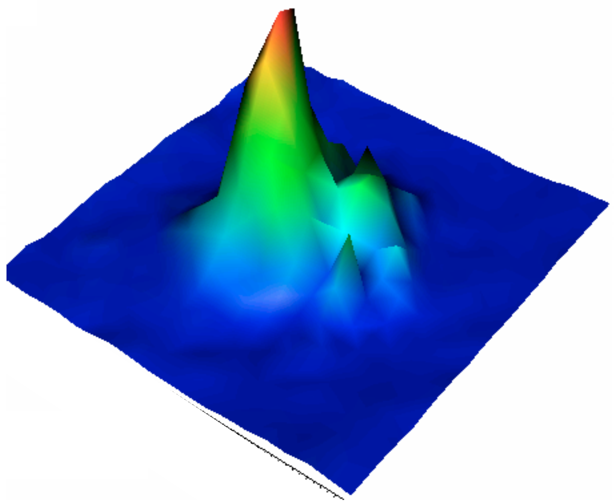

Infrared Microscopy Techniques using Synchrotron radiation

Paul Dumas
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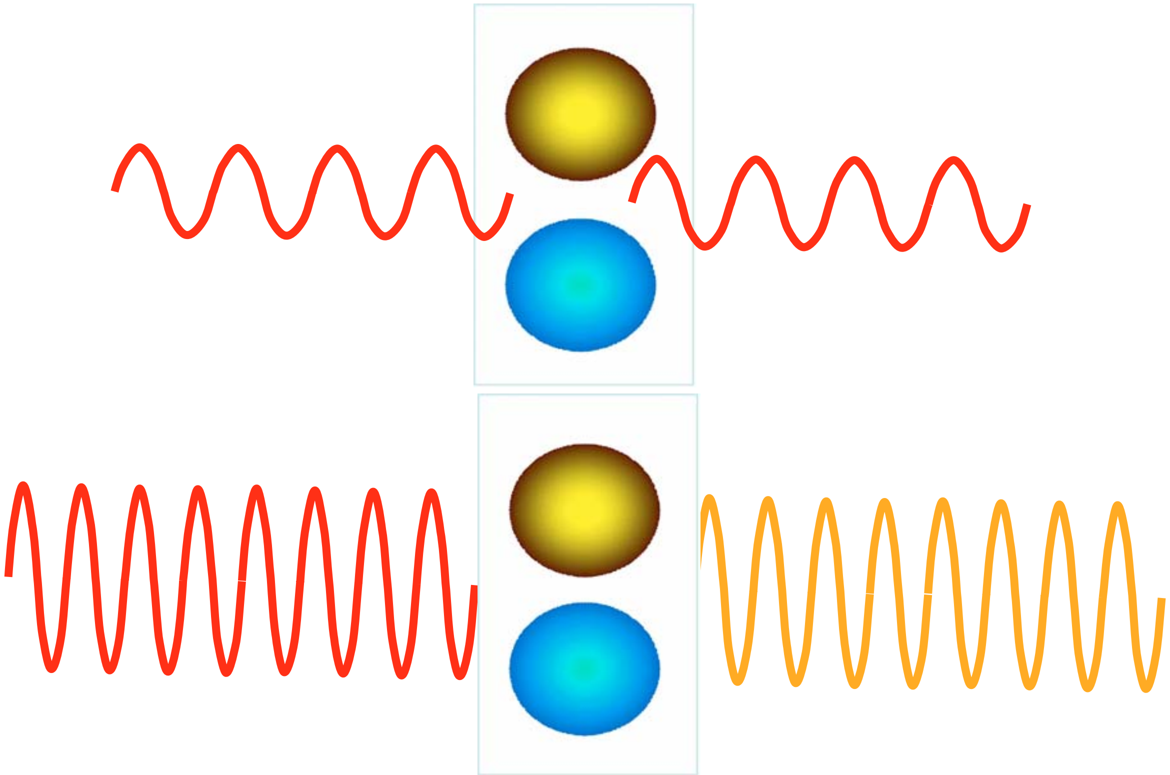
Vibrational motions

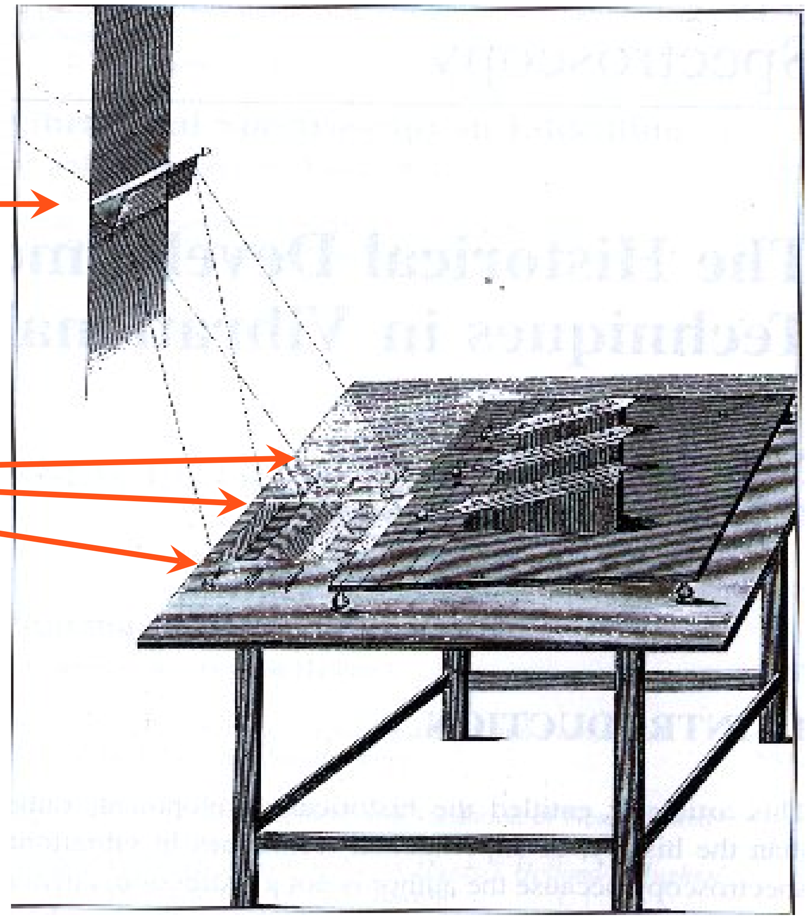
All matters, atoms, molecules and all kind of substances vibrate . Only at absolute zero temperature (-273.15 °C or -459.67°F), that all stop vibrating.



Infrared radiation: the historical starting point

The sunlight was dispersed with a calcite prism

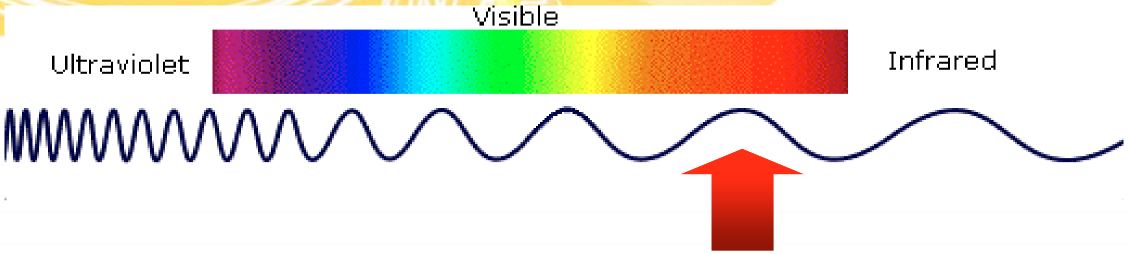
Thermometers were placed along the projected light



« A region of light extending over the visible one » was discovered by
Sir William HERSCHEL , en 1800
F.W. Herschel, Philo. Trans. Royal Soc. London **90**,49,255,284,293, 437 (1800)

From this observation, Sir Herschel concluded that the light should be composed by waves… but hypothesis immediately rejected by other scientists!!

The Infrared energy range



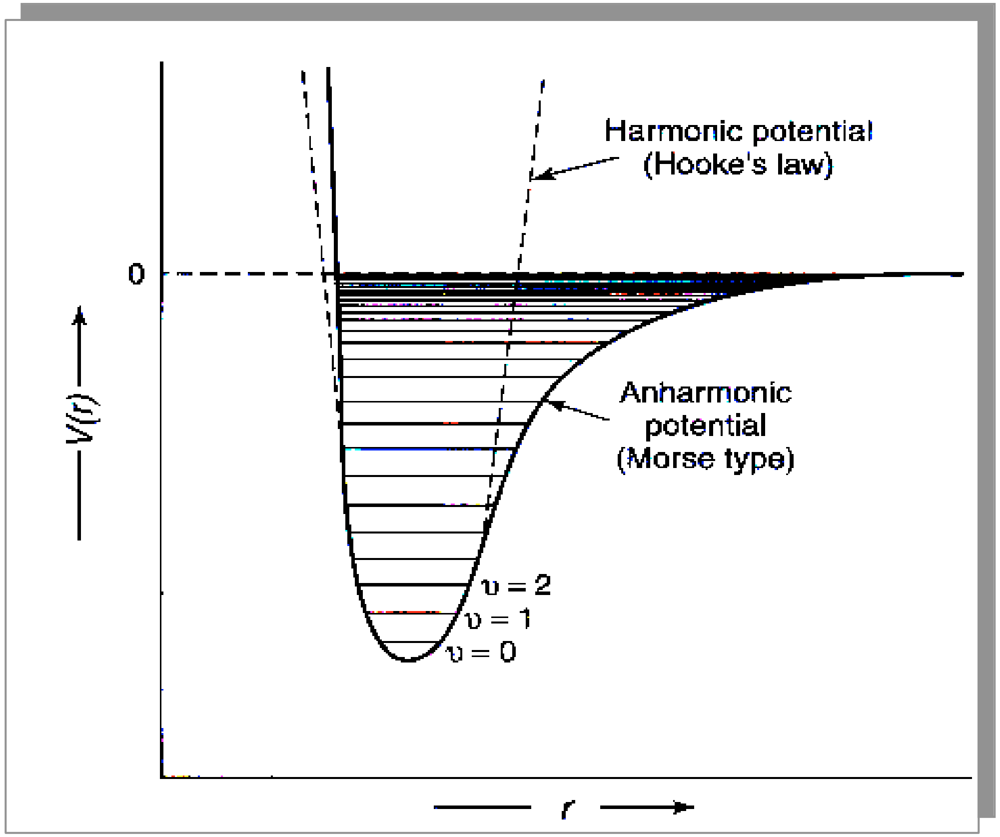
✓ **Energy range:** 1 to ~500 μm
(10000 to 20 cm-1 or 1.23 to 0.0025 eV)

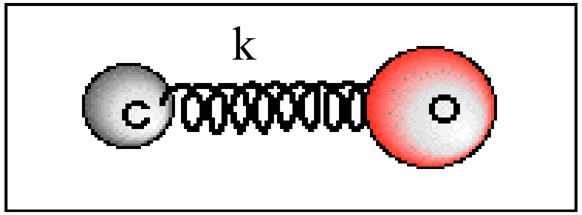
- ✓ ~1 to ~2.5 μm (10000-4000 cm^{-1}) <u>Near IR</u>
- ✓ ~2.5 à 20 μm (4000-500 cm^{-1}) <u>Mid- IR</u>
- ✓ ~20 à ~2500 μm (500-50 cm^{-1}) <u>Far IR</u>

✓ **They are long wavelengths, distributed in a wide range!**

✓ **They can be easily analysed simultaneously!**

Compound identification using vibrational motions





m_1 m_2

$$\upsilon_{osc} = \frac{1}{2\pi}\sqrt{k\frac{m_1+m_2}{m_1 m_2}}$$

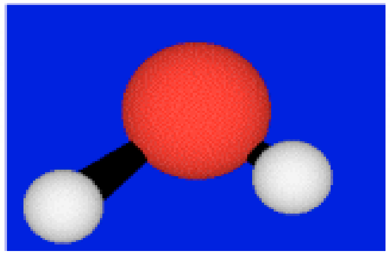
Frequency shift with:

- nature of atoms

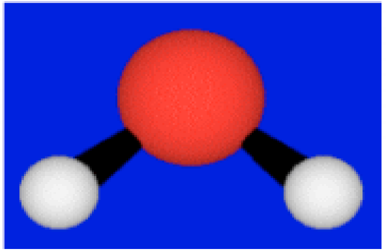
- environment change

IR frequency domain and vibrations

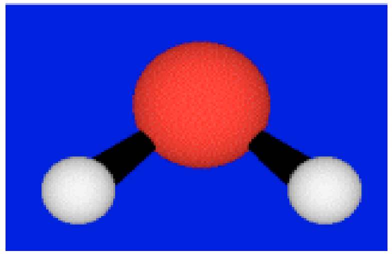
~3.3 μm



3756 cm-1

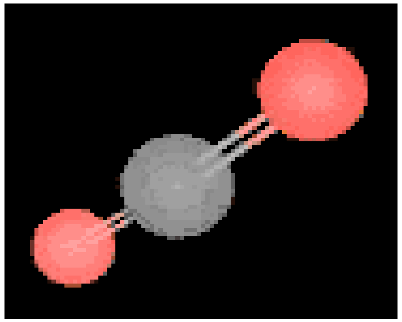


3652 cm-1

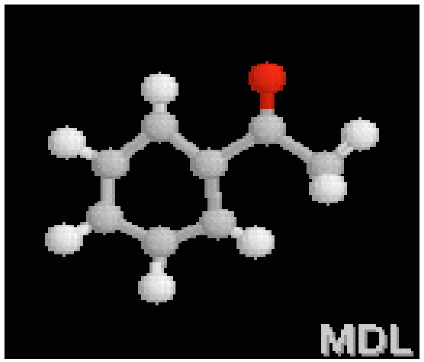


1595 cm-1

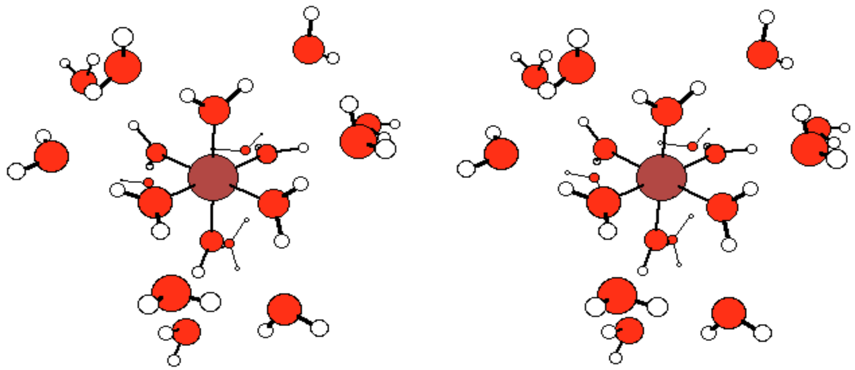
~6 μm



~10 μm



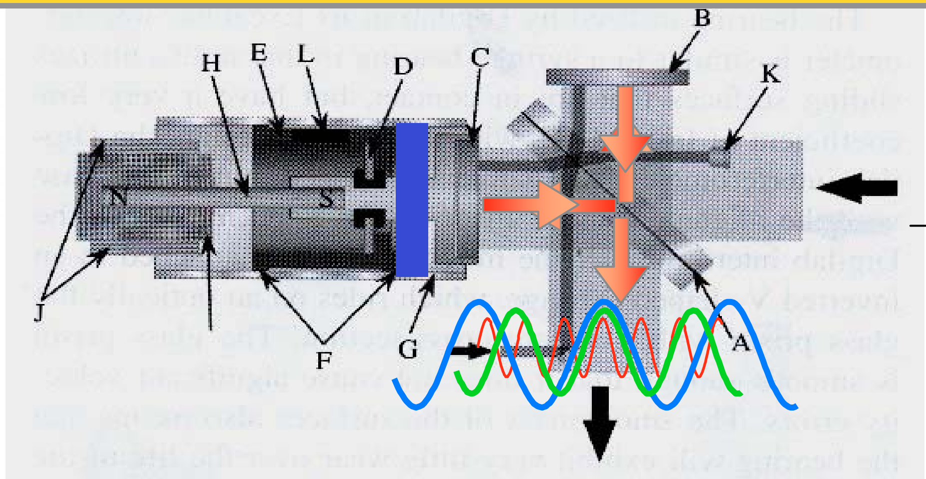
~30 μm

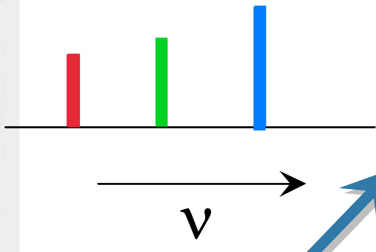


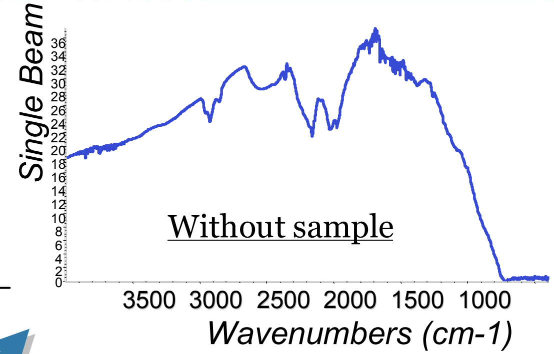
But also IR reflectivity and conductivity ….
(brodband change)

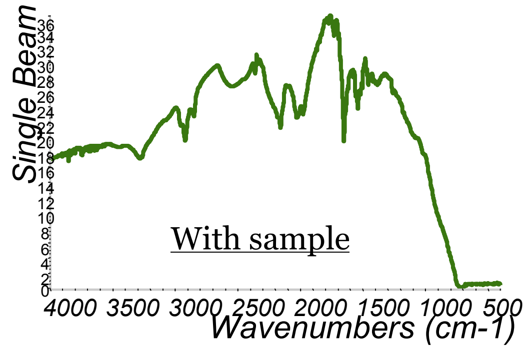
Fourier Transform Spectroscopy

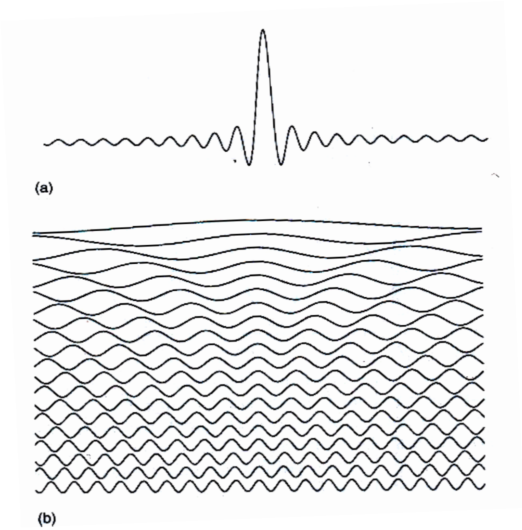
No monochromator, all wavelengths collected



