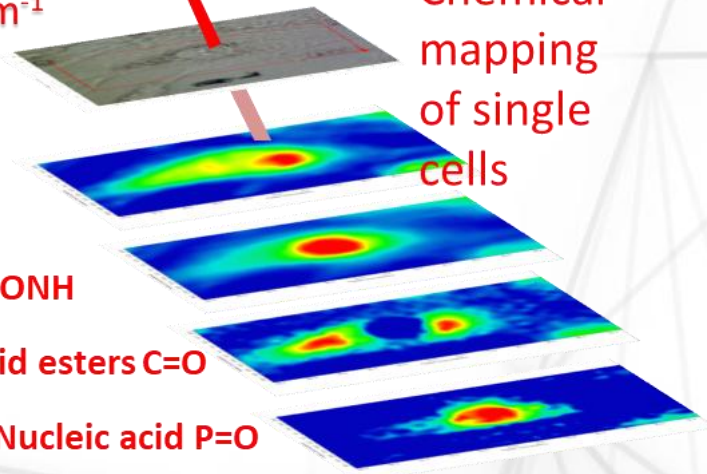


SYNCHROTRON SOURCE

SPATIAL RESOLUTION
DIFFRACTION LIMITED
3-15 µm RESOLUTION
CONFOCAL



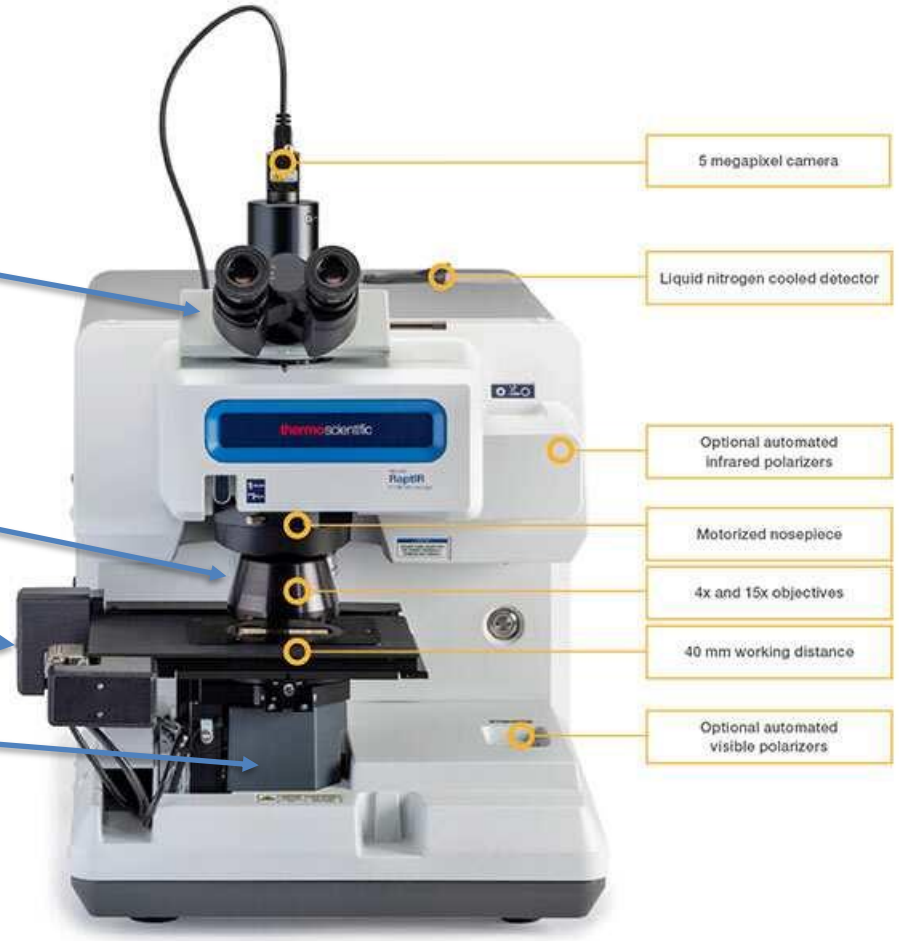
SPECTRAL RANGE: BROADBAND
50-10000 cm^{-1}



Chemical mapping of single cells

ANATOMY OF AN IR MICROSCOPE

- Microscope mainframe
- Microscope optics
- Vizulisation (Binoculars, Camera)
- Illumination
- Visible and IR objectives
- IR detector(s)
- Motorized microscope stage
- IR Condenser
- Optional filters
- Beam ports

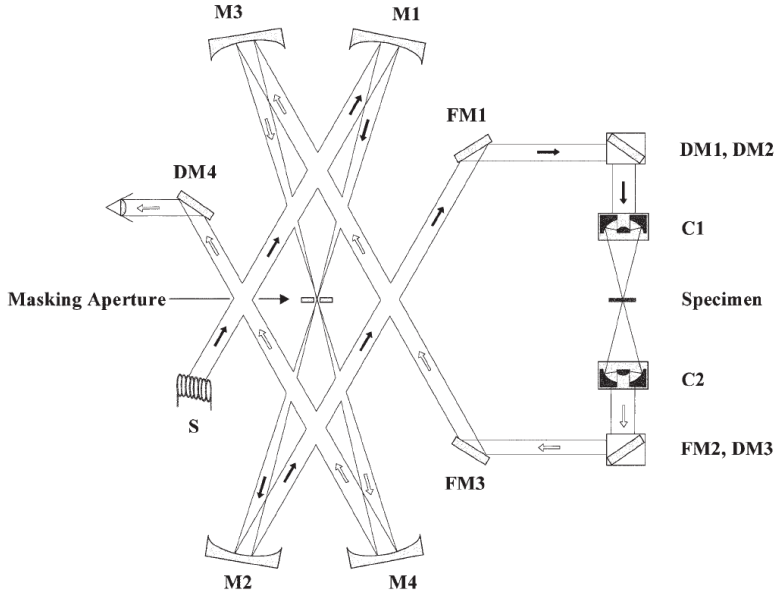


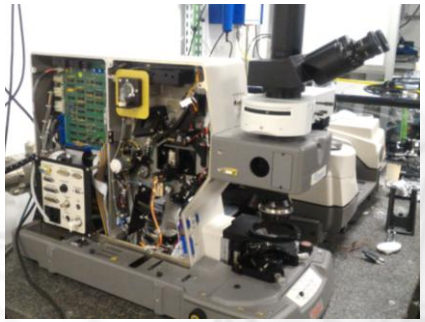
MICROSCOPE OPTIC CONFIGURATION

Dual aperture configuration

Single aperture configuration

Single aperture dual path configuration





ThermoFisher Scientific Continuum

SPATIAL RESOLUTION

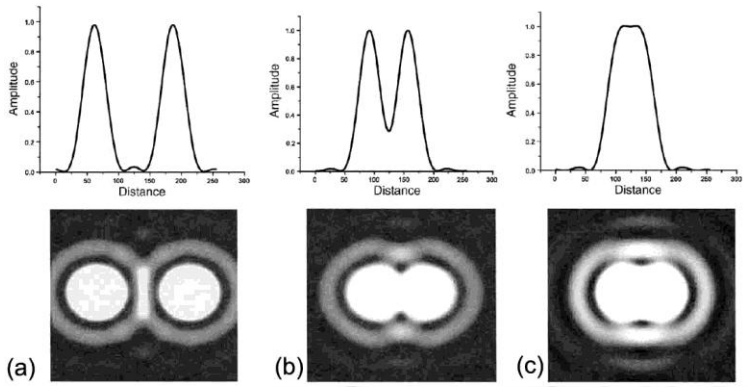
- Theoretical diffraction limit: given by Abbe equation:

$$R = \frac{0.61\lambda}{NA}$$

R: resolving power
λ: wavelength (μm)
NA: objective Numerical Aperture,
NA= nsin(θ)

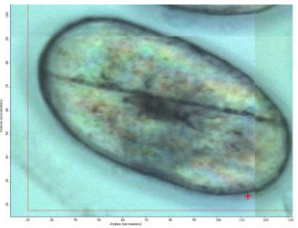
- Actual resolution will be worst due to:
  - Diffraction from sample/optics
  - Objective obscuration ratio
  - Alignment
  - In reflection mode