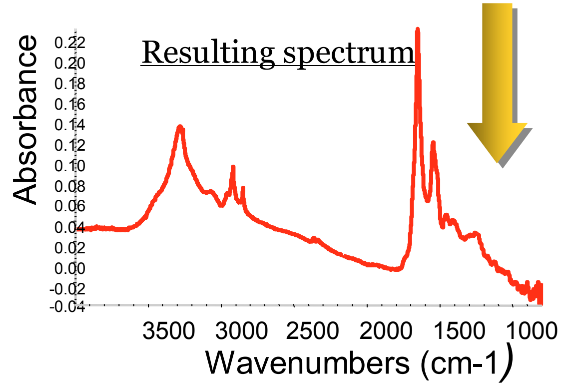








Fast Fourier Transform



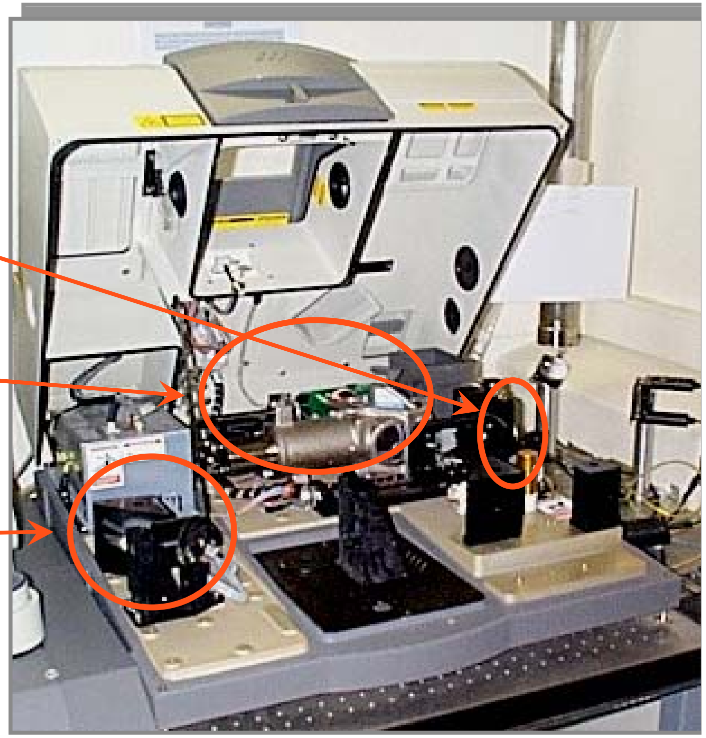
Infrared spectroscopy today…

- ✓ **Widely used in academic as well as in industry , primilarly for compound identification**
- ✓ **« Classical » infrared spectrometer is composed of three main components:**

1- An IR source (blackbody heated to about 1500K) - such as SiC

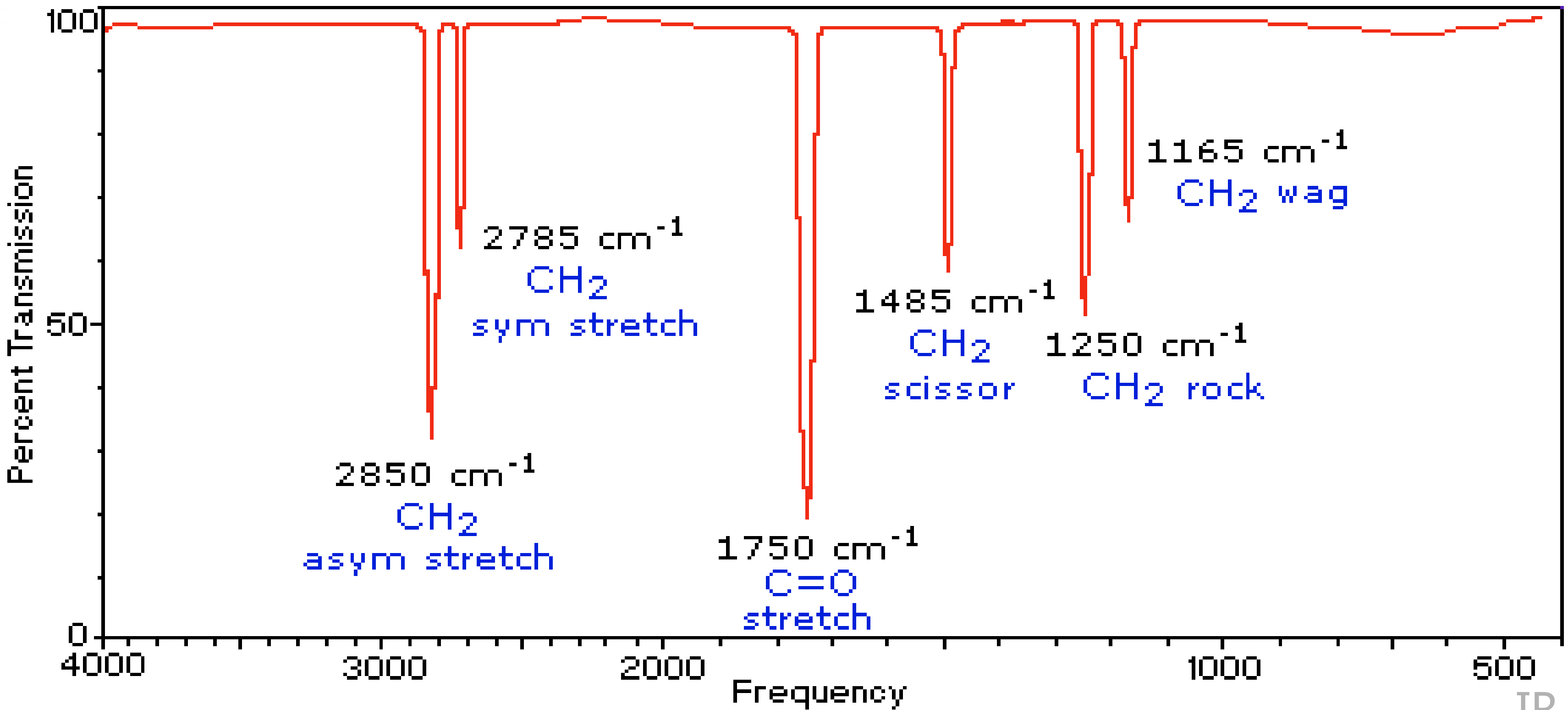
2- Interferometer to modulate all the emitted wavelengths

3- Detectors, with high responsivity in the IR frequency range



Infrared absorption phenomena: a kind of « finger print » for each ensemble of molecular groups

IR spectra of formaldehyde , $H_2C=O$



IR Tutord

Main features

✓ Each functional group has an ensemble of motions (vibrational) specific of the molecular group (fingerprint)

✓ These motions (or vibrational frequencies) are detected under « resonant » excitation in the energy domain 0.495 eV-0.062 eV or 2.5 to 20 microns or 4000-500 cm-1

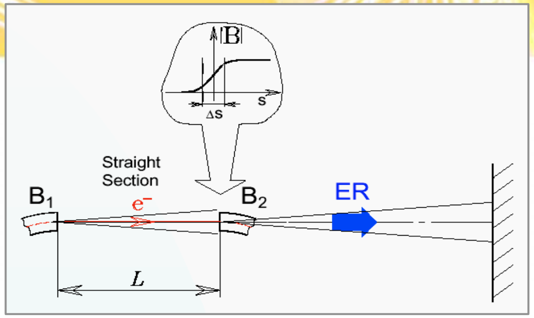
✓ There are databanks of spectra, which allow a rapid search and identification.

✓ The technology is rather simple, and the data are obtained quite quickly (few seconds).

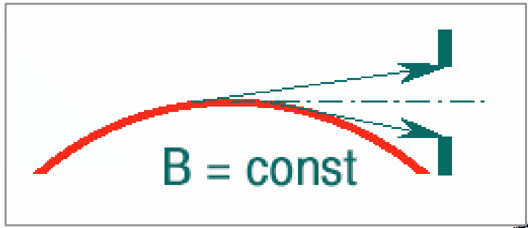
Synchrotron Infrared Emission: Properties and Characteristics

Synchrotron radiation and infrared emission

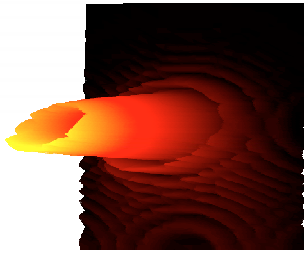
Edge emission:

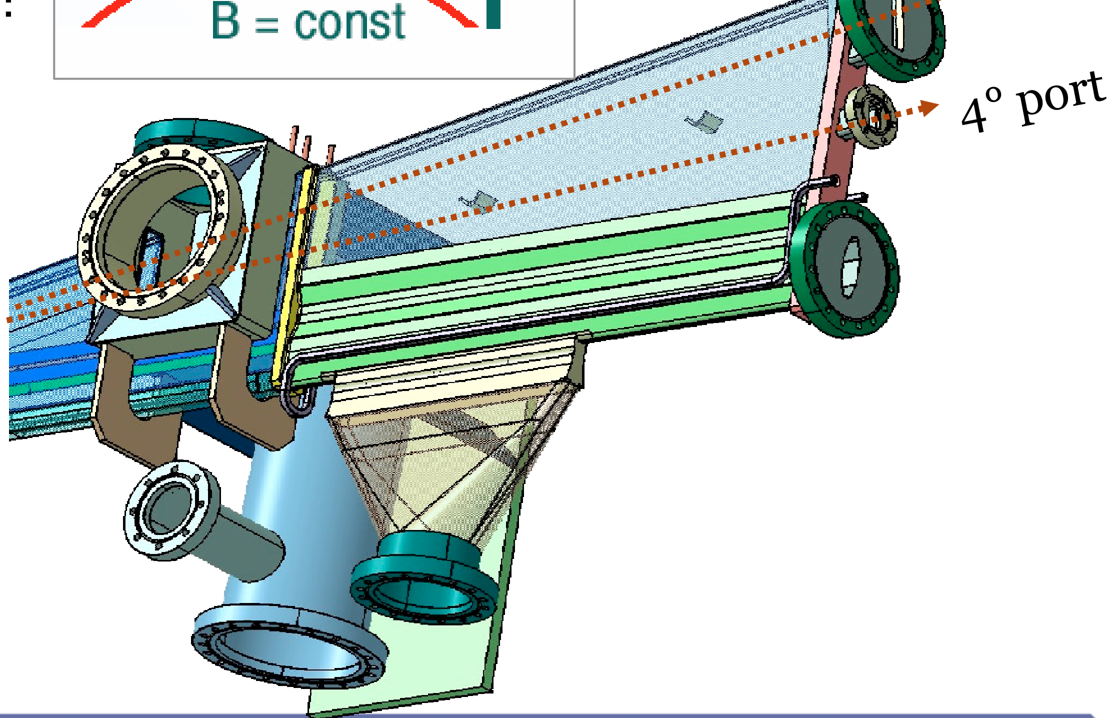


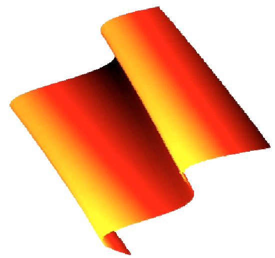
Bending magnet emission:



Exemple for 10µm wavelength

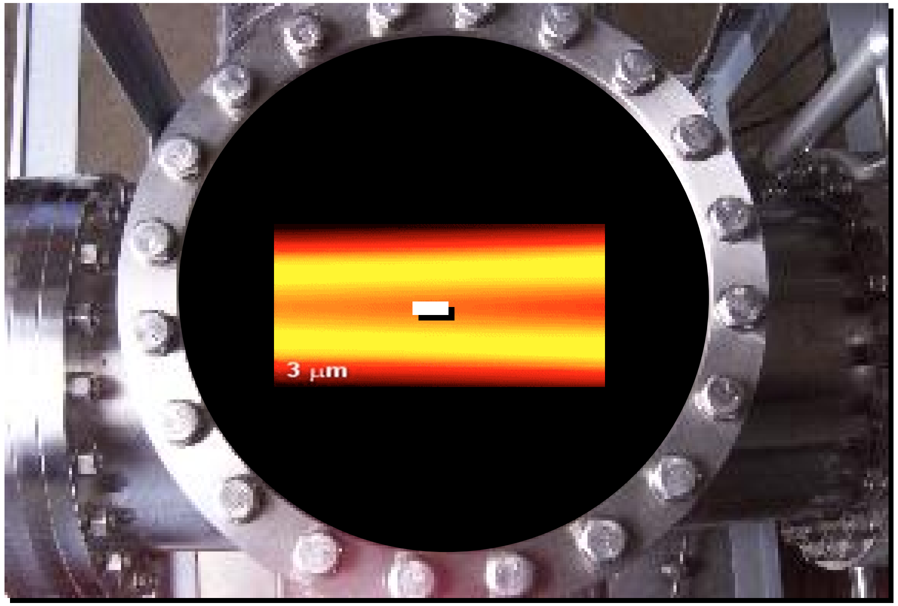




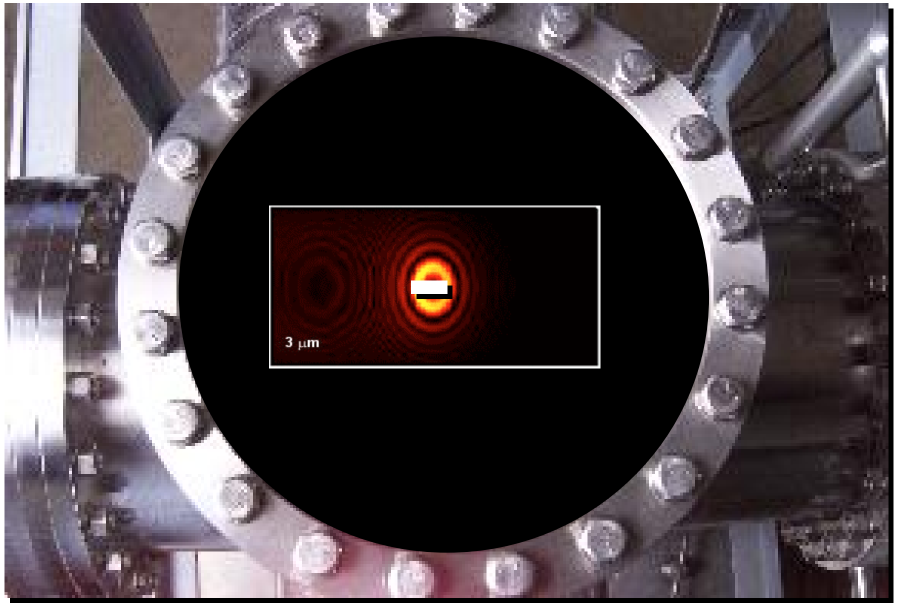


History of synchrotron IR ?

It takes much longer before being recognized as a potential source for spectroscopy



Bending magnet radiation



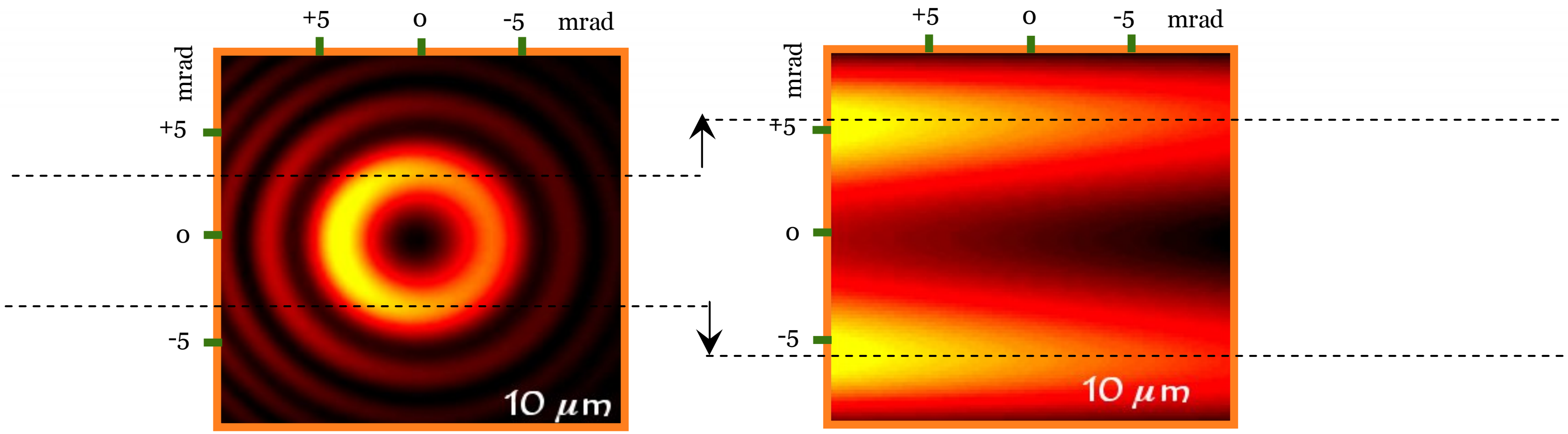
Edge radiation

*: calculated using the SRW code for E=2.75 GeV, 1.56 T, 7 meters straight section

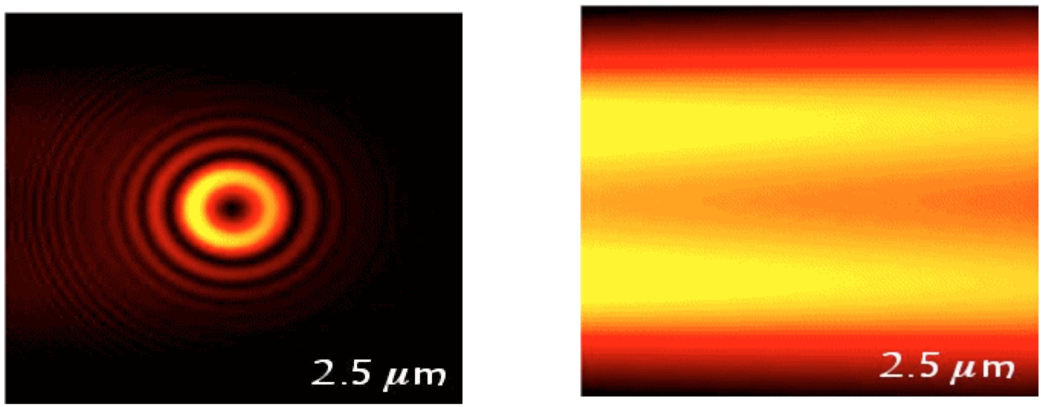
Edge radiation versus bending magnet

Calculated using SRW Code developed by O. Chubar and P. Elleaume

E= 2 GeV I= 300 mA , 1.2 T , HxV= 20x20 mrad



For a fixed wavelength, vertical angle larger for constant field emission



Formulas for calculating infrared flux

(Non-coherent) Synchrotron Radiation from Constant Field of Bending Magnet

$$\left(\frac{dW}{d(1/\lambda)}\right)_{SR}\left[\frac{W}{cm^{-1}}\right] \approx 4.88\cdot 10^{-7}\, E[GeV]\, I[A]\, \theta_x[mrad]\, G(\lambda_c/\lambda)$$

$$G(x) \equiv x\int_x^{+\infty} K_{5/3}(x')dx'$$

$\gamma = E/m_0c^2$ = electron relativistic mass enhancement factor

θ_y = aperture

$\lambda_c = 4\pi\rho/(3\gamma^3)$ = critical synchrotron radiation wavelength for the bending magnet