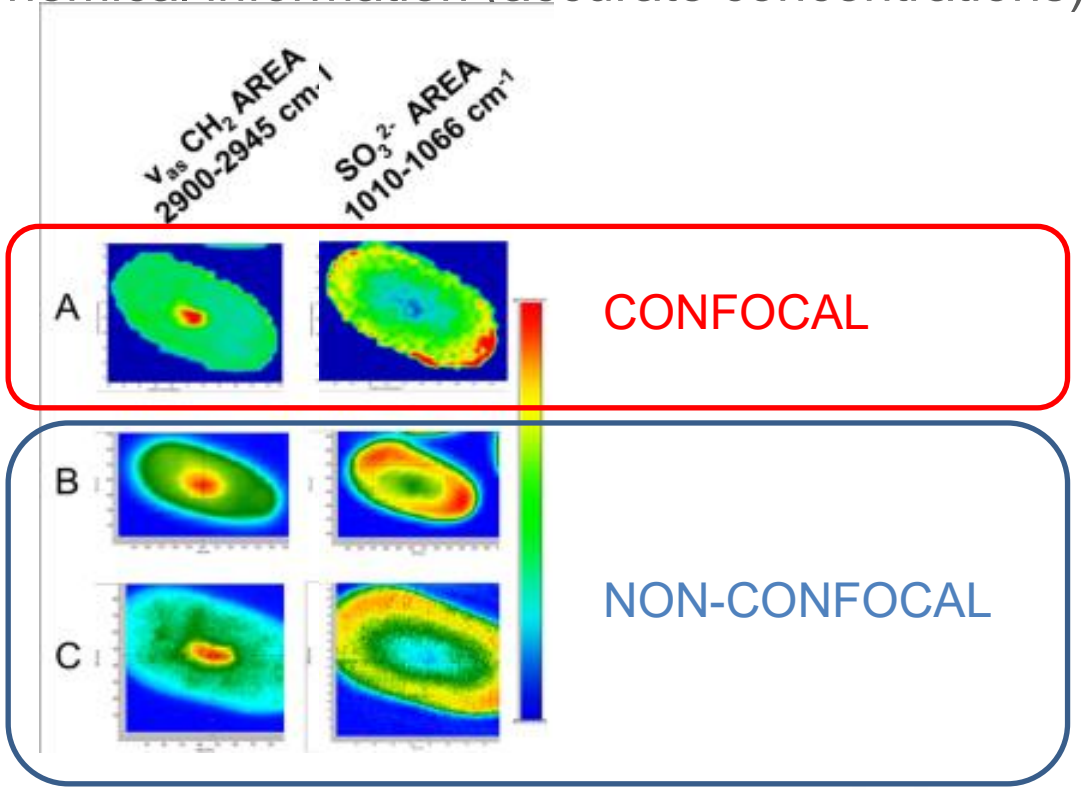
Typical NA for IR objectives:
15X objective: ~0.5
30X objective : ~0.6



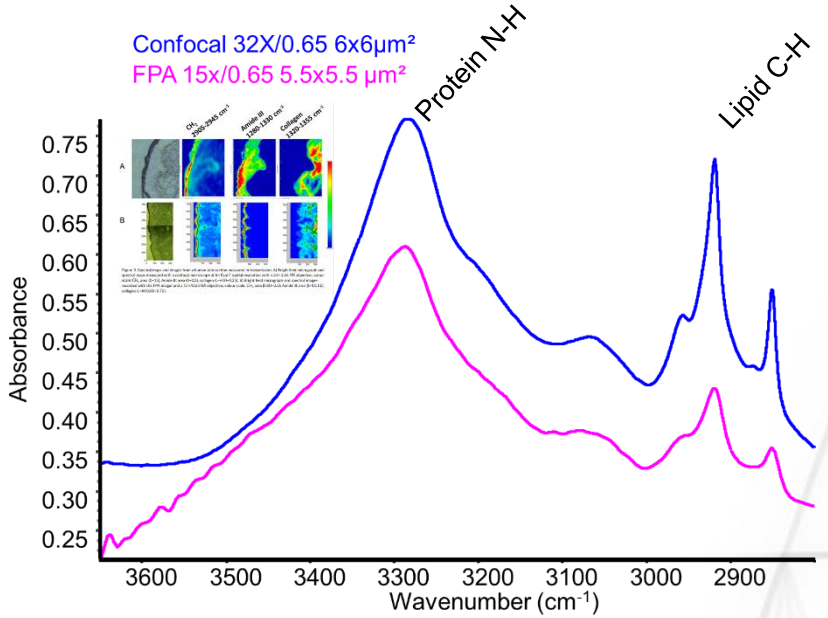
SPATIAL RESOLUTION

- Spatial resolution is important for obtaining accurate information
  - Spatial information (accurate images)
  - Chemical information (accurate concentrations)





Spectral images and maps of the same hair medulla
A. Confocal microscope with synchrotron source
B. Low magnification imaging system (15x)
C. High magnification imaging system (62x)



Spectra of the medulla of the same skin stratum corneum layer measured with either:

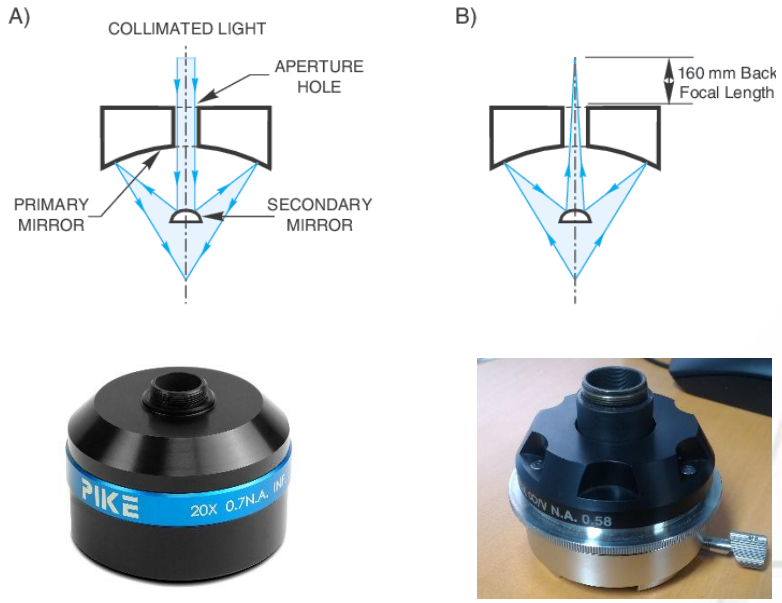
- A confocal microscope with synchrotron source at 6x6 µm² resolution
- A non-confocal IR microscope with FPA detector at 5x5 µm² projected pixel size

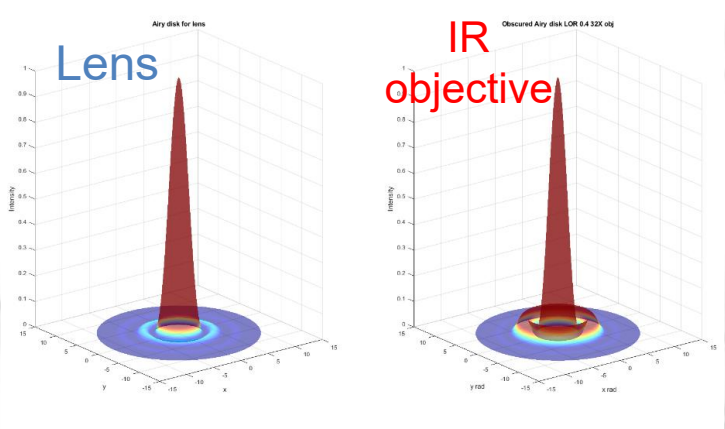
OBJECTIVES

- IR objectives
  - All reflective spherical objectives
    - Avoid chromatic aberrations over the whole spectral range
  - Schwarzschild: focus to infinity
  - Cassegrain: focus to a focal point
- Central obscuration
  - Reduced throughput
  - Reduced resolution
  - Lower energy in the central lobe
  - Higher energy in the lateral lobes
- Objective magnifications
  - 15X
  - 25X, 30X, 32X, 36X, 40X
  - N.A. 0.5 - 0.8