$K_{5/3}$ = modified Bessel function

For a storage ring with parameters E = 2.75 GeV, I = 0.5 A, λ_c = 1.43 Å,

horizontal angular aperture θ_x = 40 mrad, at the wavelength λ= 10 μm

$$\frac{dW}{d(1/\lambda)}\left[\frac{W}{cm^{-1}}\right] \approx 2\cdot 10^{-20}\,\frac{dN}{dt\,(d\lambda/\lambda)}\left[\frac{Photons}{s\,(0.1\%bw)}\right]$$

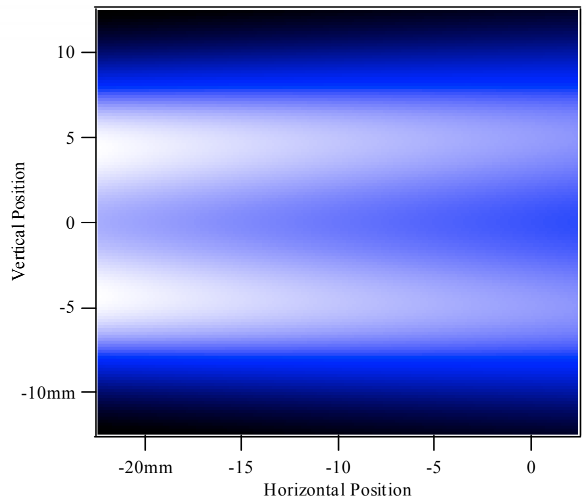
$$\left(\frac{dW}{d(1/\lambda)}\right)_{SR} \approx 1.40\cdot 10^{-6}\,\frac{W}{cm^{-1}}$$

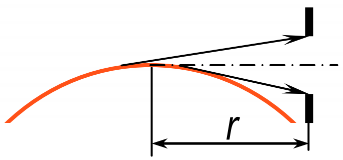
Multichannel Detection with a Synchrotron Light Source G.L. Carr, O. Chubar and P. Dumas

Australian Light Source

Infrared Synchrotron Radiation from Bending Magnet

Intensity Distribution in transverse plane close to the source



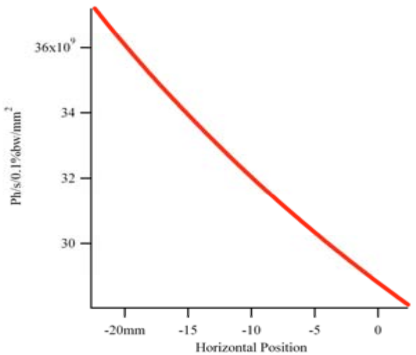


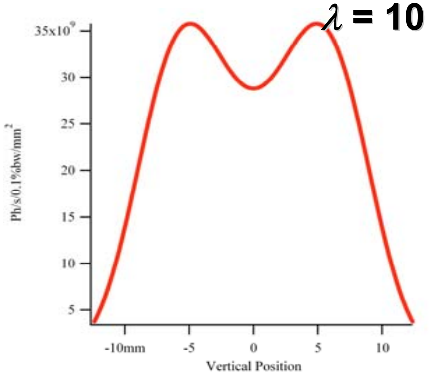
Natural Opening Angle:

$$\psi \sim (\lambda/\rho)^{1/3}$$

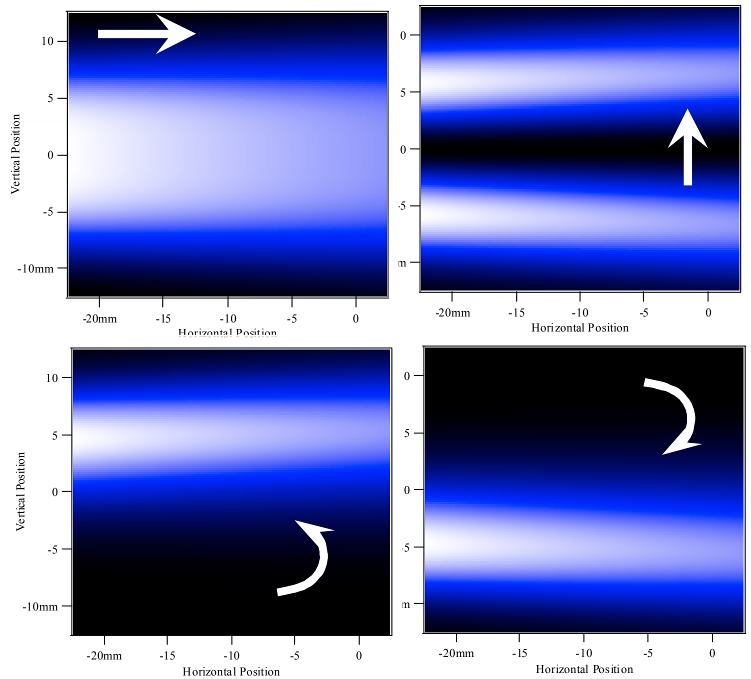
$$(\lambda >> \lambda_c)$$

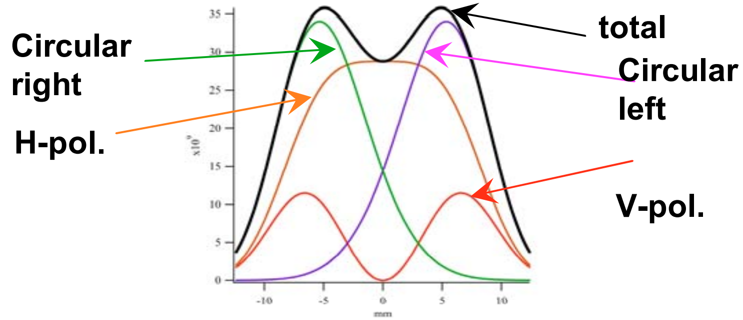
E **= 3.0 GeV;** ***B*** **= 1.30 T**
ρ=7.69 m
I **= 200 mA**
λ = 10 μm,r= 1.23 m





Intensity Distributions at Various Polarizations





Practical Formulas for calculating infrared flux

SOLEIL SYNCHROTRON

(Non-coherent) Edge Radiation from Extremities of Bending Magnet

$$\left(\frac{dW}{d(1/\lambda)}\right)_{ER}\left[\frac{W}{cm^{-1}}\right] \approx 5.76\cdot 10^{-7}\, I[A]\, H\left[\frac{\pi\cdot\theta_r^{\,2}[mrad]}{\lambda[\mu m]}\,\frac{zL}{z+L}[m]\right]$$

where $H(x) \equiv \ln(x) - \mathrm{ci}(x) + C$,

$\mathrm{ci}(x) \equiv -\int_x^{+\infty} \cos(t)t^{-1}dt$ is the cosine integral function

$C \approx 0.577216$ is the Euler constant

L is the distance between bending magnet edges

z is distance from downstream bending magnet edge to observation plane

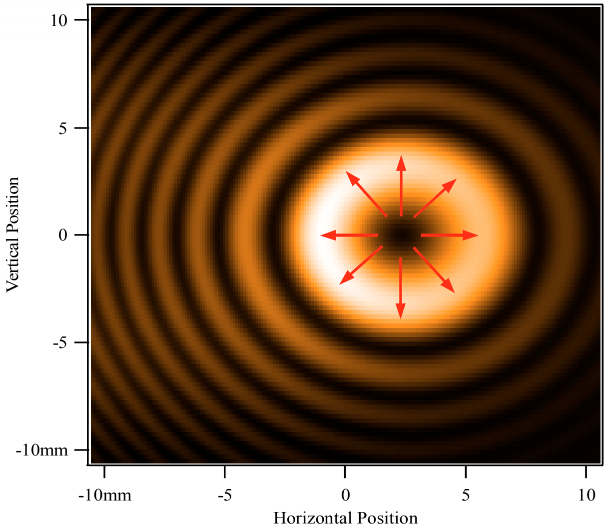
Taking the following realistic parameters: I = 0.5 A, L = 10 m, z = 5 m, θ_r = 10 mrad
λ = 10 μm

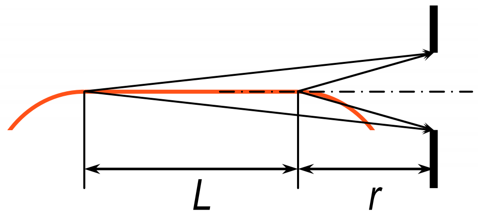
$$\left(\frac{dW}{d(1/\lambda)}\right)_{ER} \approx 1.5\cdot 10^{-6}\,\frac{W}{cm^{-1}}$$

Multichannel Detection with a Synchrotron Light Source *G.L. Carr, O. Chubar and P. Dumas*

Infrared Synchrotron Radiation from Edge of bending magnet

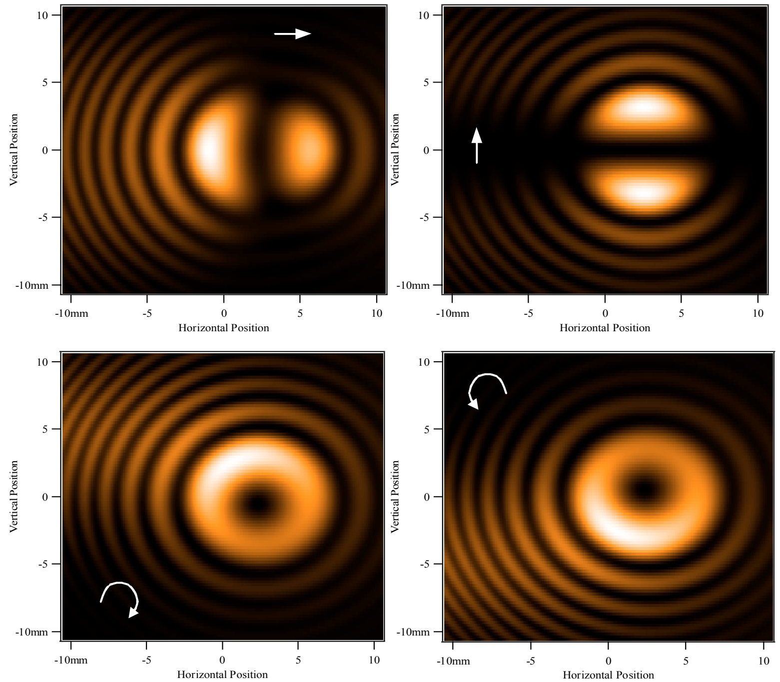
"Pure ER" is polarized "Radially"





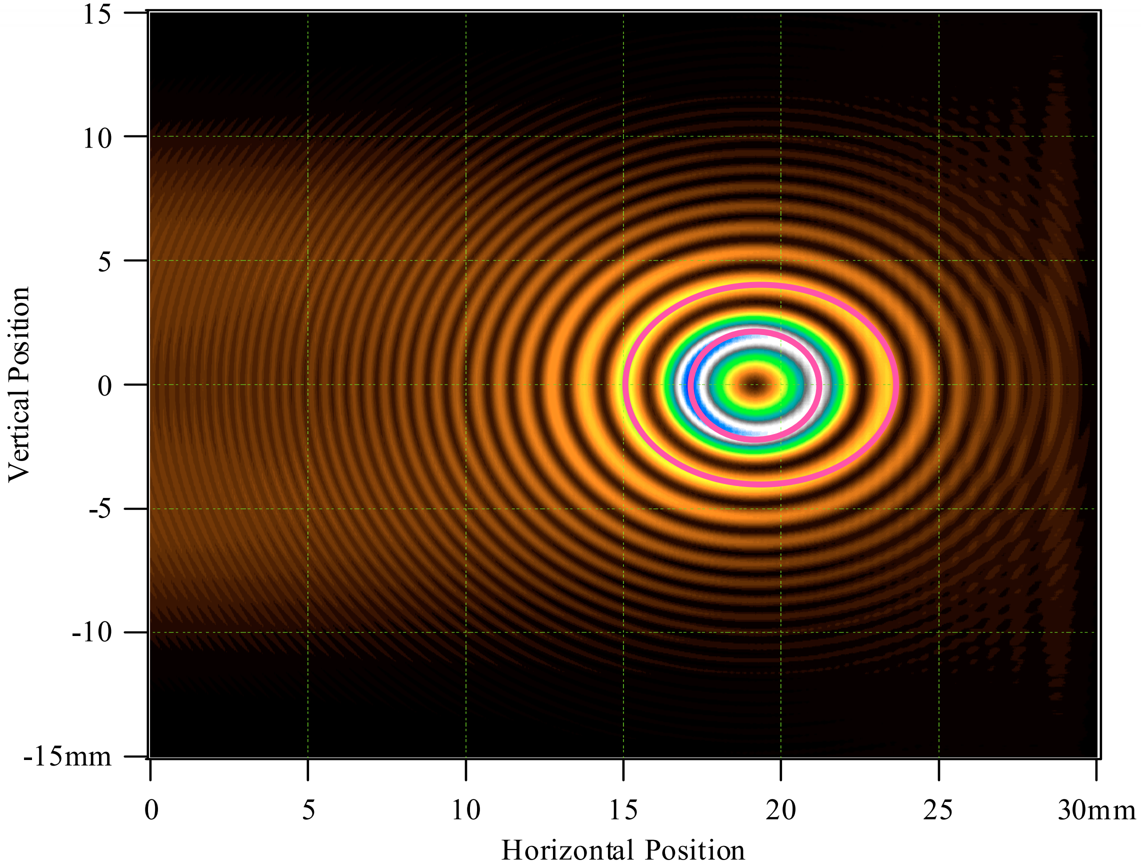
E = 3.0 GeV
B_{max} = 1.30 T
I = 200 mA
L = 5 m
r = 1.23 m
λ = 10 μm

Intensity Distributions at Various Polarizations



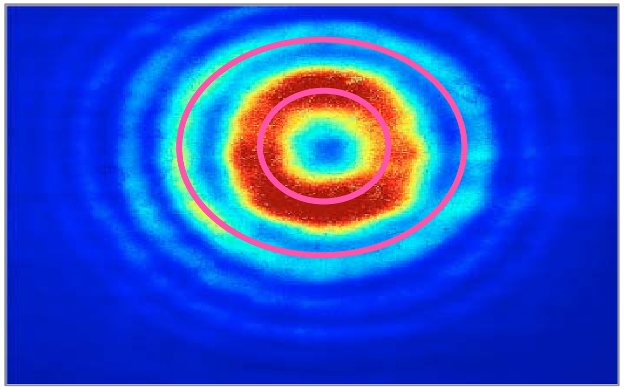
Are we confident with the simulations?

Calculated intensity profile
at 6.2 meters from source
λ=0.52 microns



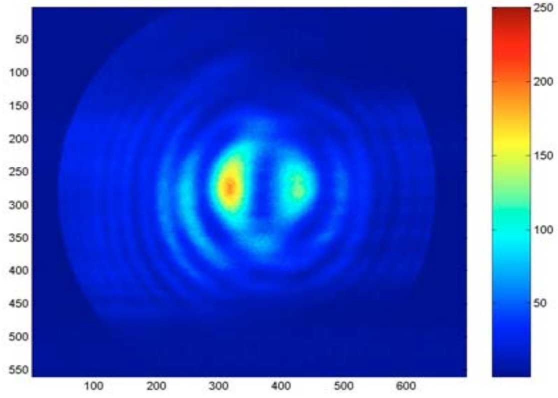
Measured at the ESRF beamline

Recorded with a CCD camera
at 6.2 meters from source
λ= 0.52 microns

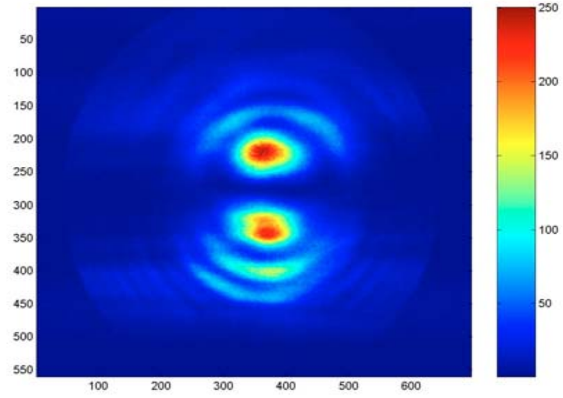


Edge radiation observed at IR beamline ESRF

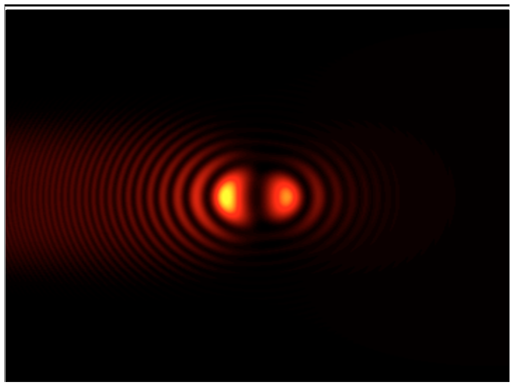
Measurements done with a CCD camera, 10m from source, filter=700nm