Schwarzschild

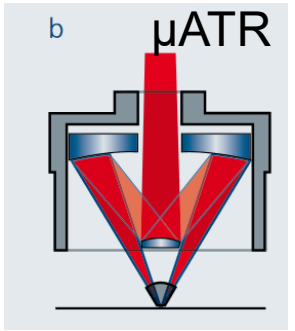
Cassegrain



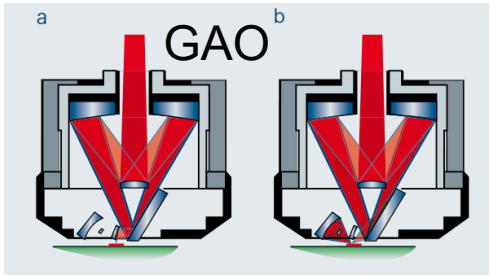


Special ir objectives

- Attenuated Total Reflection (μATR)
  - Used for thick, non-reflective samples
  - Contact sample: potentially destructive
  - Diamond, ZnSe, Ge
  - **Improved spatial resolution**: refractive index
    - Diamond 2.4
    - ZnSe 2.2
    - **Ge: 4**

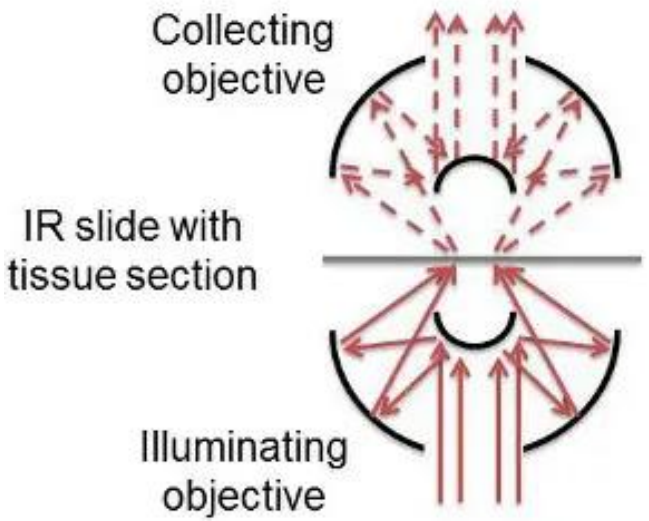


- Grazing incidence objective (GAO)
  - Improved sensitivity for oriented materials

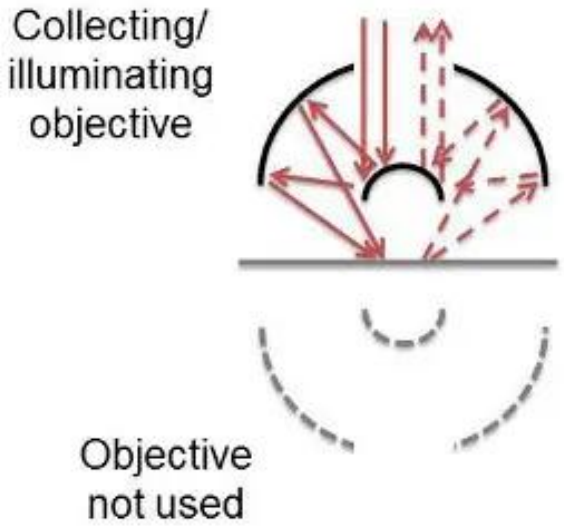


MEASUREMENT MODES

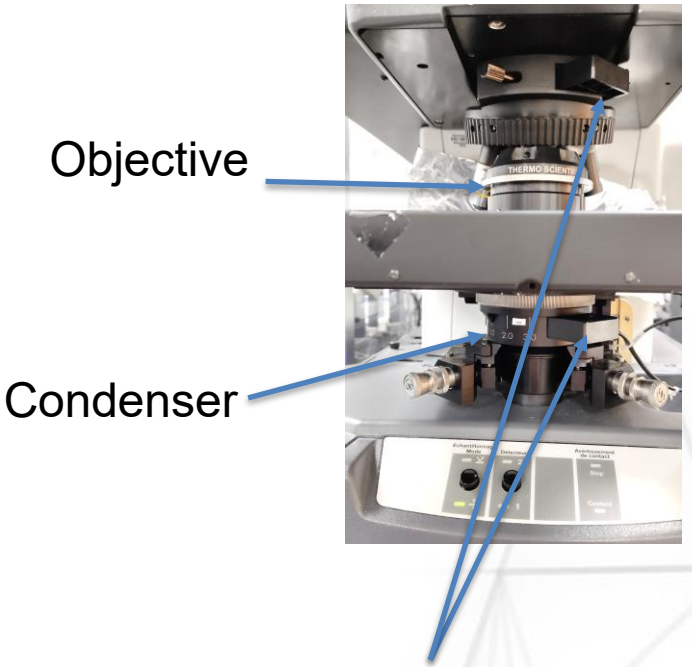
A) Transmission-mode



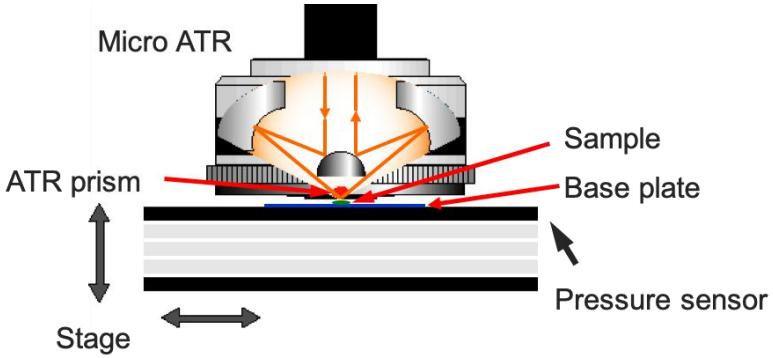
B) Reflection-mode



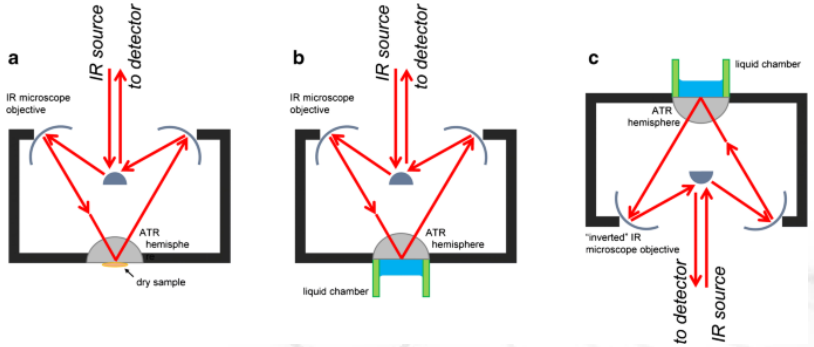
Transmission mode



C) micro ATR mode

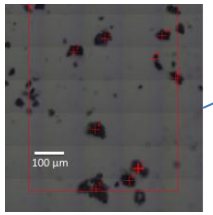


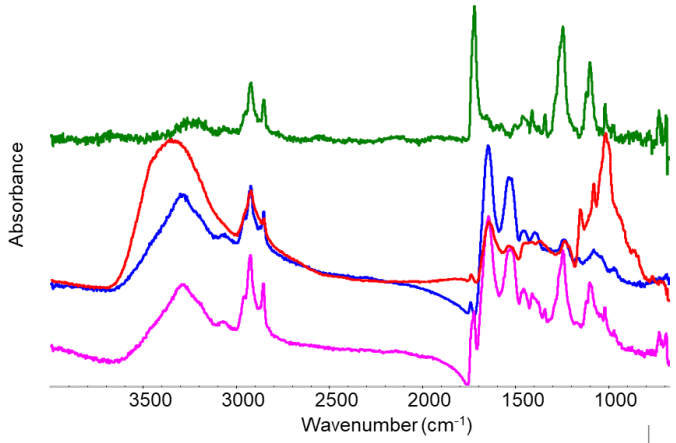
D) Inversed micro ATR mode

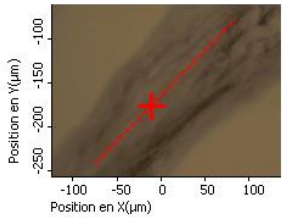


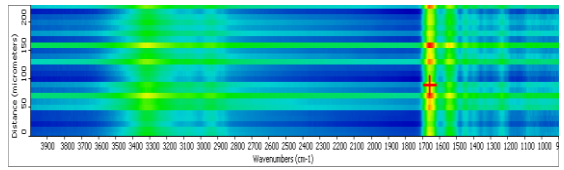
MAPPING MODES

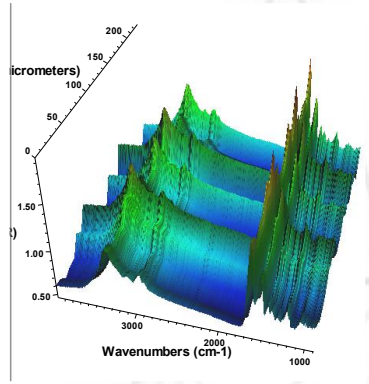
- Computer controlled motorized stage
  - 1 µm precision (0.1 µm optional)
- Discrete maps
  - Point by point
- Line maps
  - Across interfaces
- Area maps
  - Raster scanning
  - Sequential: slow

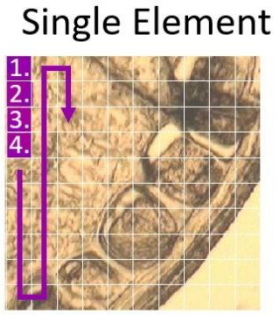








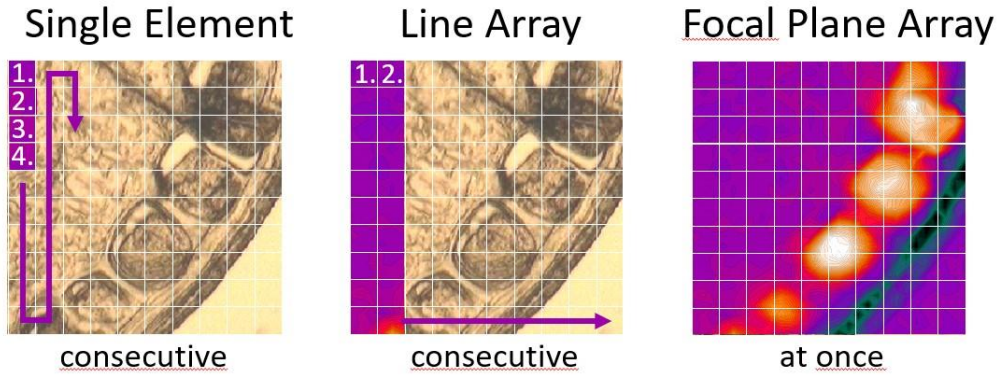


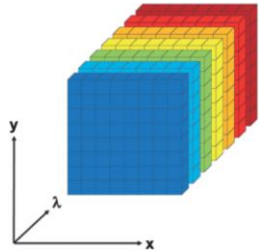


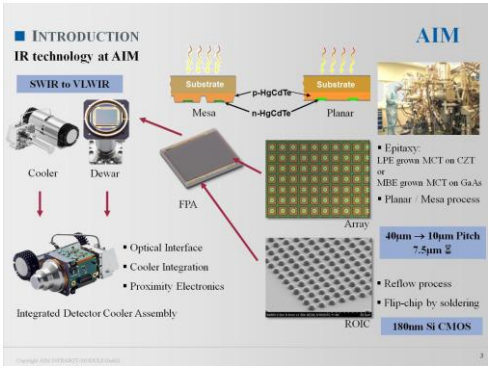
Time consuming

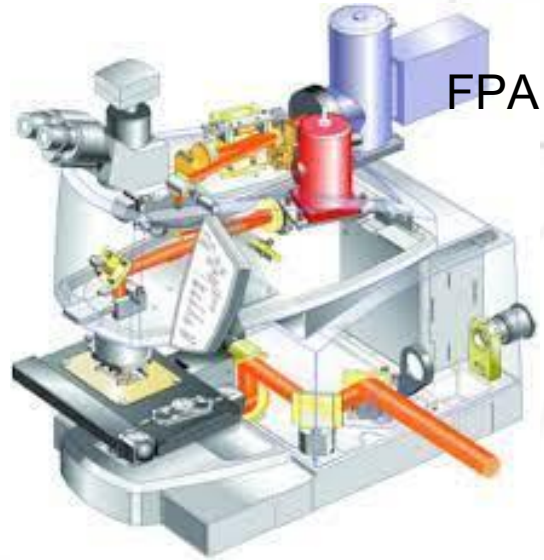
IMAGING MODES: HYPERSPECTRAL IMAGING

- Array detectors
  - Linear arrays
  - Focal Plane Arrays (FPA)
  - Use globar source
- Each pixel contains a full spectrum
  - Hyperspectral image/hypercube of data
- Detector technology: narrow-band MCT





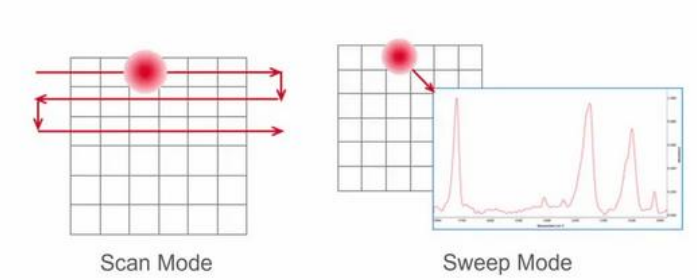




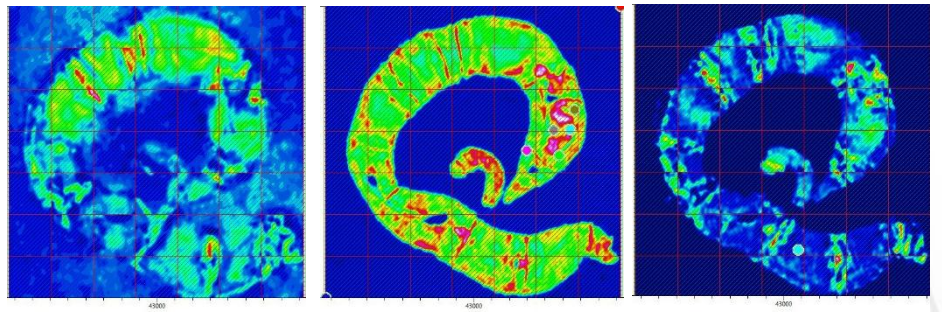
Agilent Cary 620 + Lancer FPA

IMAGING MODES: LDIR

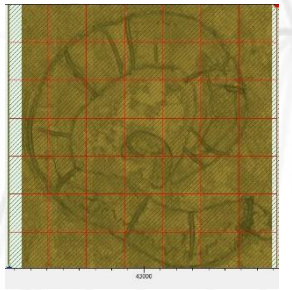
- LDIR: LASER DIRECT IMAGING



- Couple QCL source and point MCT or FPA detector
- Can operate in two modes:
  - Imaging/scan mode: single wavelength
  - Spectral/sweep mode: acquisition of a full spectrum
- Transmission or reflection modes



S. mansonii worm

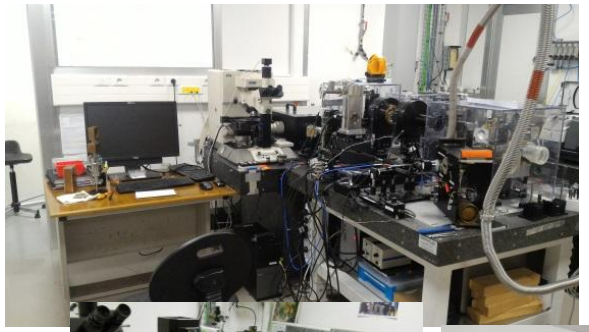
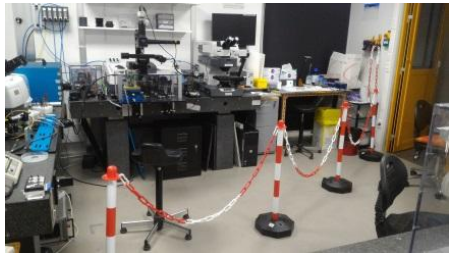