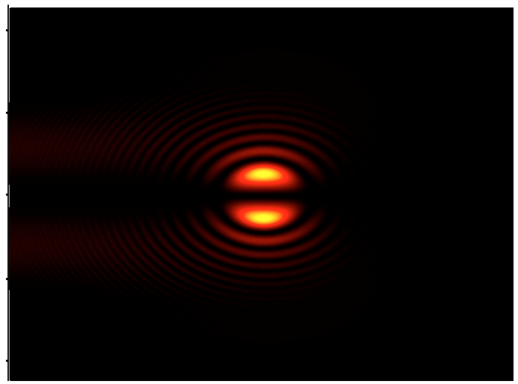


H-polarized

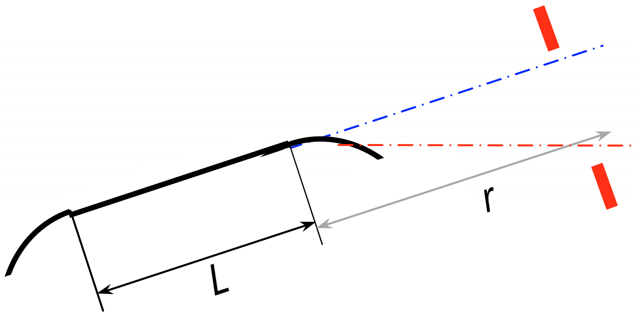


V-polarized



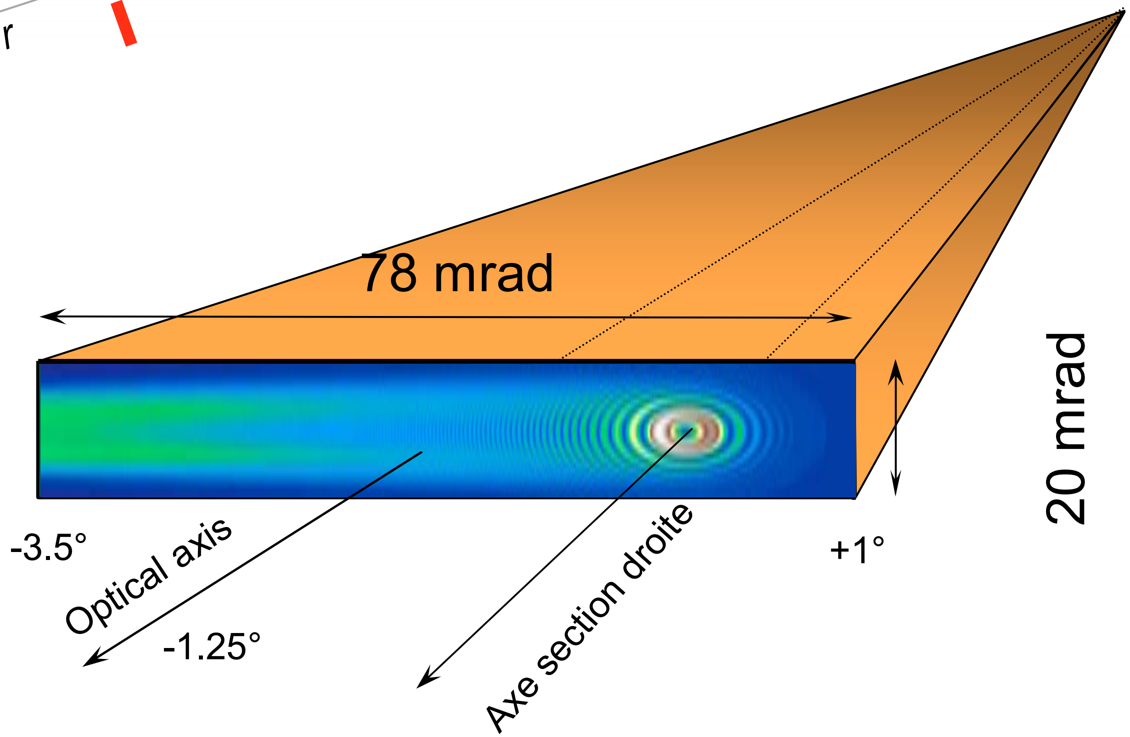


Collecting the two sources

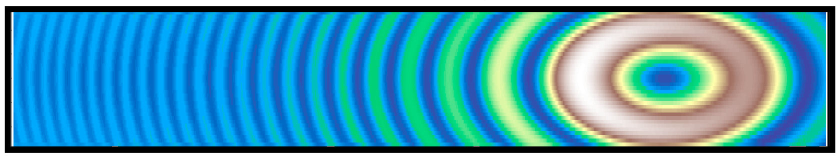


SOLEIL's case

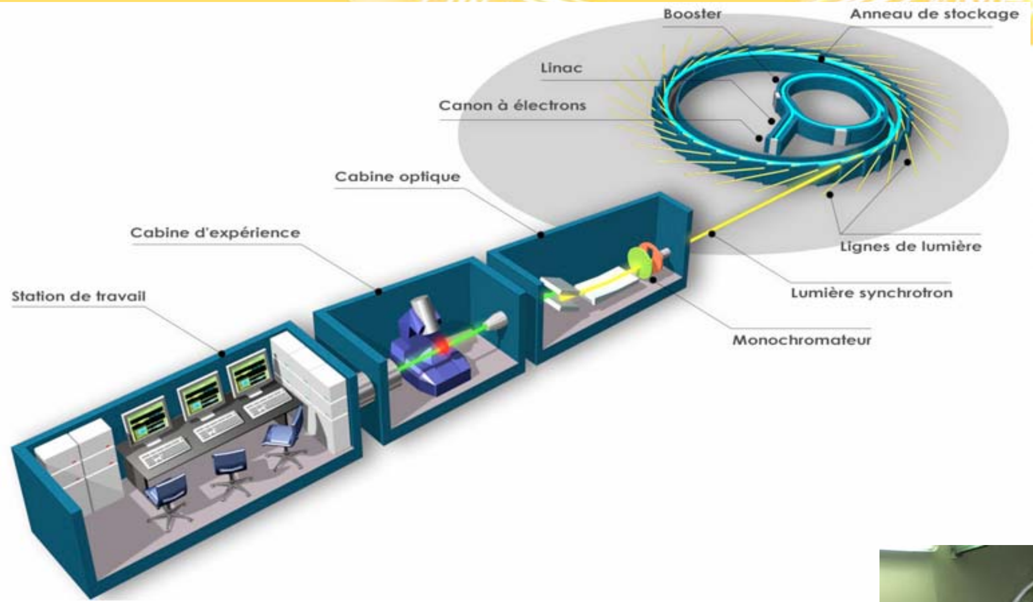
Emission @ 10 μm

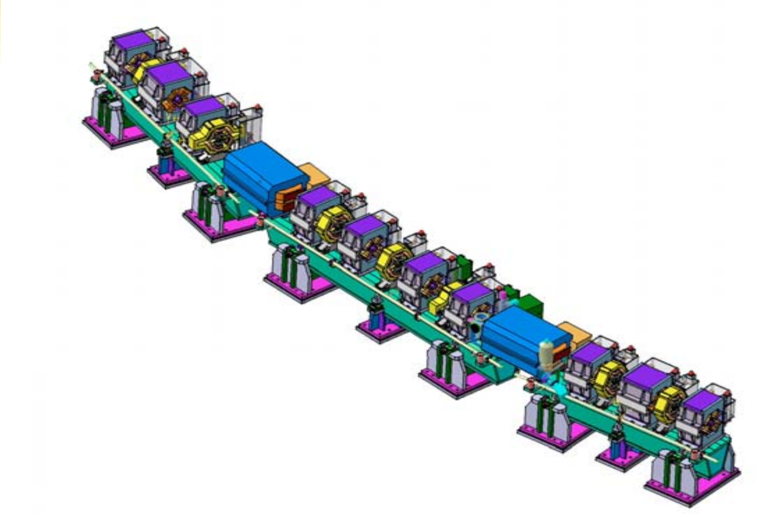


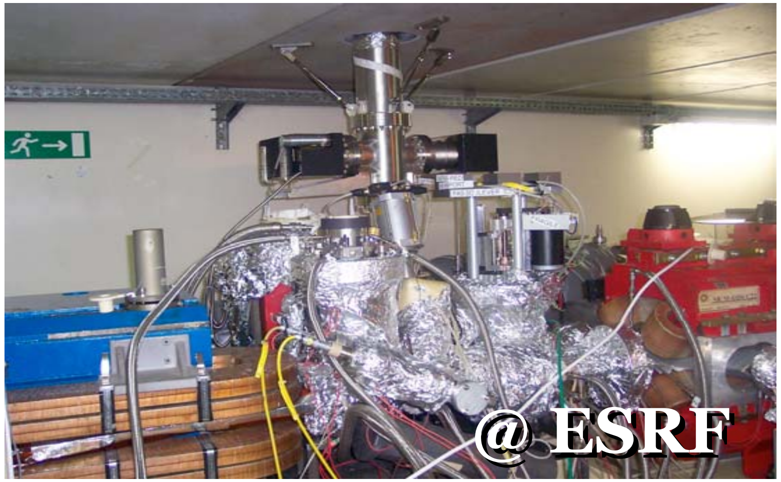
Emission @ 100 μm

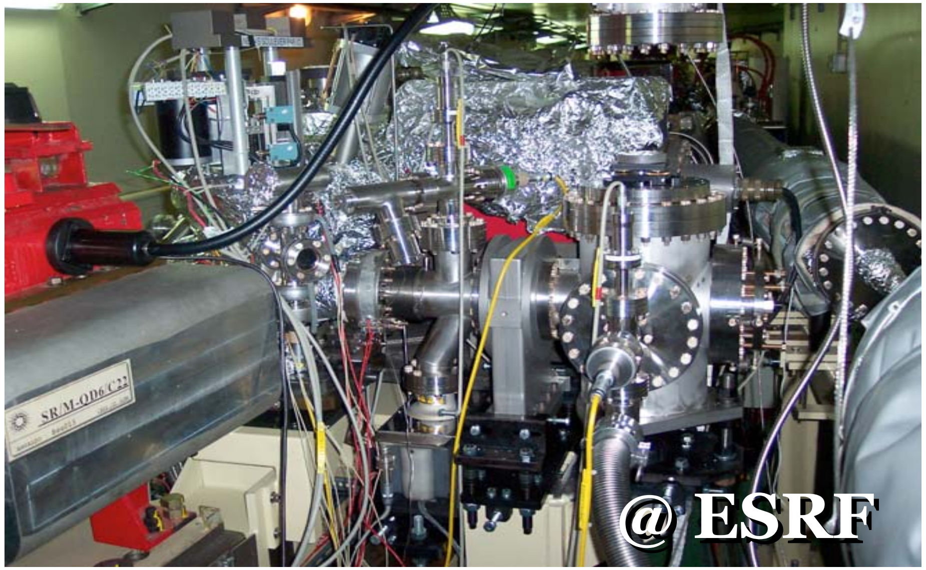


Synchrotron radiation in the infrared



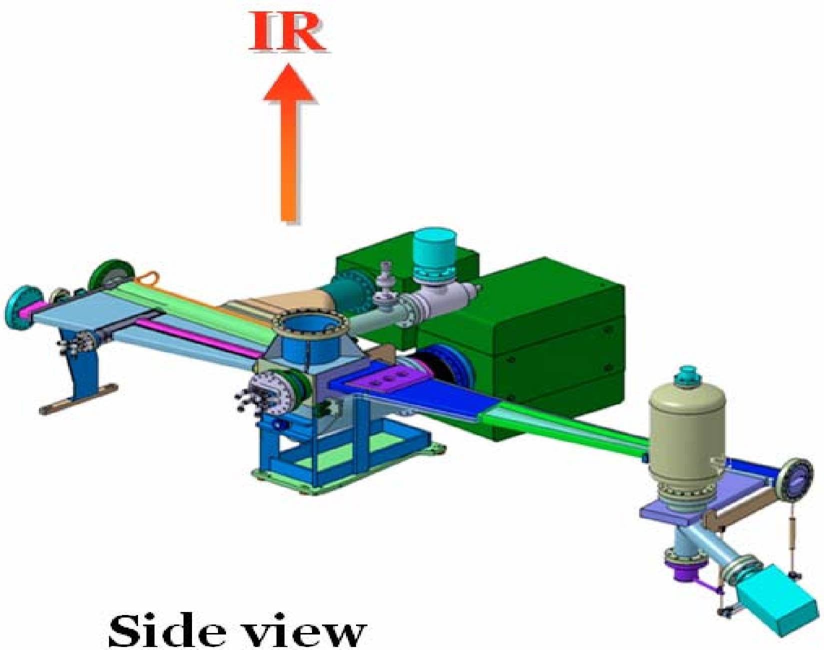




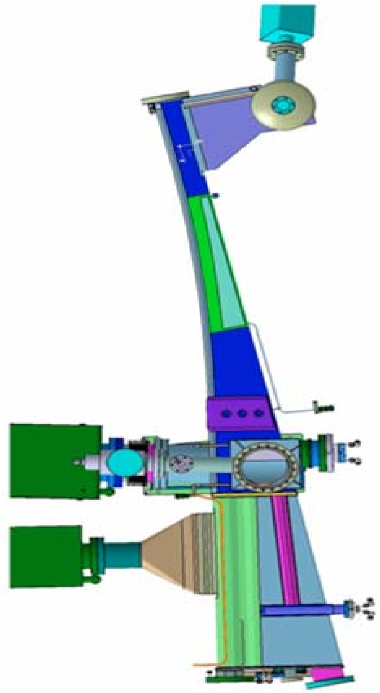


Extraction optics

Allows to collect 20 mrad vertical and 78 mrad horizontal



Side view



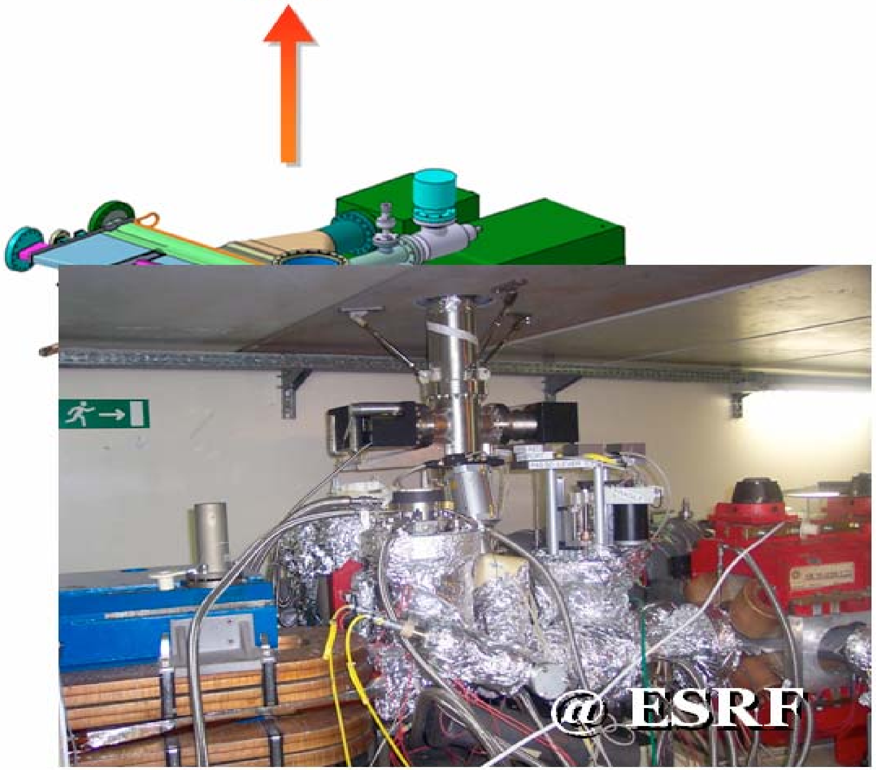
crotch

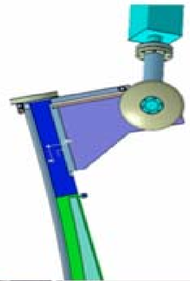
Top view

Extraction optics

Allows to collect 20 mrad vertical and 78 mrad horizontal

IR





Brightness in the infrared region(1)

Synchrotron Center	Energy (GeV)	Maximum operating current (mA)	Horizontal electron source size (µm)	Vertical electron source size (µm)
*ESRF(France)**	6.0	200	~44	~9
*Spring-8(Japan)**	8.0	100	~83	~19.5
Elettra(Italie)	2.0	300	~239	~13.5
MaxII(Sweden)	1.5	200	~350	~14.5
SOLEIL (France)	2.75	500	~180	~8
NSLS-Brookhaven(USA)	0.80	1000	~550	~70
Australian Synchrotron	3.0	200	~389	~19.7

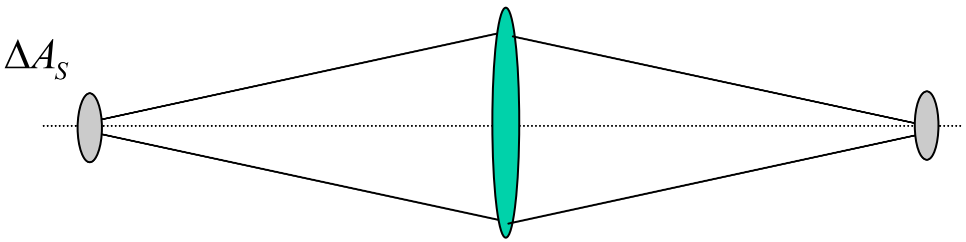
It's not dependant on the electron source size!
Source size is diffraction-limited (apparent source size)

Brightness in the infrared region(2)

To obtain a rough estimation of the diffraction-limited SR source size :

$$\sim \left(\lambda^2 \rho\right)^{1/3}$$

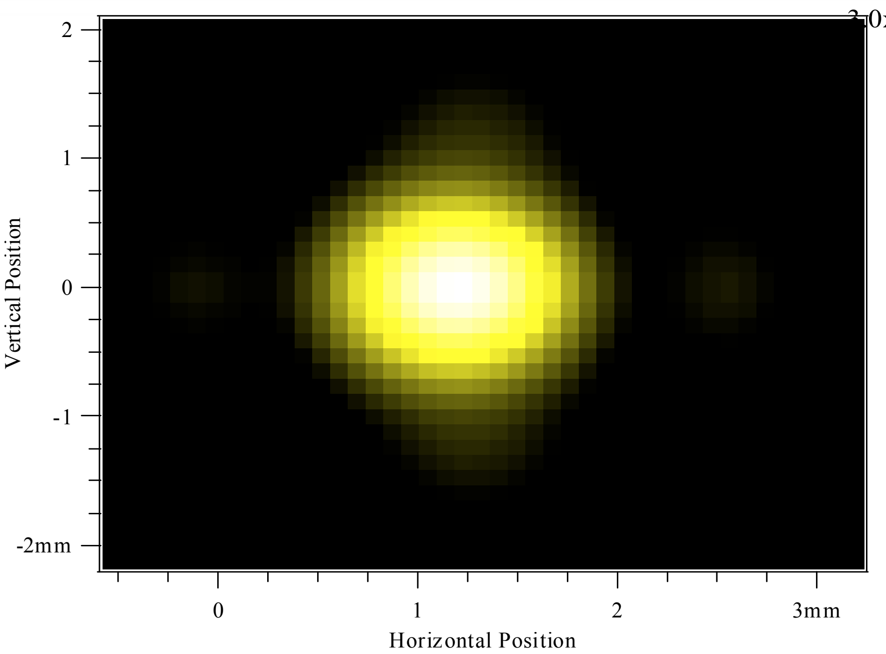
Numerical methods of Fourier optics can be used :back-propagation of the wavefront (at a specific wavenumber) to the source position, or by simulating of the radiation focusing at optical magnification equal to 1