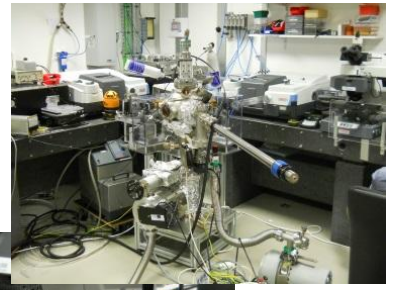
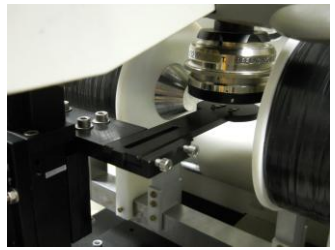
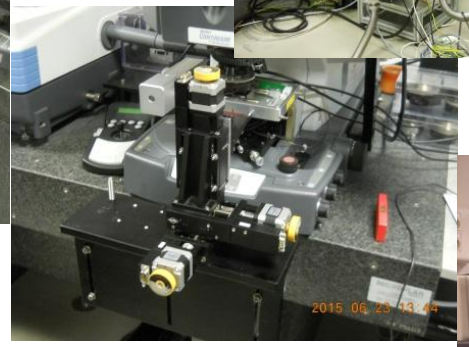
Agilent 8700 LDIR Chemical Imaging System

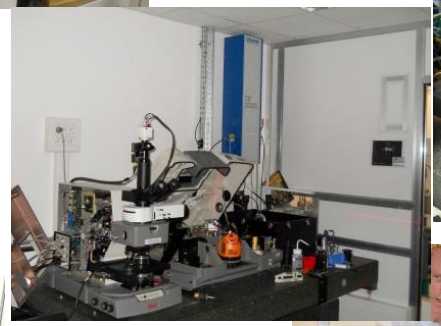
Bruker Hyperion II ILIM

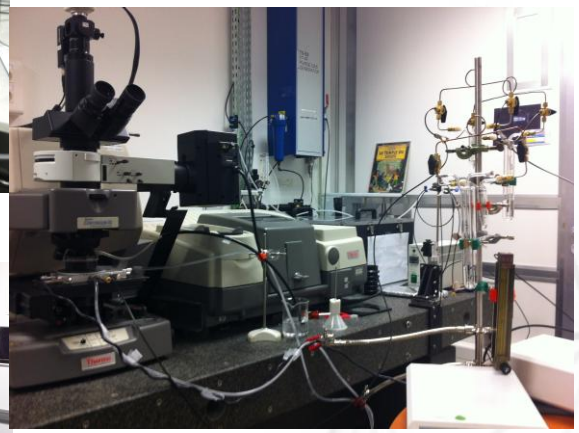
SAMPLE ENVIRONMENTS

Endless possibilities

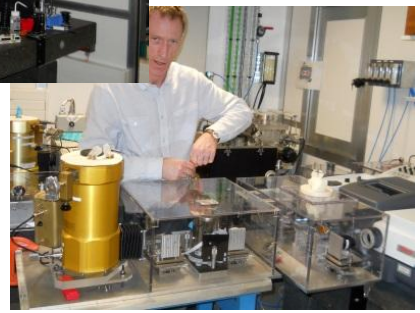



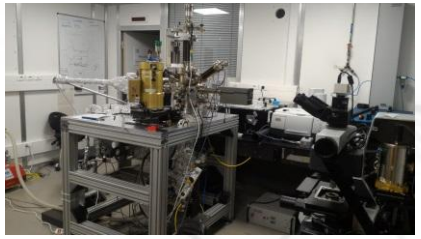










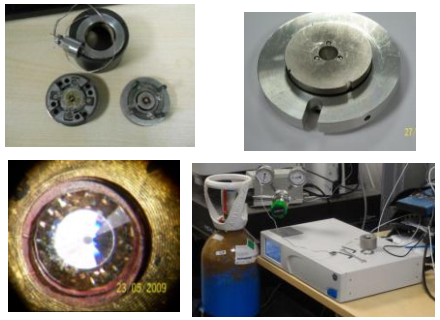


SAMPLE ENVIRONMENTS

Physico-chemcial constraints

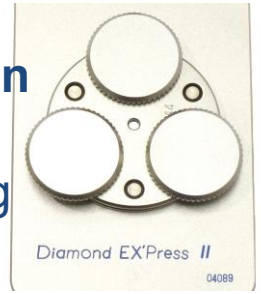
Compression

Diamond Anvil Cells

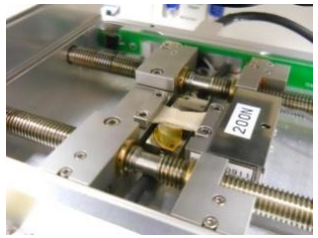


10^1 – 10^6 bars

Diamond compression cells
For flattening samples



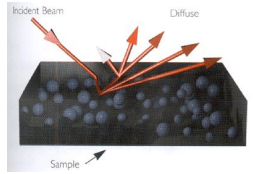
Stretching

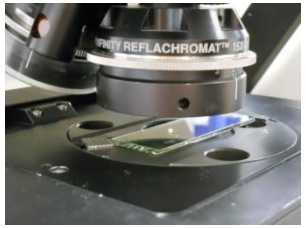


Heating/cooling atmospheric control

Fluorescence Imaging

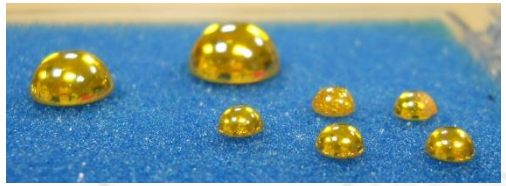
Réflexion



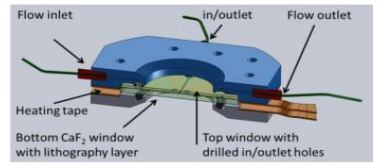


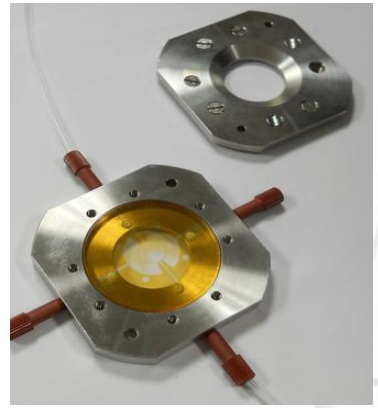
Micro-ATR

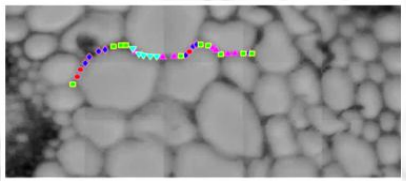
Inverted ATR



Microfluidics







PLAN

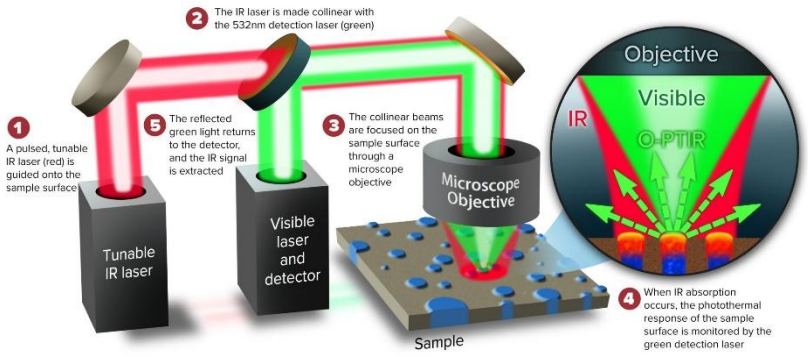
General introduction → Applications → Introduction to FTIR Spectroscopy

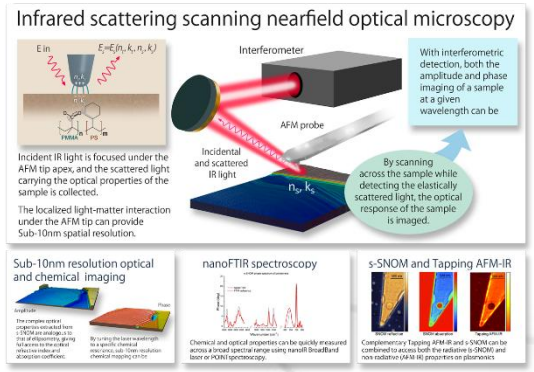
↓

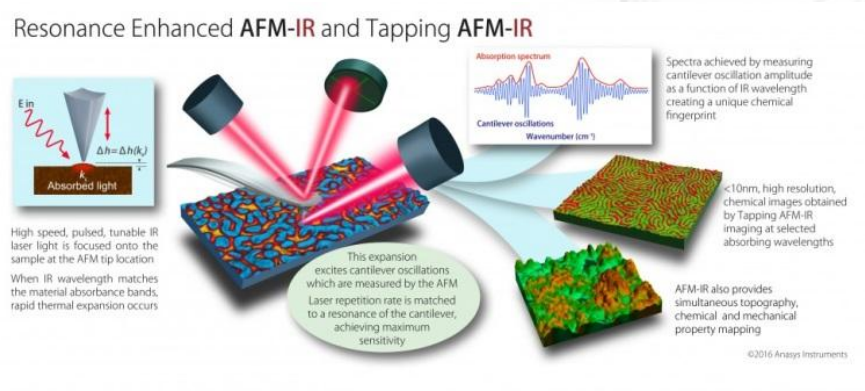
Introduction ot FTIR Microspectroscopy → Instrumentation → Beyond the diffraction limit

BEYOND THE DIFFRACTION LIMIT

- Spatial resolution of IR microspectroscopy inherently limited by diffraction
  - 2.5-25 µm in the mid-IR
- Most of modern microscopy is done below the diffraction limit of IR:
  - Confocal laser fluorescence microspectroscopy
  - Nano particles (< 100 nm)
- New methods:
  - Optical PhotoThermal IR (OPTIR) : 250-500 nm resolution
  - NanoIR: 10-50 nm resolution

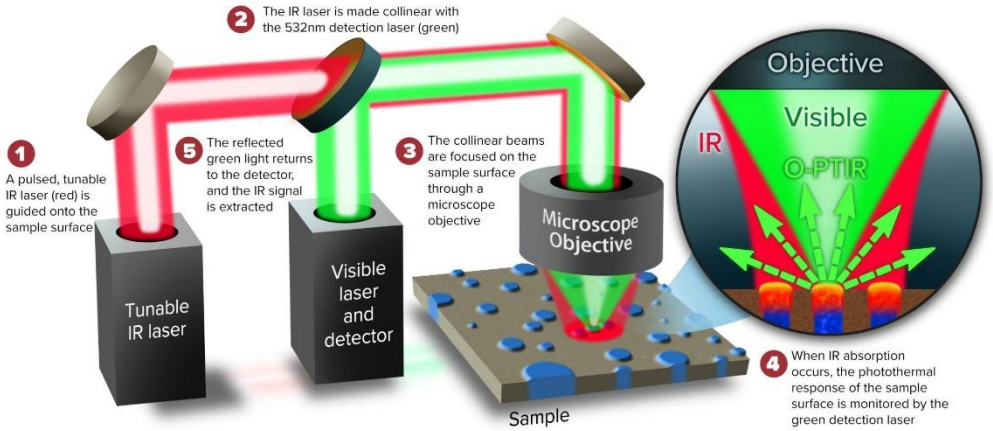


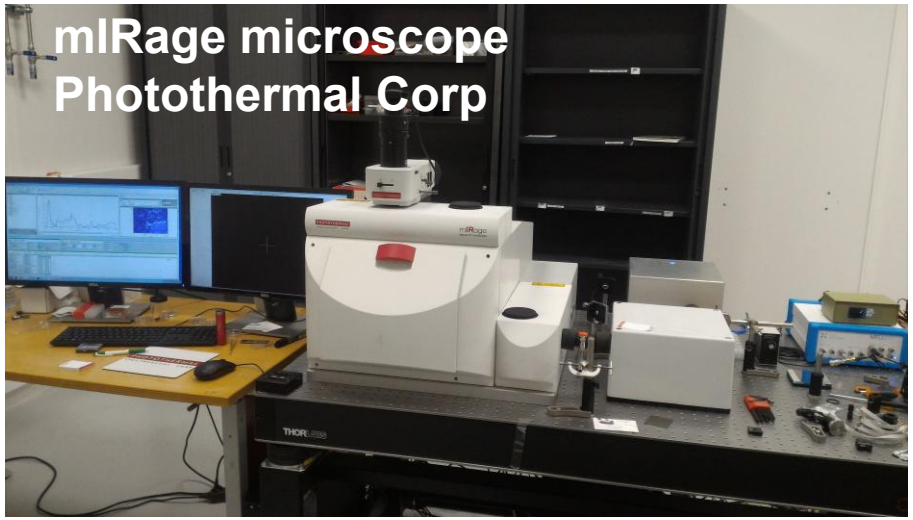




Optical PhotoThermal IR (OPTIR)

- Pump probe technique
  - QCL pump
  - Visible laser probe
- Measures change in sample refractive index η (''Mirage'' effect)
  - η changes by a few % upon IR excitation
  - Triggers change in sample reflectivity
  - Green light can be monitored by very sensitive visible detectors (CCD, PMT, APD…)
- Spatial resolution given by the green laser
  - Diffraction limited in the visible
  - Co-propagation/counter-propagation the lasers
- Hardly compatible with synchrotron at the moment





Synchrotron OPTIR !!

Article

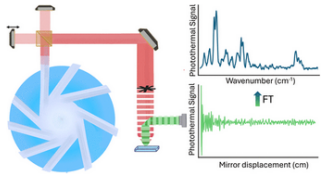
Broadband Fourier-Transform Optical Photothermal Infrared Spectroscopy and Imaging

Aleksandr Razumtcev, Gwendylan A. Turner, Sergey Zayats, Ferenc Borondics, Aris Polyzos, Garth J. Simpson*, and Hans A. Bechtel*

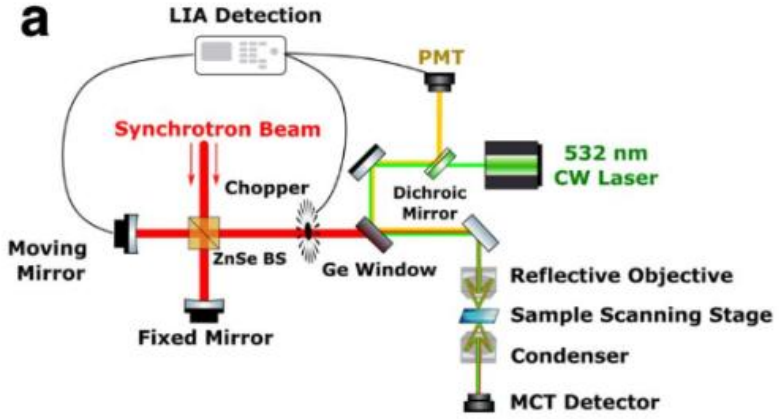
Analytical Chemistry 2025, 97, 37, 20117-20126 **(Article)** Open Access
Publication Date (Web): September 11, 2025
DOI: 10.1021/acs.analchem.5c02493