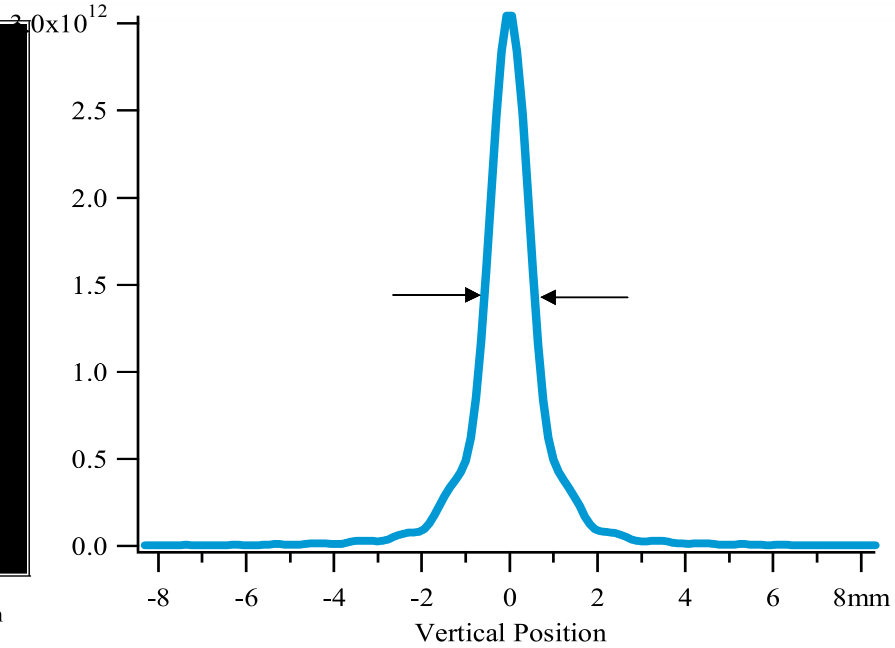


Brightness in the infrared region(3)

Apparent source size @ Australian synchrotron

λ=10 µm



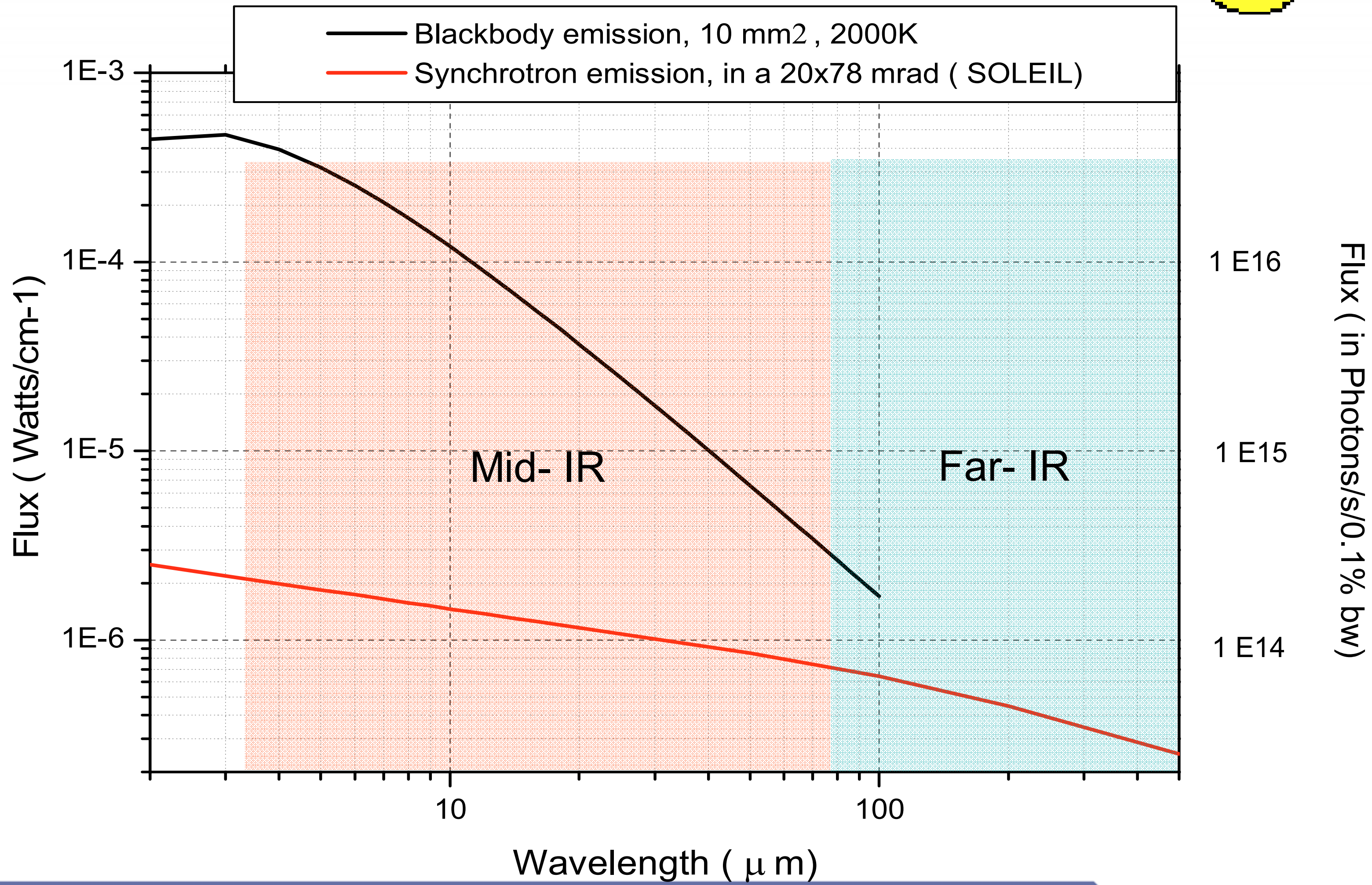


$$\sim\left(\lambda^2\rho\right)^{1/3}$$

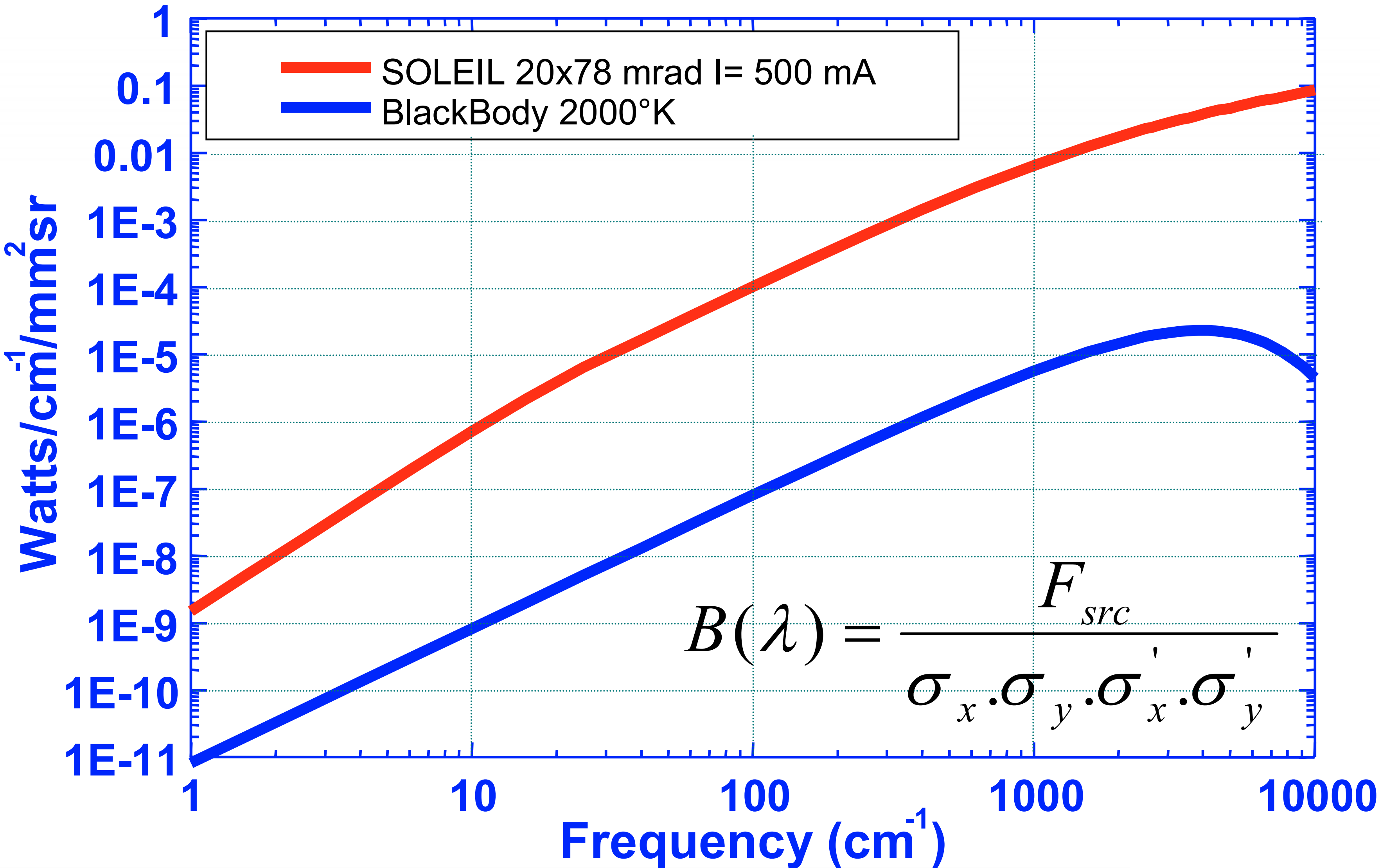
0.9 mm

Synchrotron Infrared properties

Is the synchrotron IR beam very intense?



Universal Brightness Curves



$$B(\lambda) = \frac{F_{src}}{\sigma_x . \sigma_y . \sigma'_x . \sigma'_y}$$

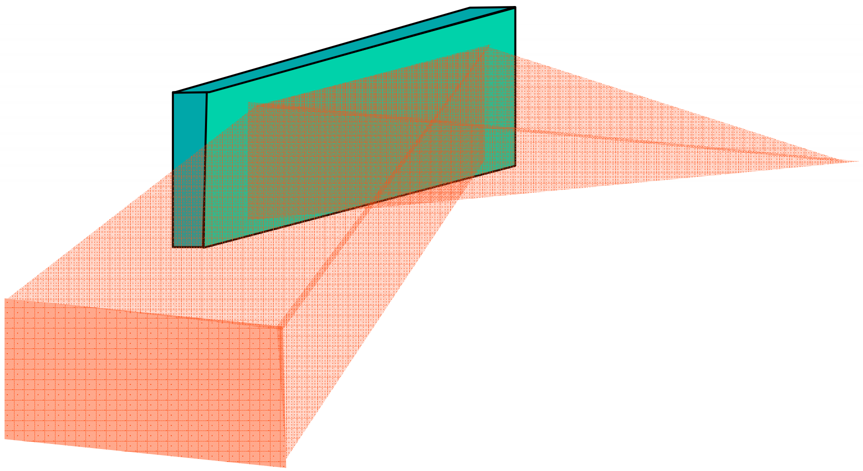
Brightness, or brilliance, or spectral radiance

Low brightness source

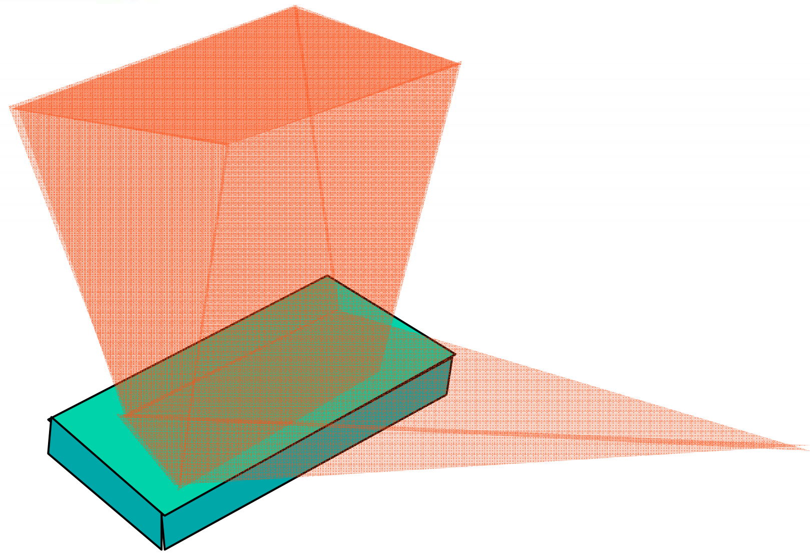
High brightness source

Infrared beamlines at Synchrotron facilities

Extracting the beam



Horizontal deflection

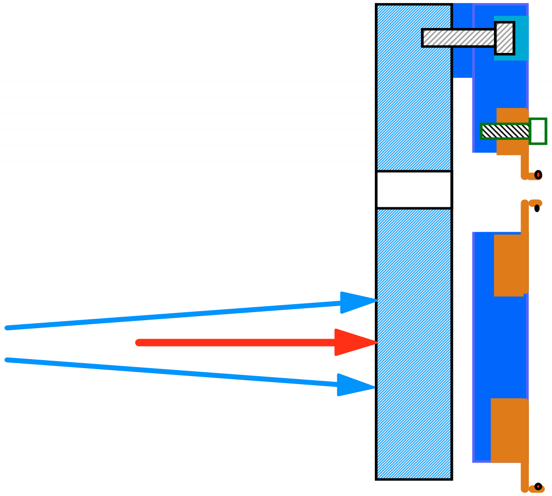


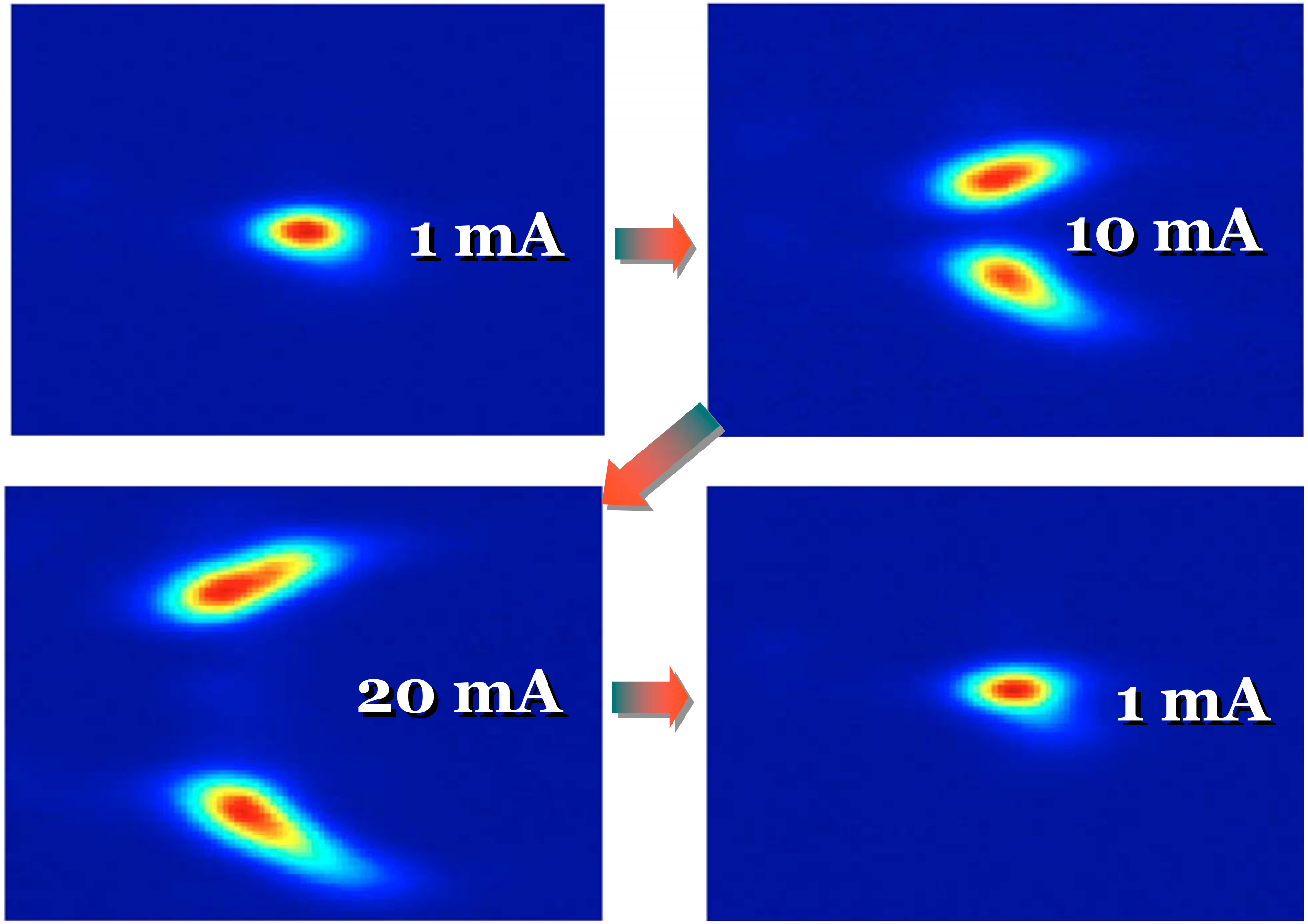
Vertical (upward) deflection

High power density on the mirror!