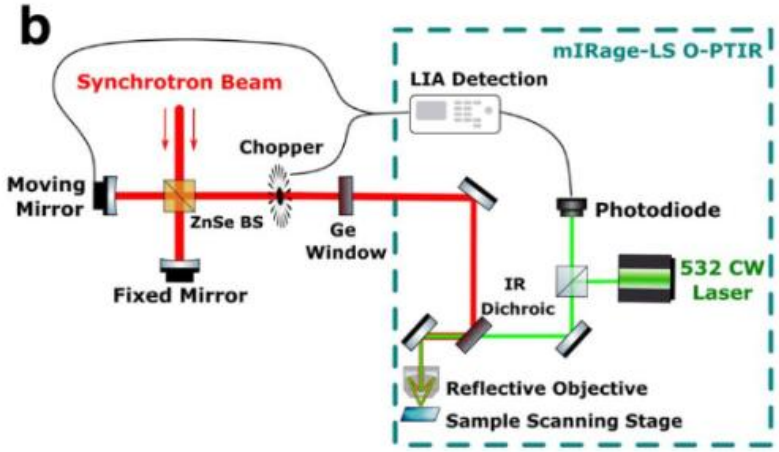
Abstract | Full text | PDF

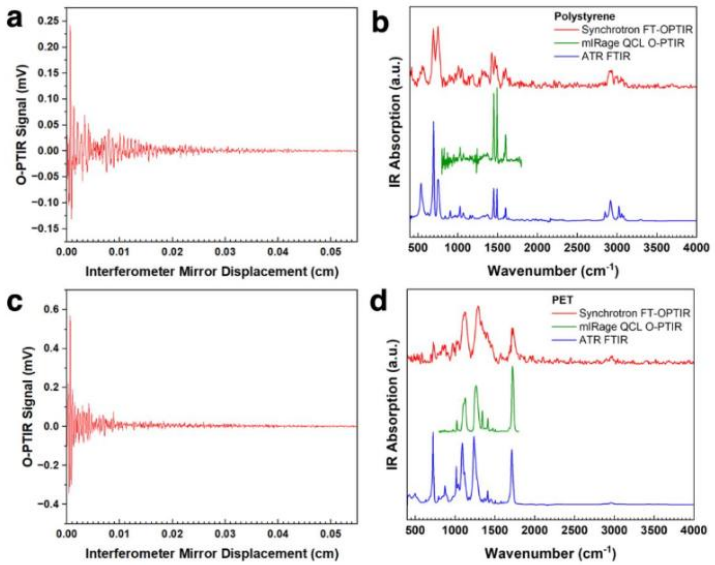
ABSTRACT



analytical chemistry







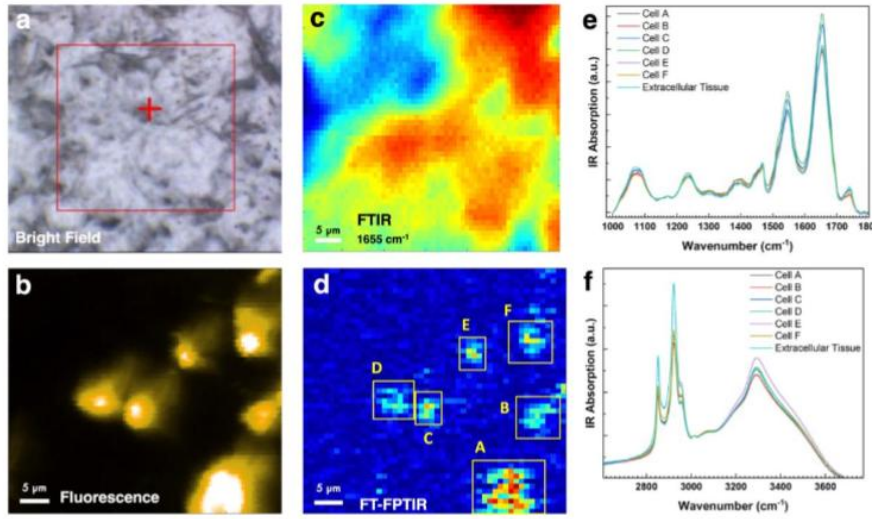
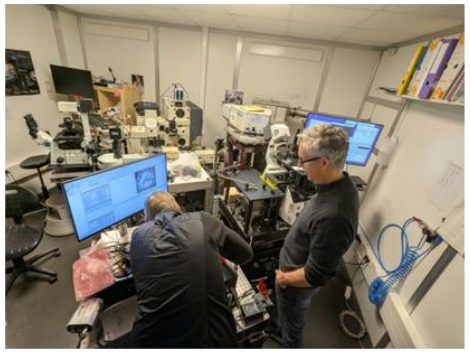
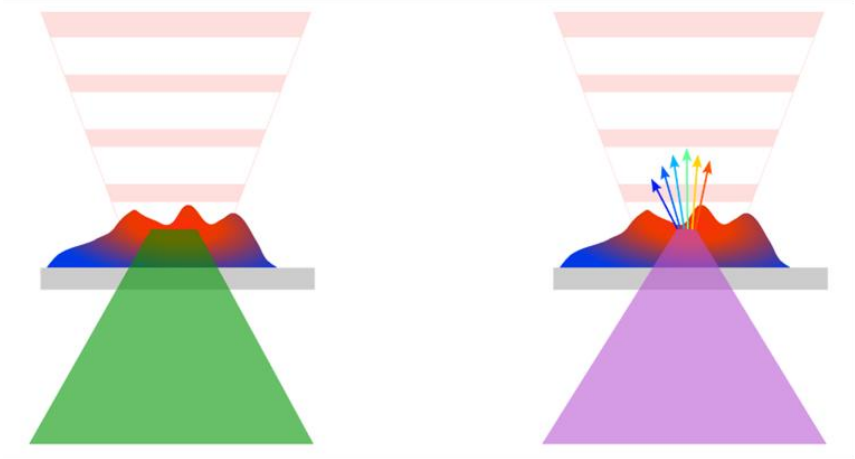


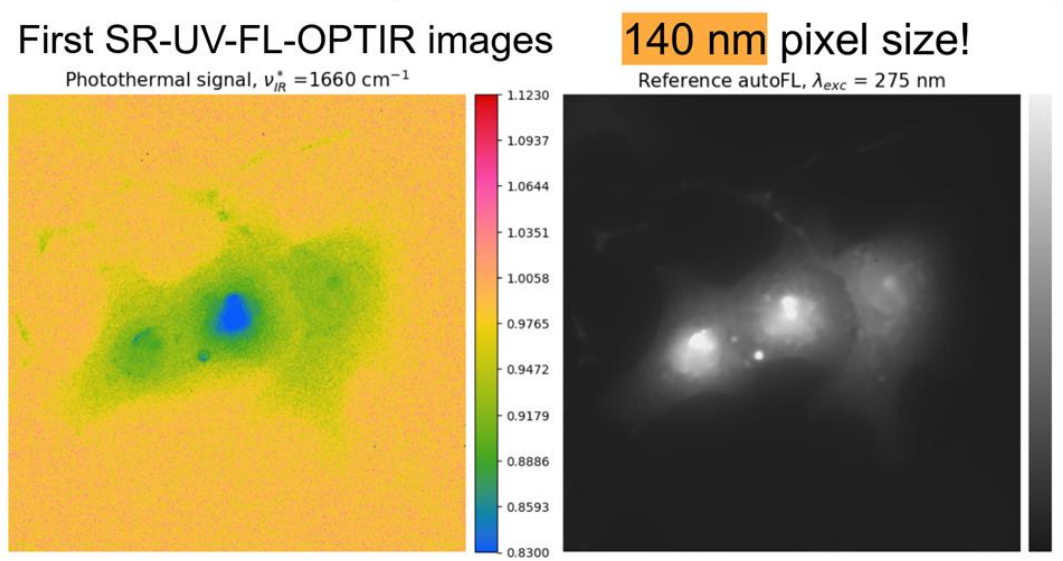
Figure 4. Cell-specific broadband FT-FPTIR chemical imaging of a fluorescently-labeled mouse tissue

Synchrotron Radiation – UV – FLuorescence OPTIR

HIGHER RESOLUTION OPTIR

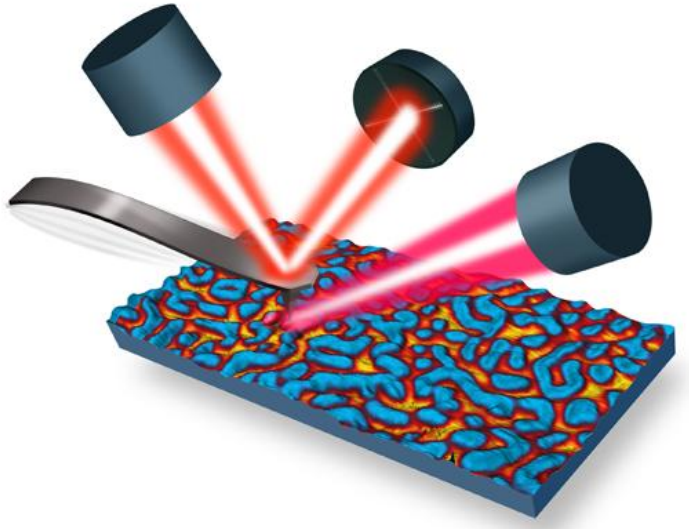






Nano IR

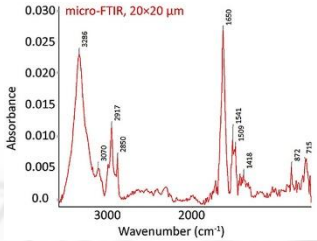
- **Near-field** measurements
  - Detector-sample distance << wavelength
  - Diffractio ndoes not occur in the nier-field
- Nanometer resolution
- Sample constraints
  - Ultrathin samples
  - Ultrasmooth samples (rugosity < 1 µm)
- Nano IR couple AFM probes with IR beam
- Several measurement modes
  - Micro-thermocouples
  - Photothermal AFM-IR
  - Scattering Surface Near Field Optical Microscopy (sSNOM)
- IR sources
  - QCL
  - OPO
  - Synchrotrons