Dealing with high incident power

Recorded at ESRF IR-beamline

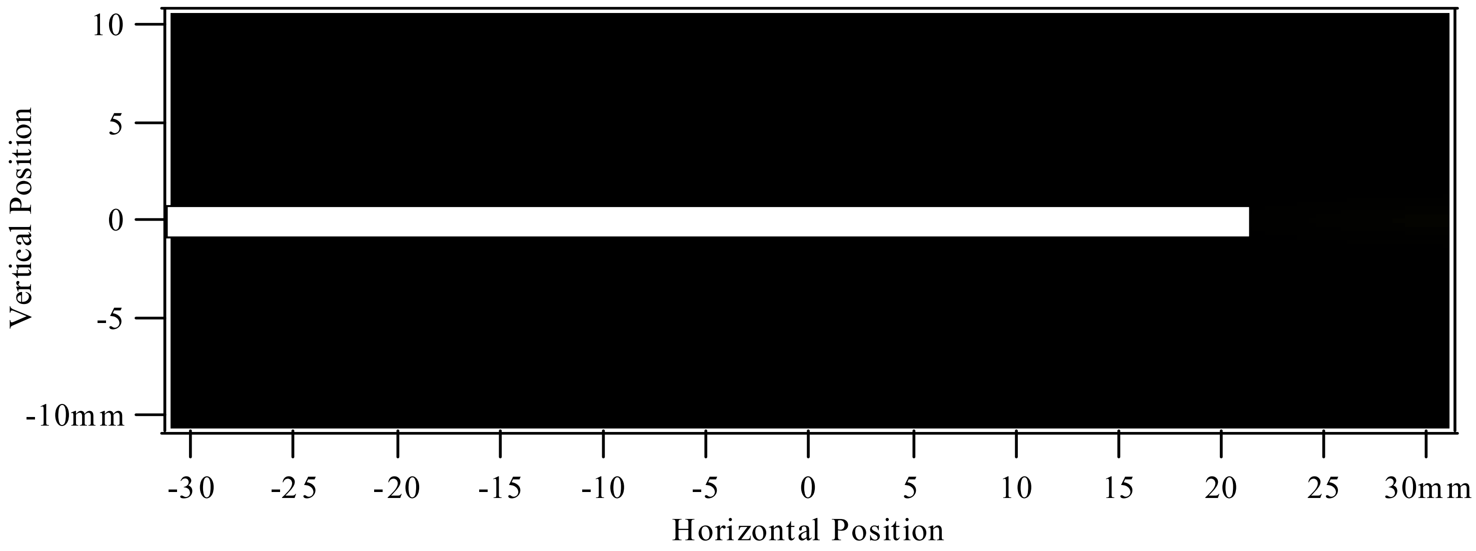


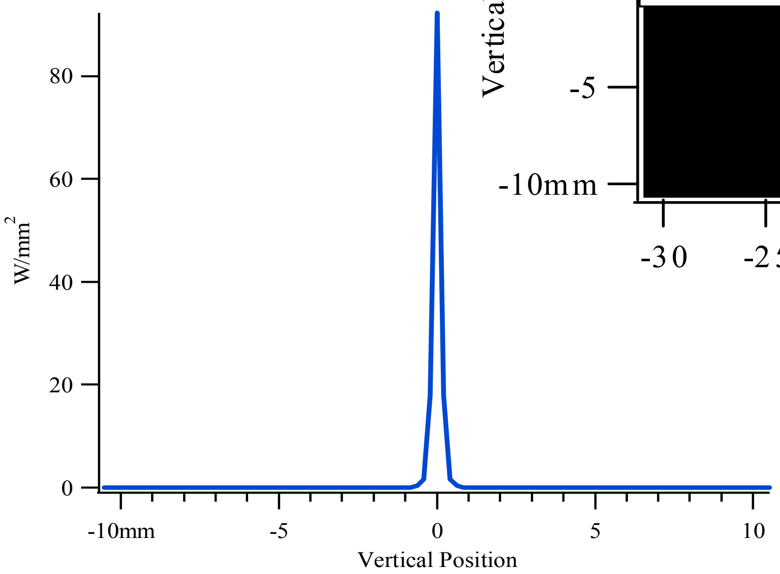


Calculating power on the first mirror

SRW- O. Chubar

At Australian Synchrotron





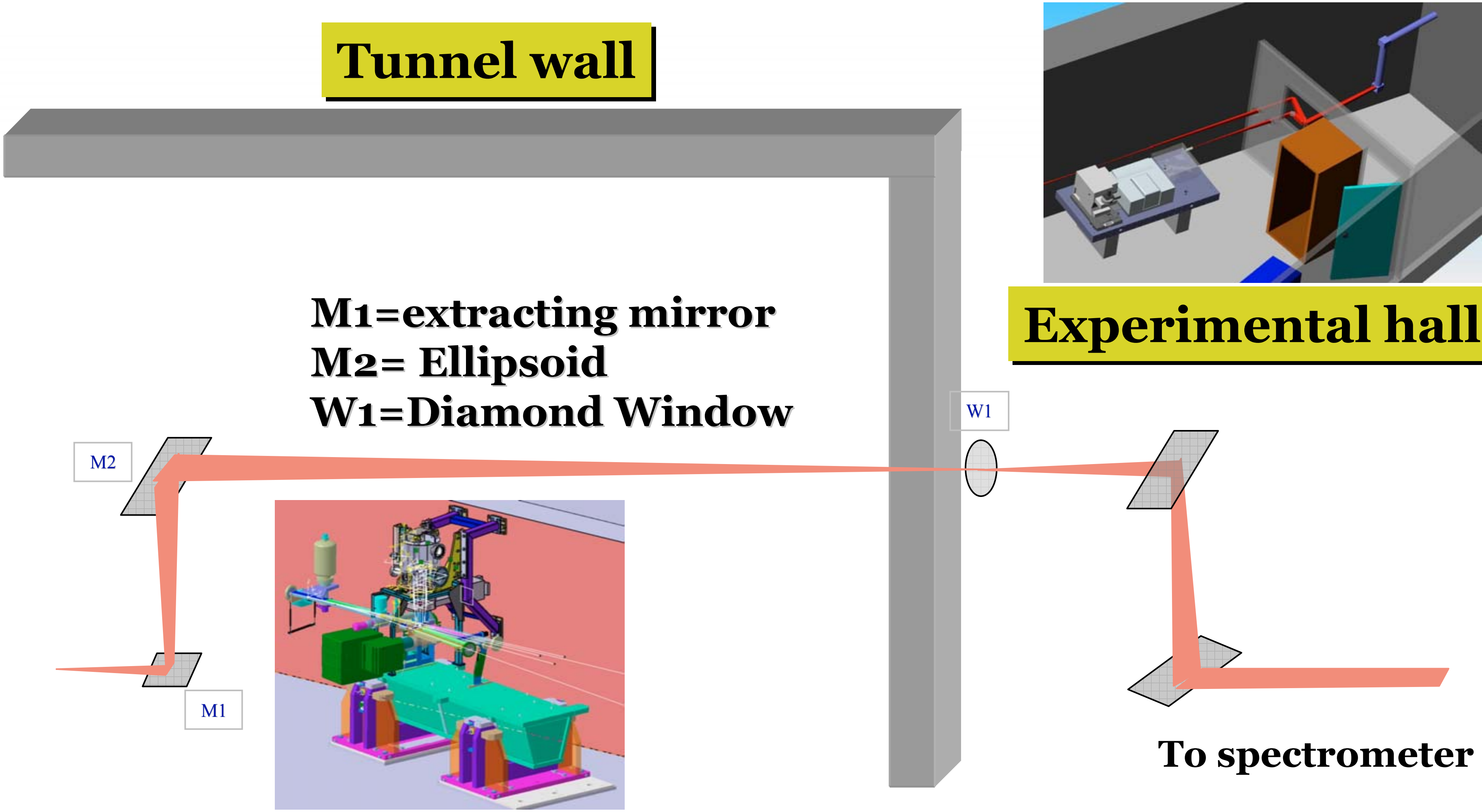
- ✓ **Slot in the mirror**
- ✓ **Water-cooled tubing**

Beamline schematic

Tunnel wall

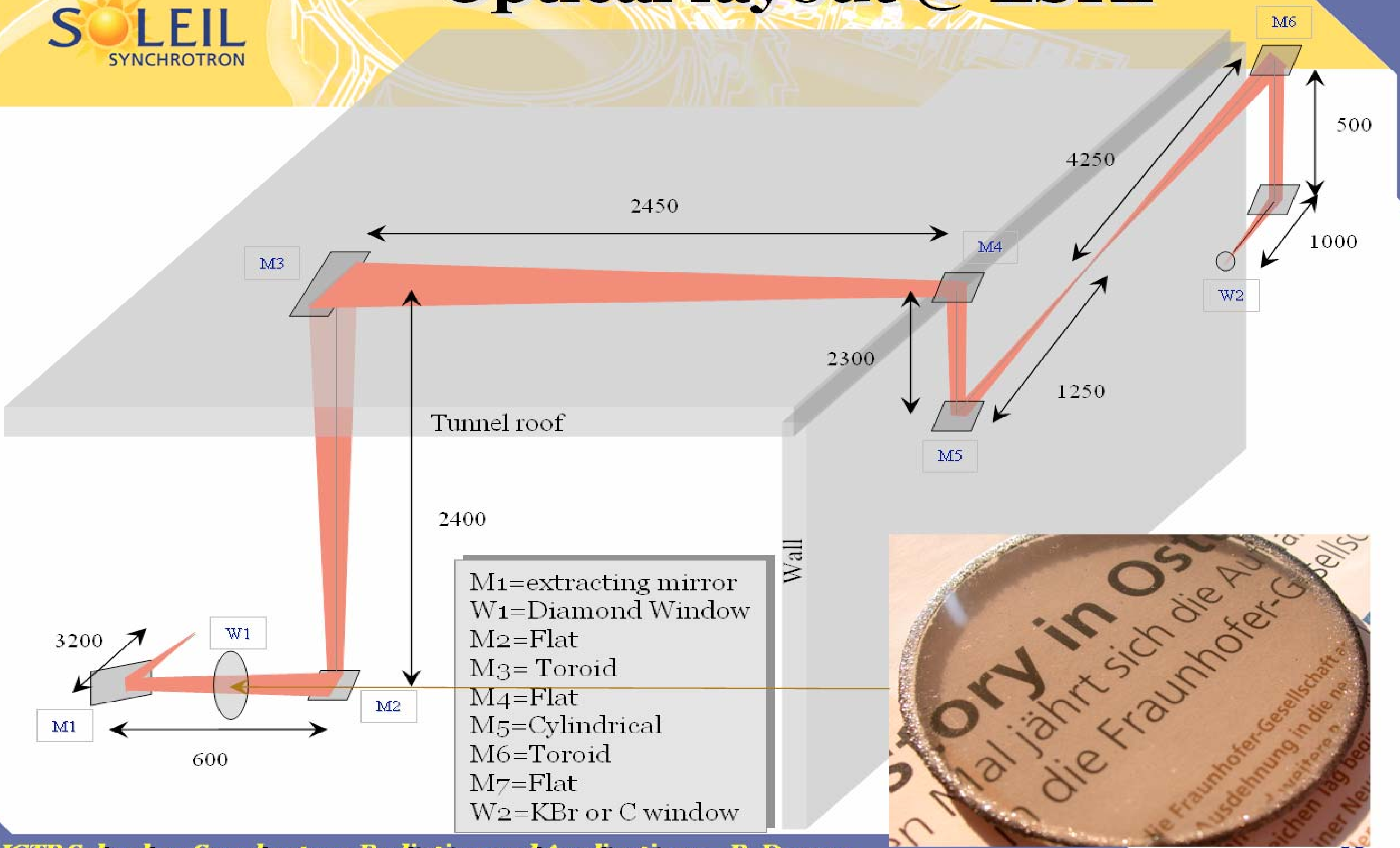
Experimental hall

M1=extracting mirror
M2= Ellipsoid
W1=Diamond Window



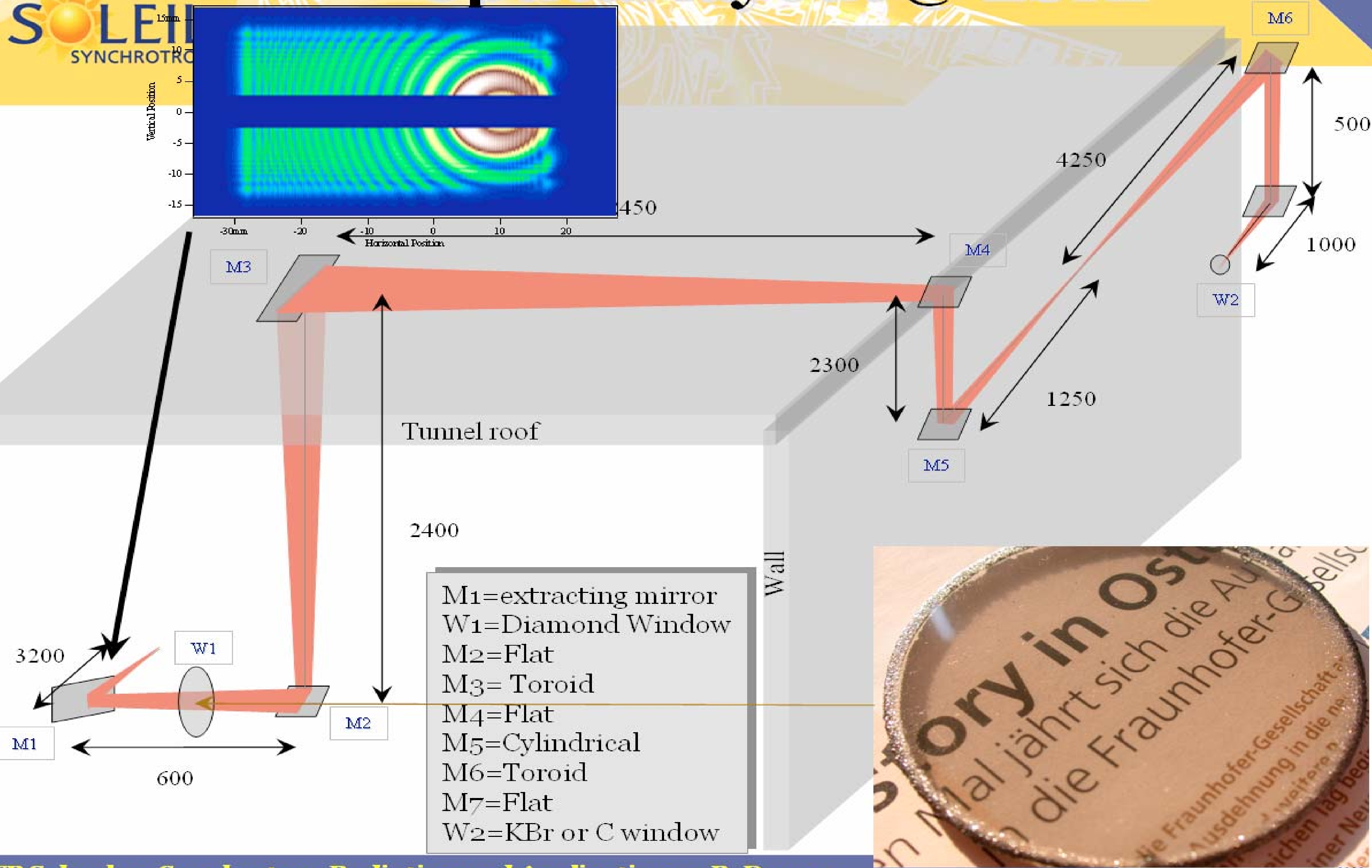
To spectrometer

Optical layout @ ESRF



M1=extracting mirror
W1=Diamond Window
M2=Flat
M3= Toroid
M4=Flat
M5=Cylindrical
M6=Toroid
M7=Flat
W2=KBr or C window

Optical layout @ ESRF



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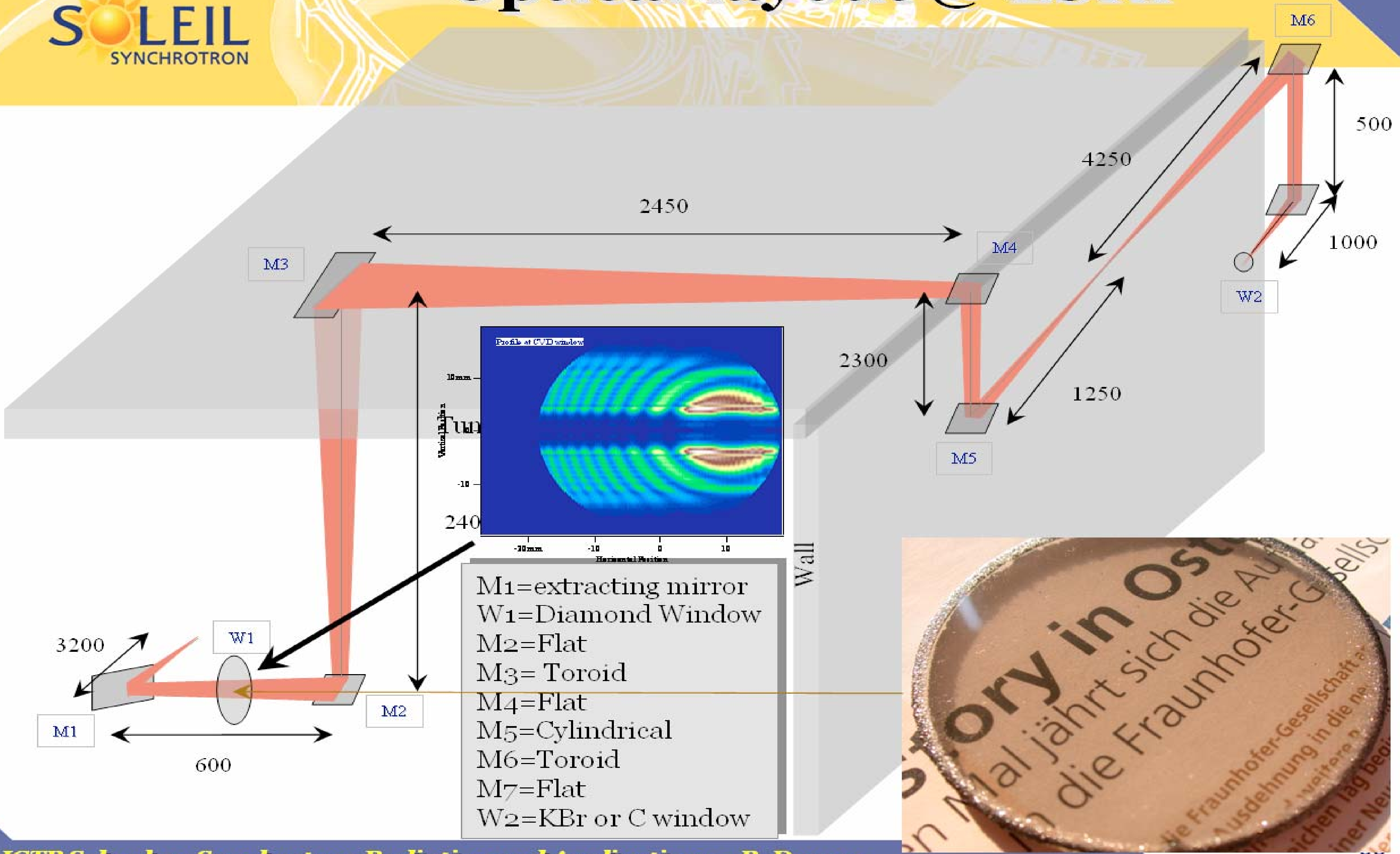
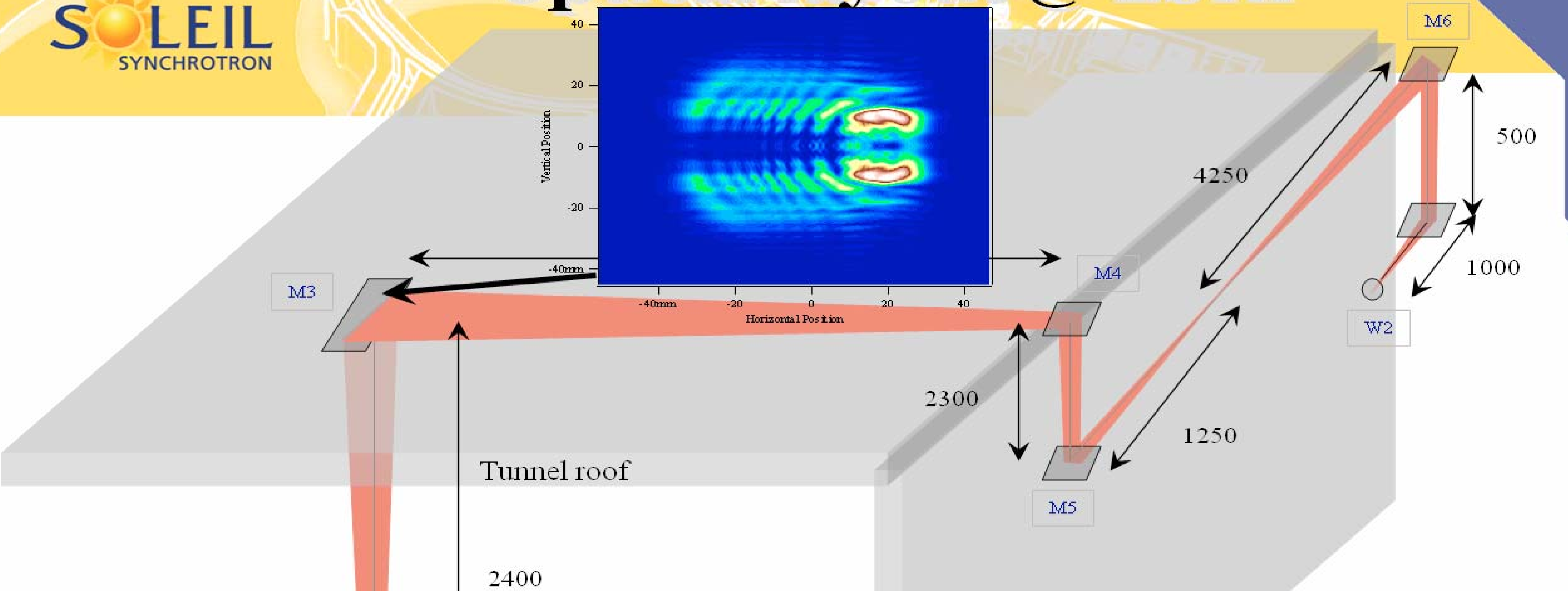
W1=Diamond Window
M2=Flat
M3= Toroid
M4=Flat
M5=Cylindrical
M6=Toroid
M7=Flat
W2=KBr or C window

Optical layout @ ESRF

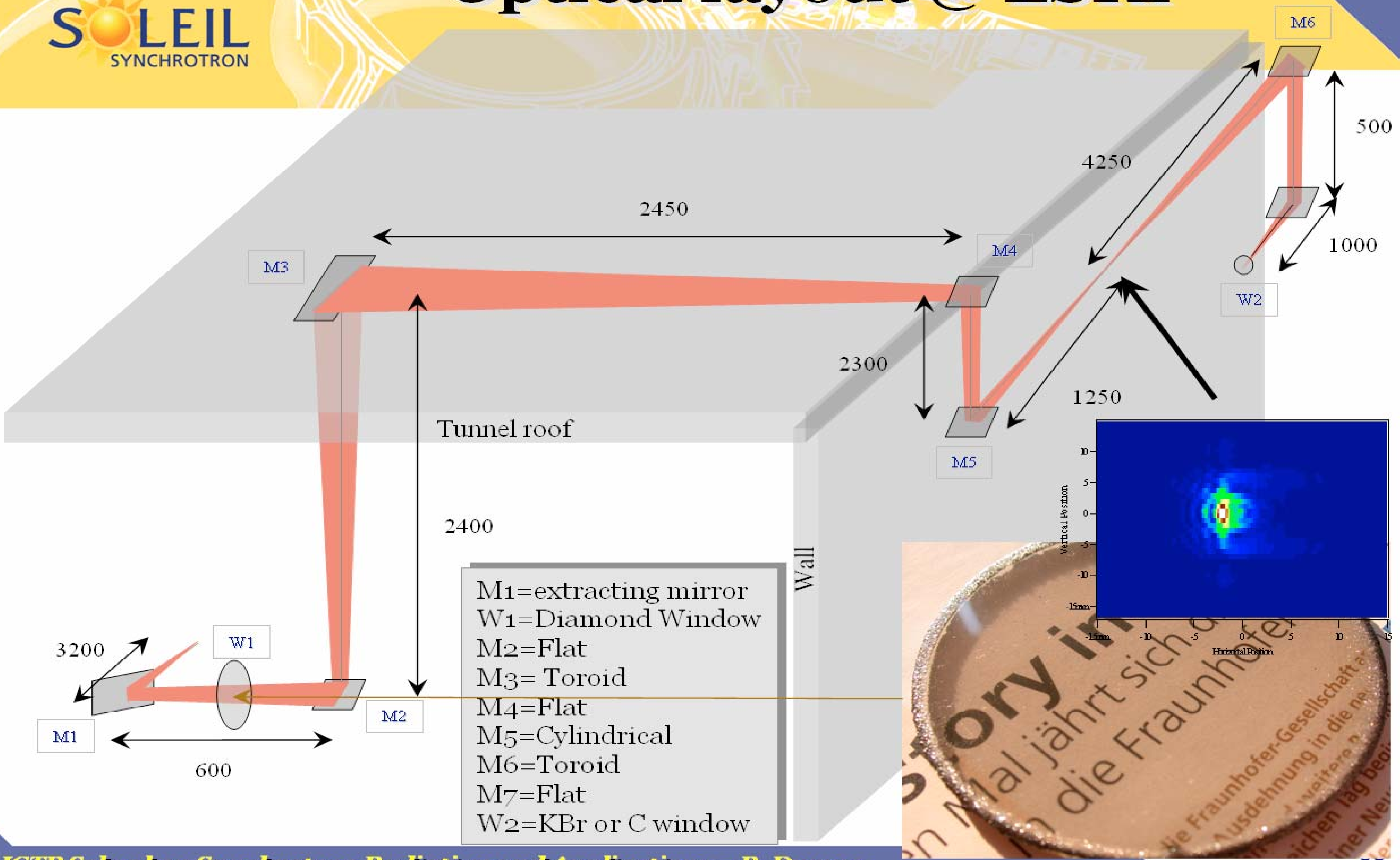


Optical layout @ ESRF

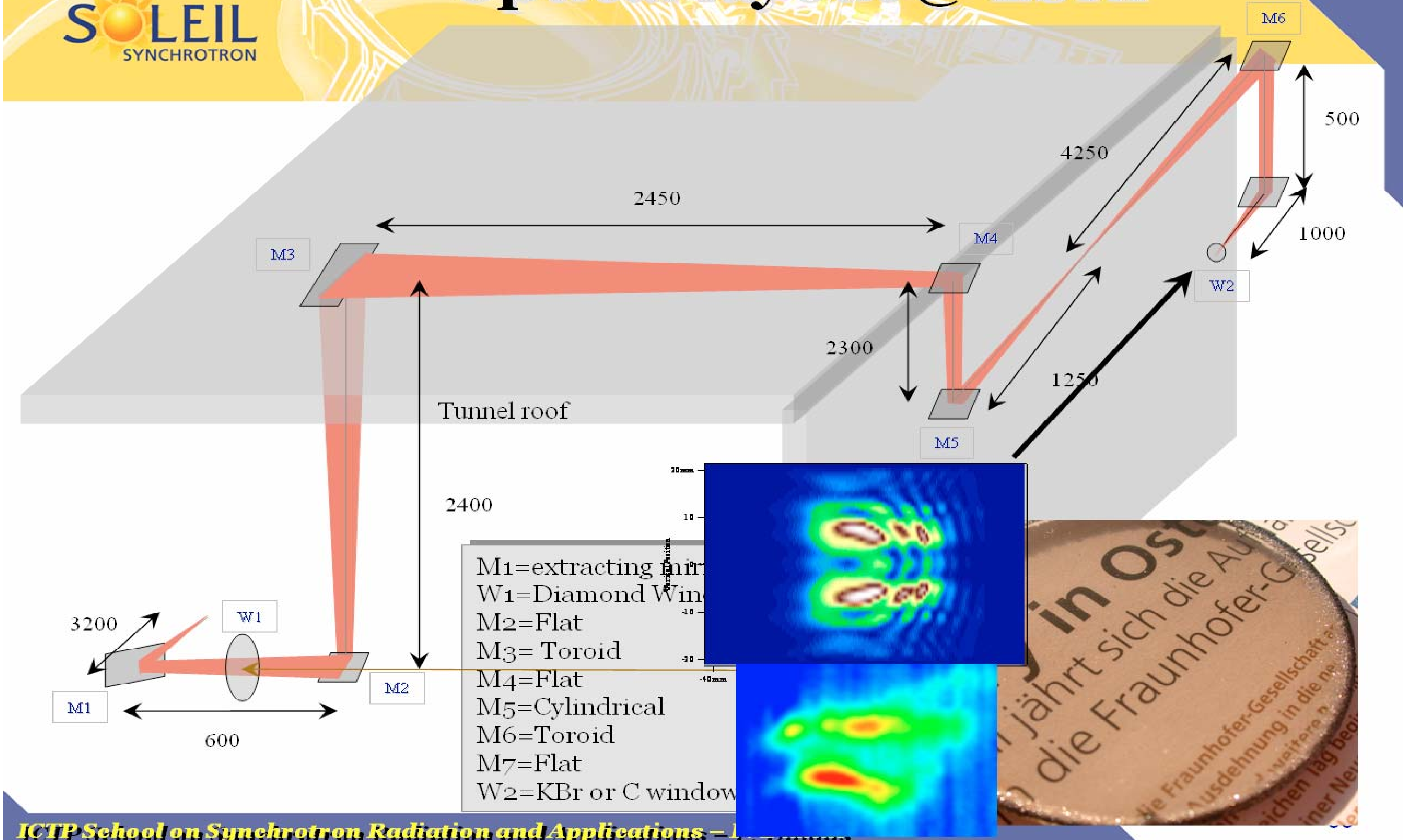


M1=extracting mirror
W1=Diamond Window
M2=Flat
M3= Toroid
M4=Flat
M5=Cylindrical
M6=Toroid
M7=Flat
W2=KBr or C window