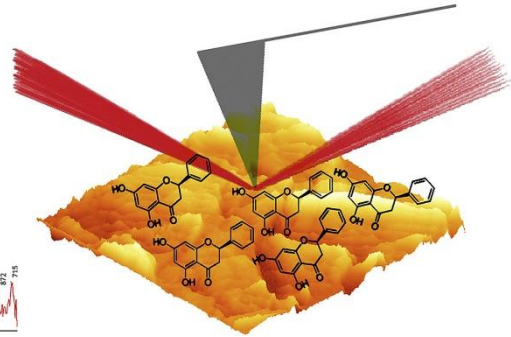


FTIR > FTIR microscopy > nano-FTIR

AFM-IR

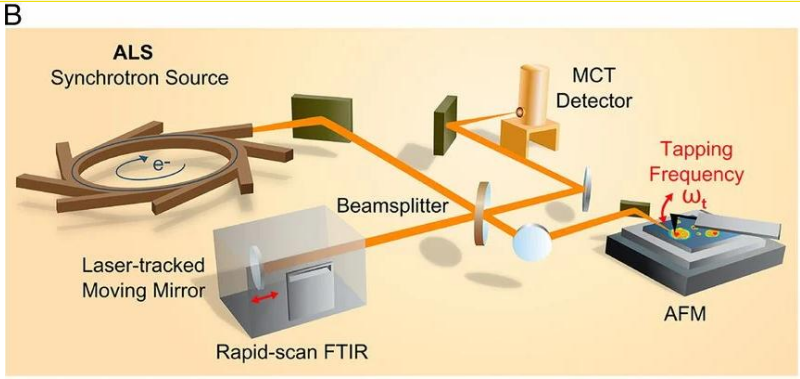
SNOM





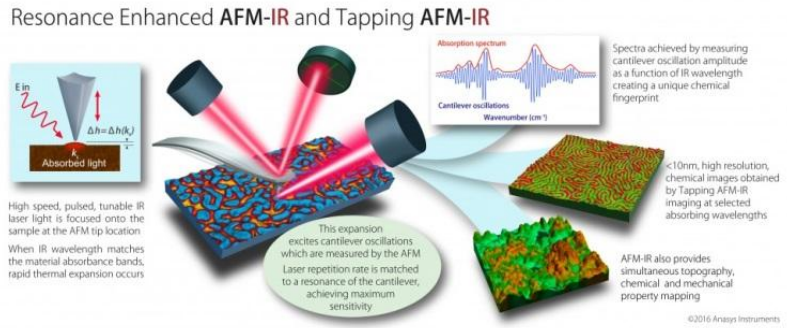
Nano IR

- Compatible with synchrotron source

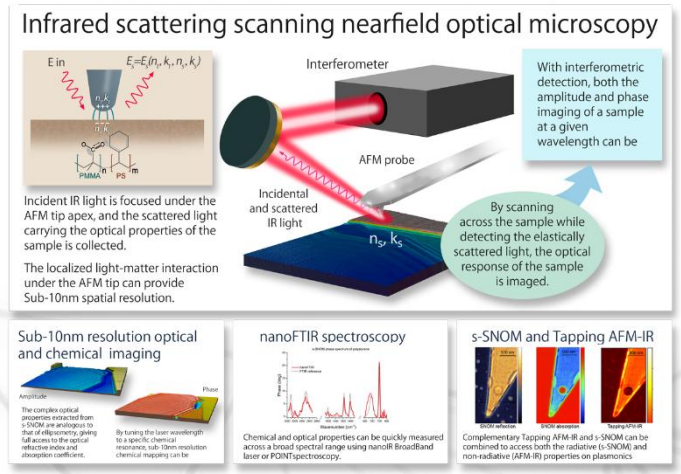


Bechtel et al.

- AFM IR
  - Photothermal
  - For soft materials



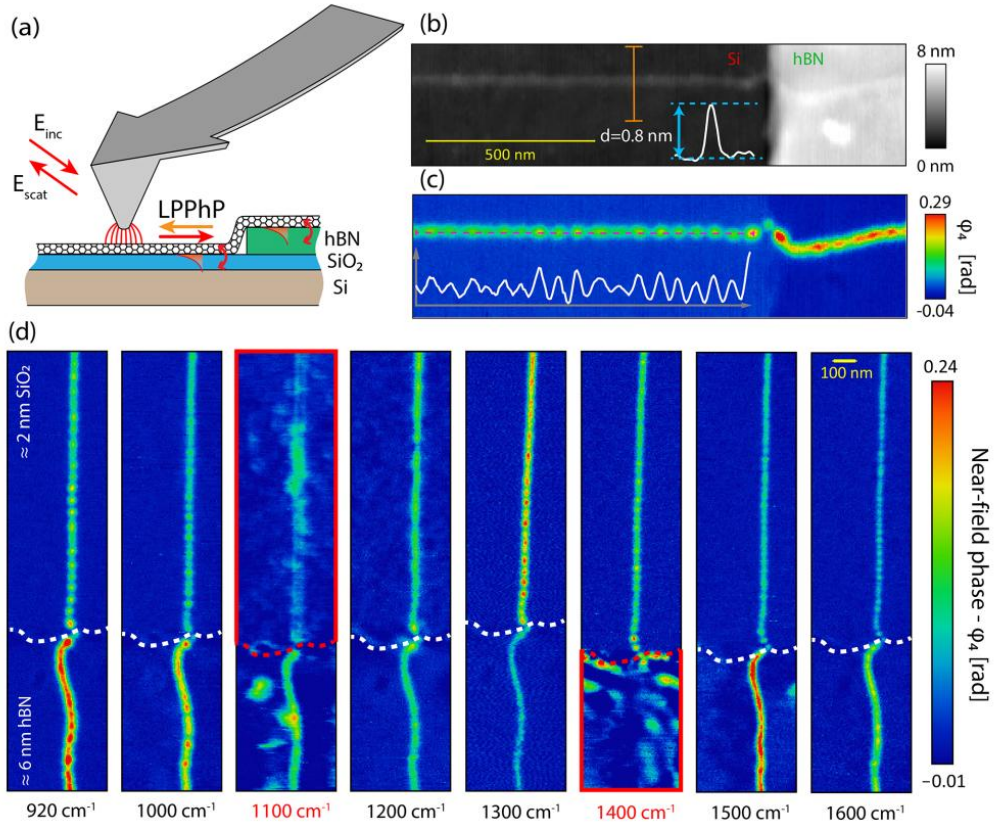
- scattering SNOM
  - Scattering
  - For hard materials

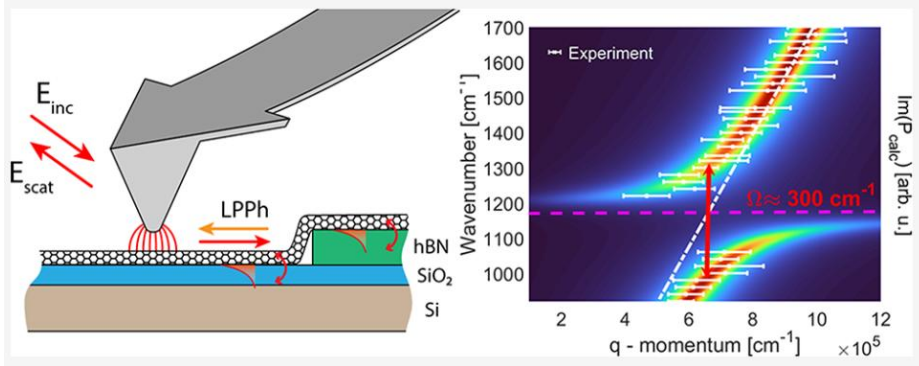


Bruker website

Synchrotron nano-IR

- One dimensional plasmon coupling in metallic carbon nanotubes





Direct Visualization of Ultrastrong Coupling between LuttingerLiquid Plasmons and Phonon Polaritons
Gergely Németh,* Keigo Otsuka, Dániel Datz, Áron Pekker, Shigeo Maruyama, Ferenc Borondics,*
and Katalin Kamarás, Nano Lett 2022

Thanks for your attention

The end