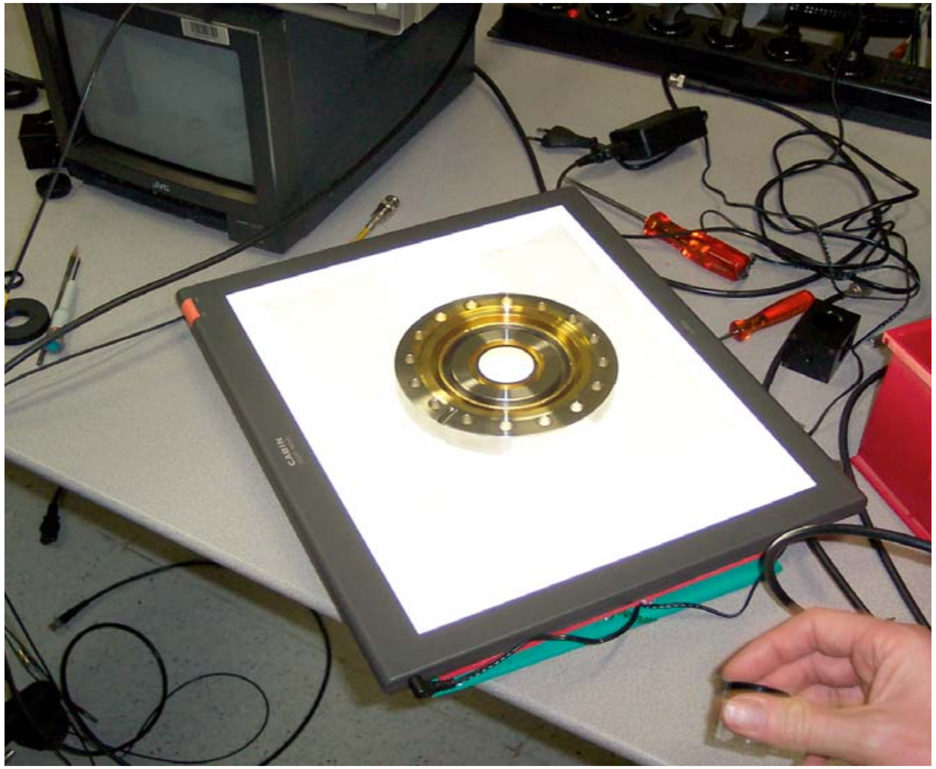
Optical layout @ ESRF

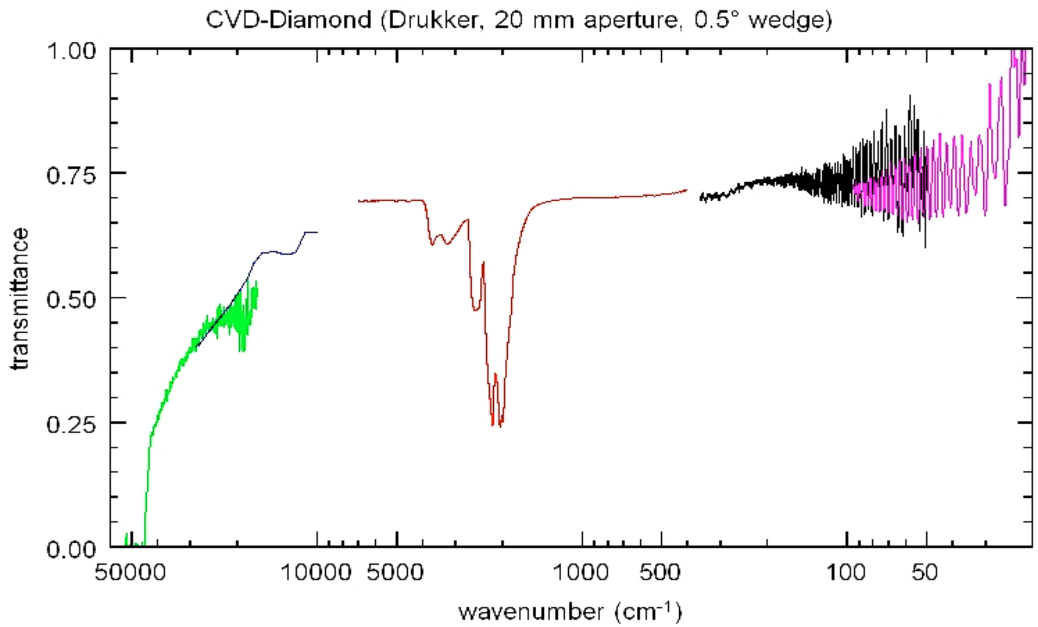


Optical layout @ ESRF

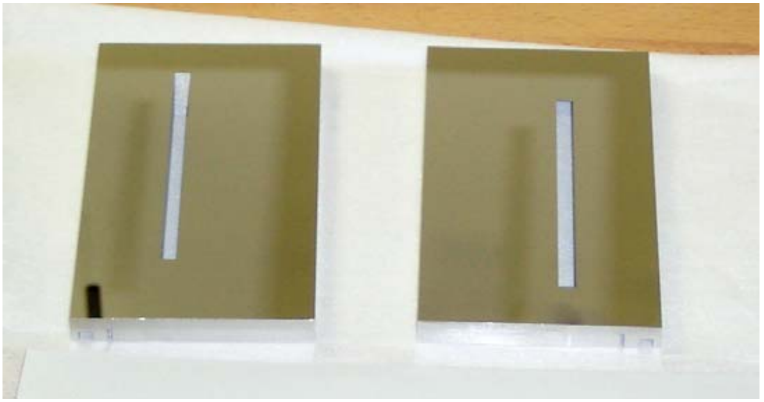


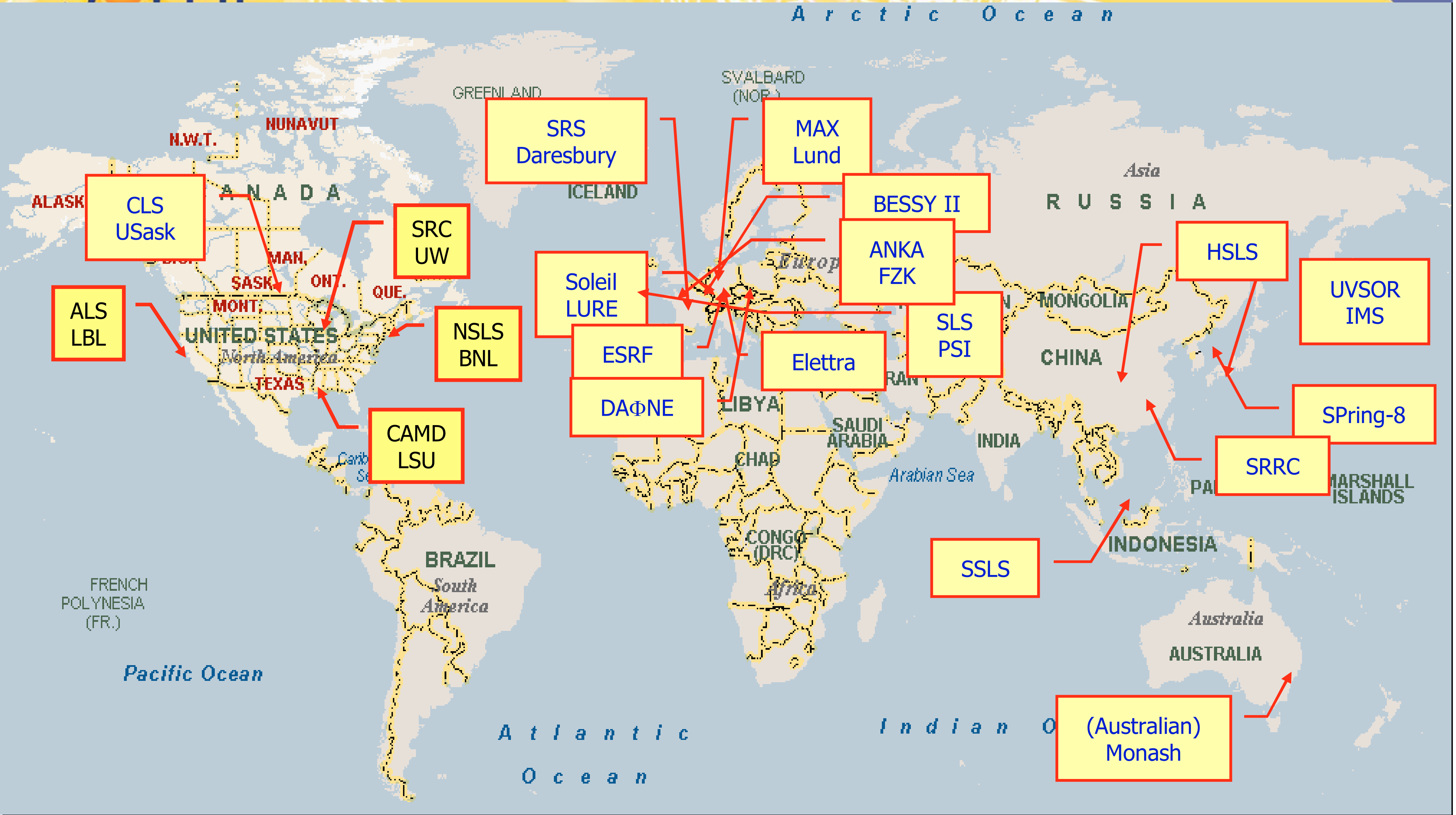
CVD diamond window@ ESRF





First mirror - slotted





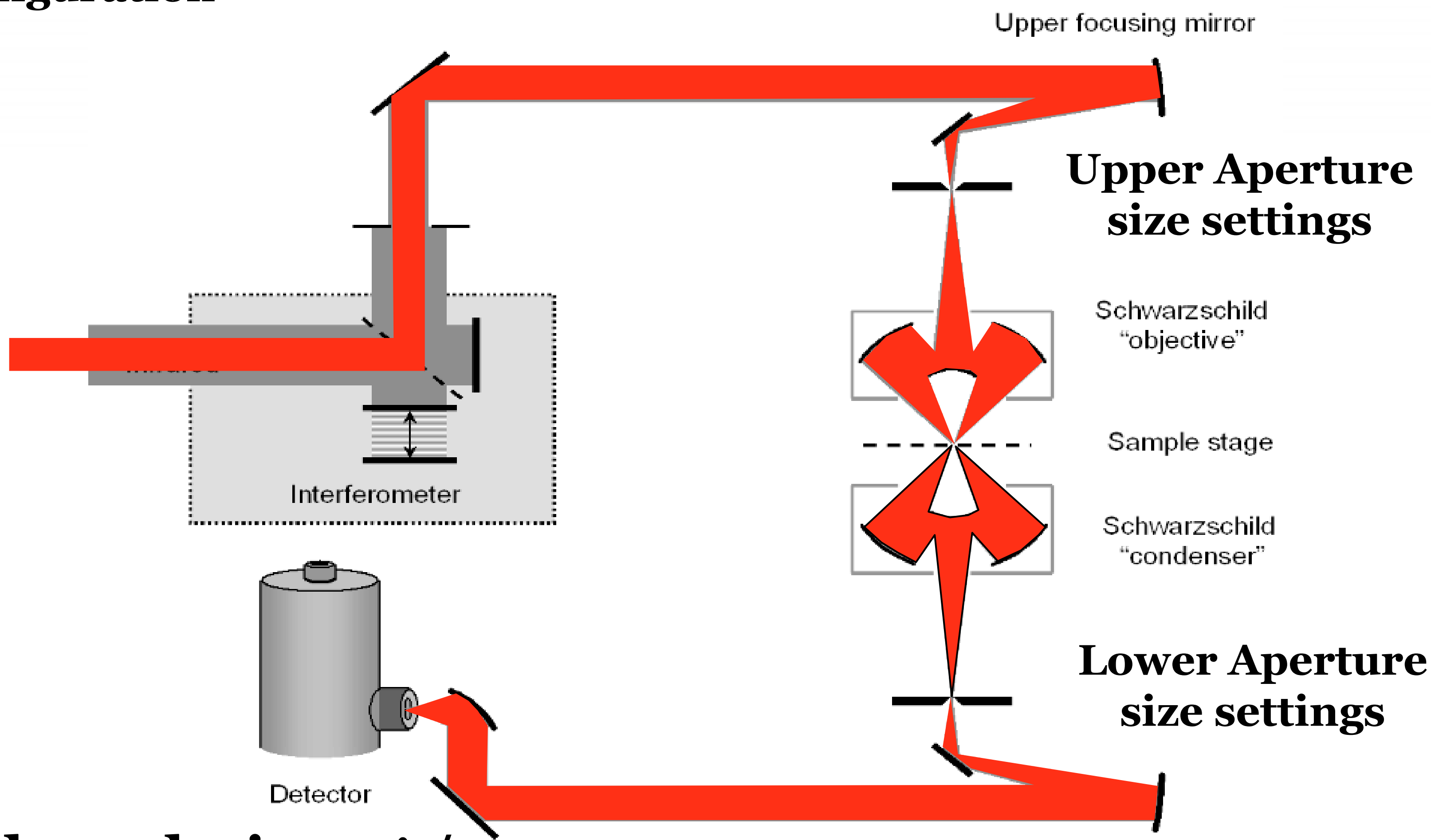
Arctic Ocean
SRS Daresbury
MAX Lund
BESSY II
ANKA FZK
SLS PSI
Elettra
Soleil LURE
ESRF
DAΦNE
CLS USask
SRC UW
ALS LBL
NSLS BNL
CAMD LSU
HSLS
UVSOR IMS
SPring-8
SRRC
SSLS
(Australian) Monash
GREENLAND
SVALBARD (NOR.)
ICELAND
NUNAVUT
N.W.T.
ALASK
CANADA
MAN.
SASK.
ONT.
QUE.
MONT.
UNITED STATES
North America
TEXAS
Asia
RUSSIA
MONGOLIA
CHINA
INDIA
Europ
LIBYA
SAUDI ARABIA
CHAD
Arabian Sea
CONGO (DRC)
Africa
BRAZIL
South America
FRENCH POLYNESIA (FR.)
Pacific Ocean
Atlantic Ocean
Indian O
INDONESIA
MARSHALL ISLANDS
Australia
AUSTRALIA

Synchrotron Infrared micro-spectroscopy
Molecular imaging

From Spectroscopy to Microscopy

Synchrotron infrared and Microscope

The brightness of the synchrotron source allows to use a confocal configuration

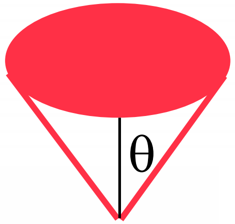


Lateral resolution ~$\lambda/2$

Diffraction-limited Point Spread Functions

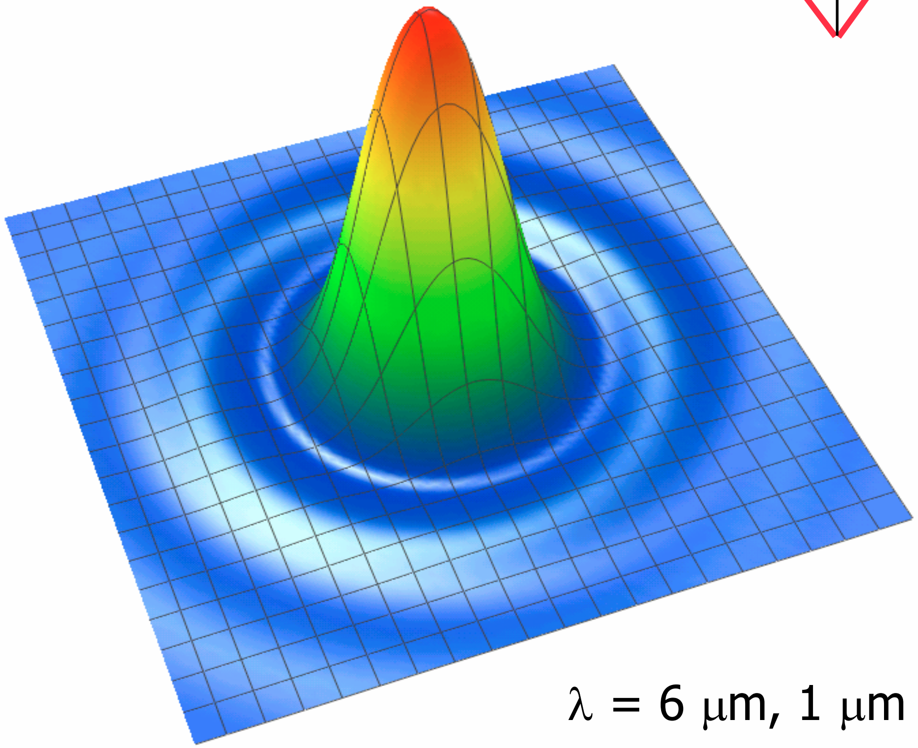
"Normal" (circular aperture)

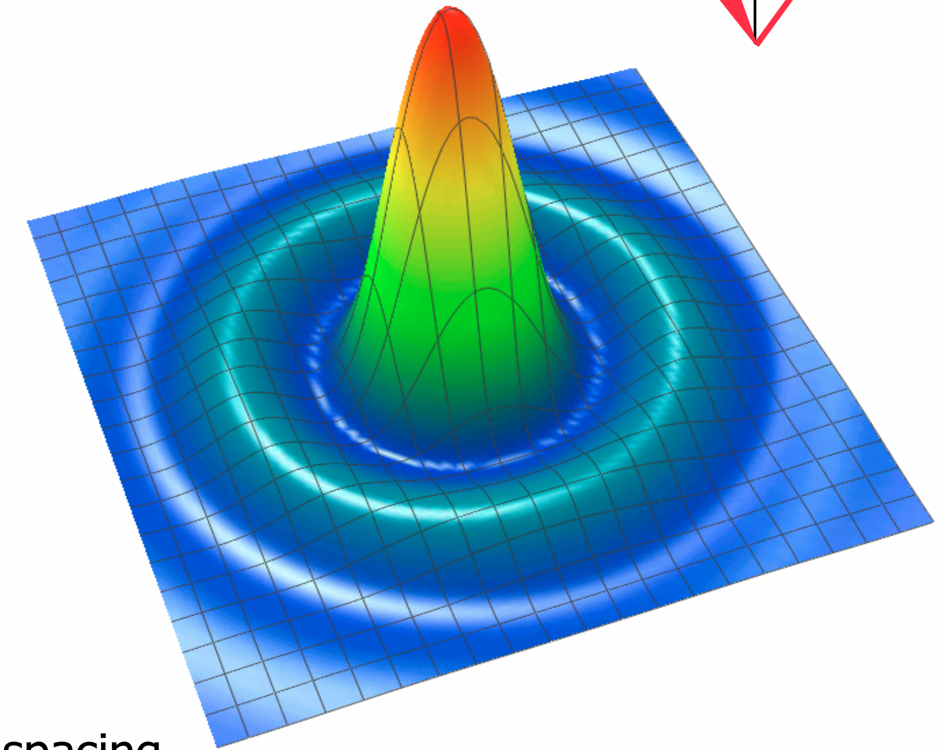
$d = 1.22\lambda/(n \sin\theta)$



Schwarzschild

$d \approx \lambda/(n \sin\theta)$



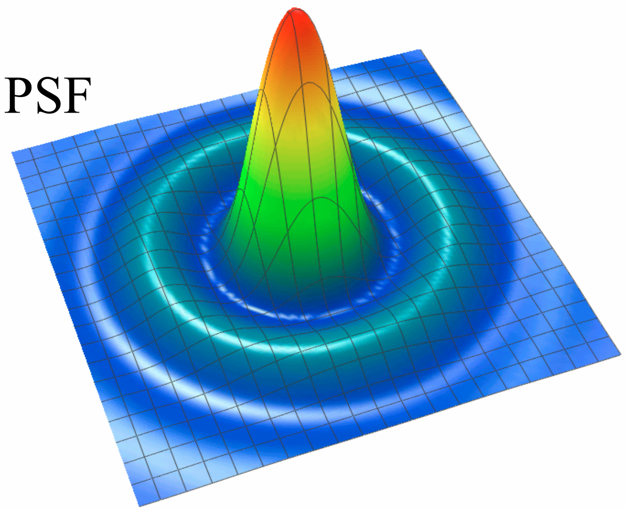


λ = 6 μm, 1 μm grid spacing

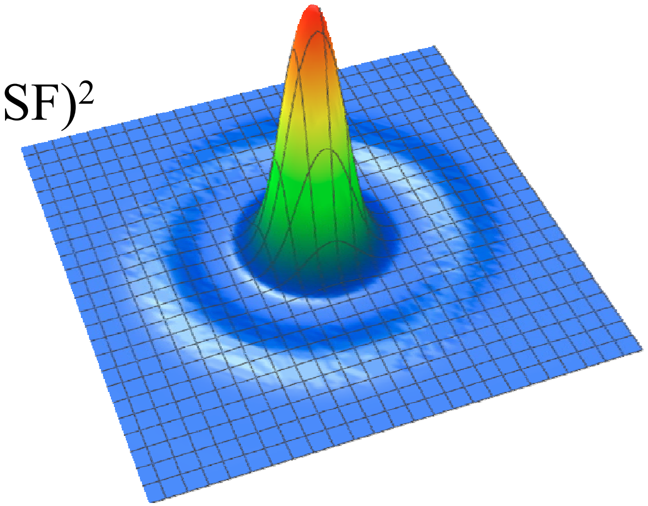
"fat" 1st order diffraction ring for Schwarzschild

Confocal versus non-confocal

PSF

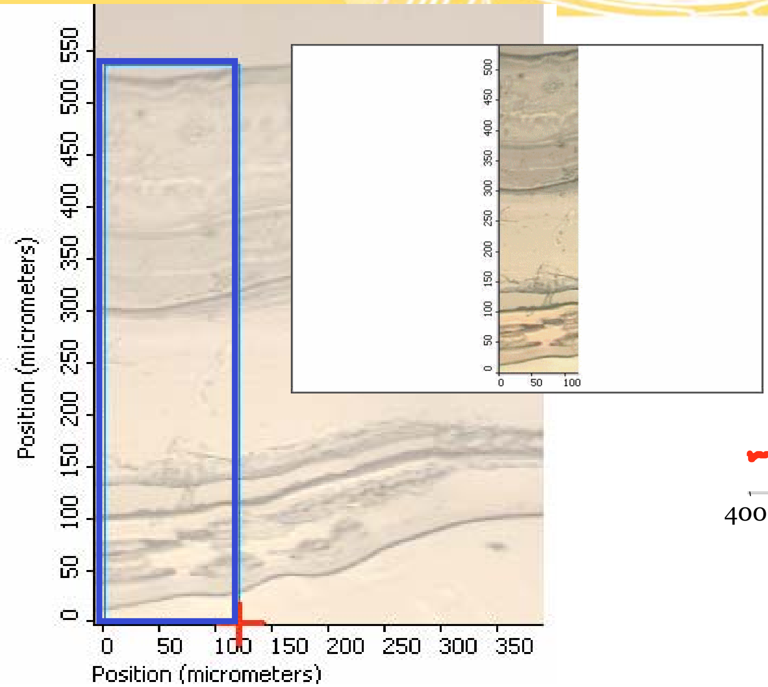


$(PSF)^2$

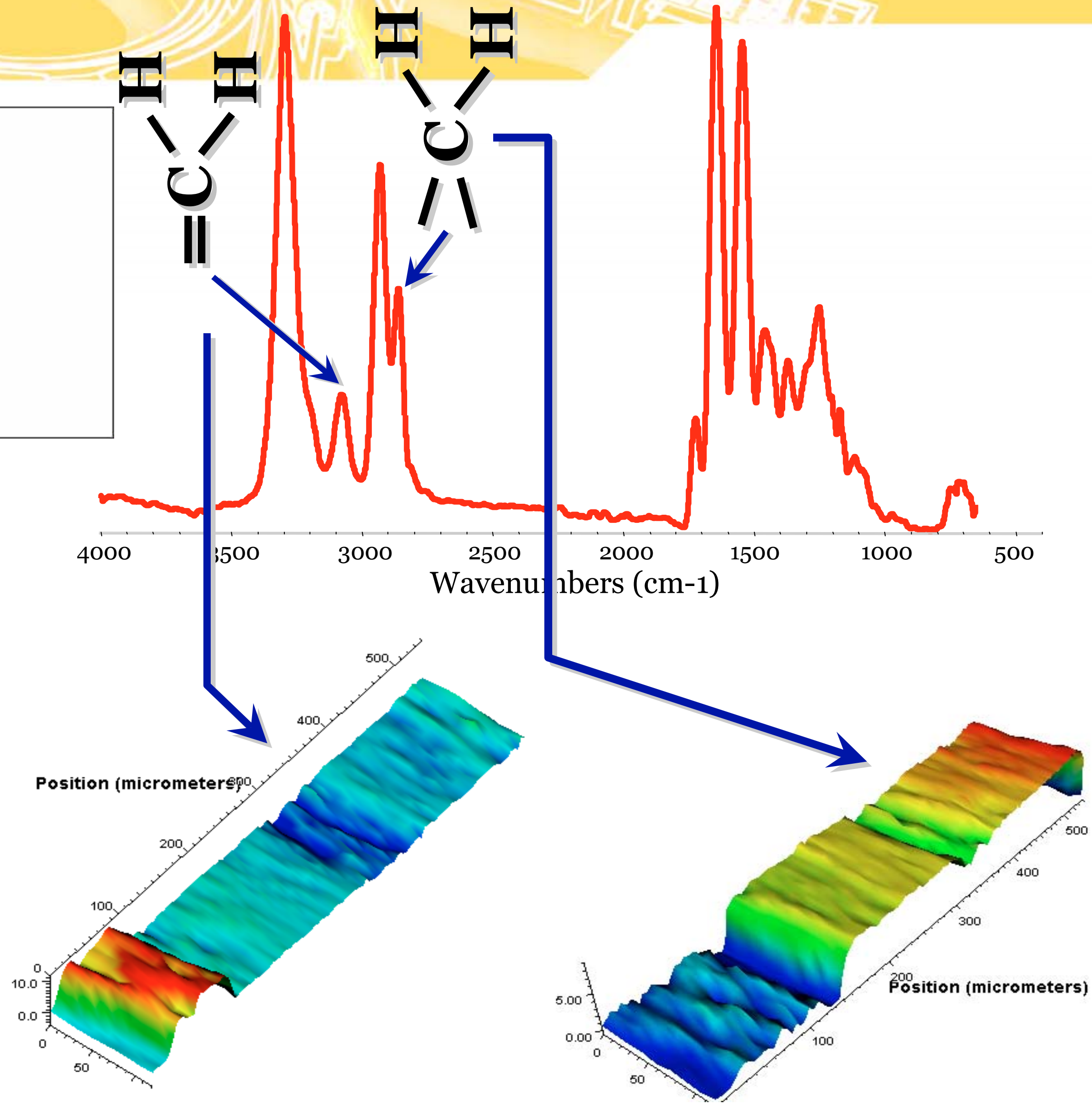


Confocal results in narrower central peaks, and also reduces effect of 1st order diffraction ring.

Chemical imaging and contrast fidelity



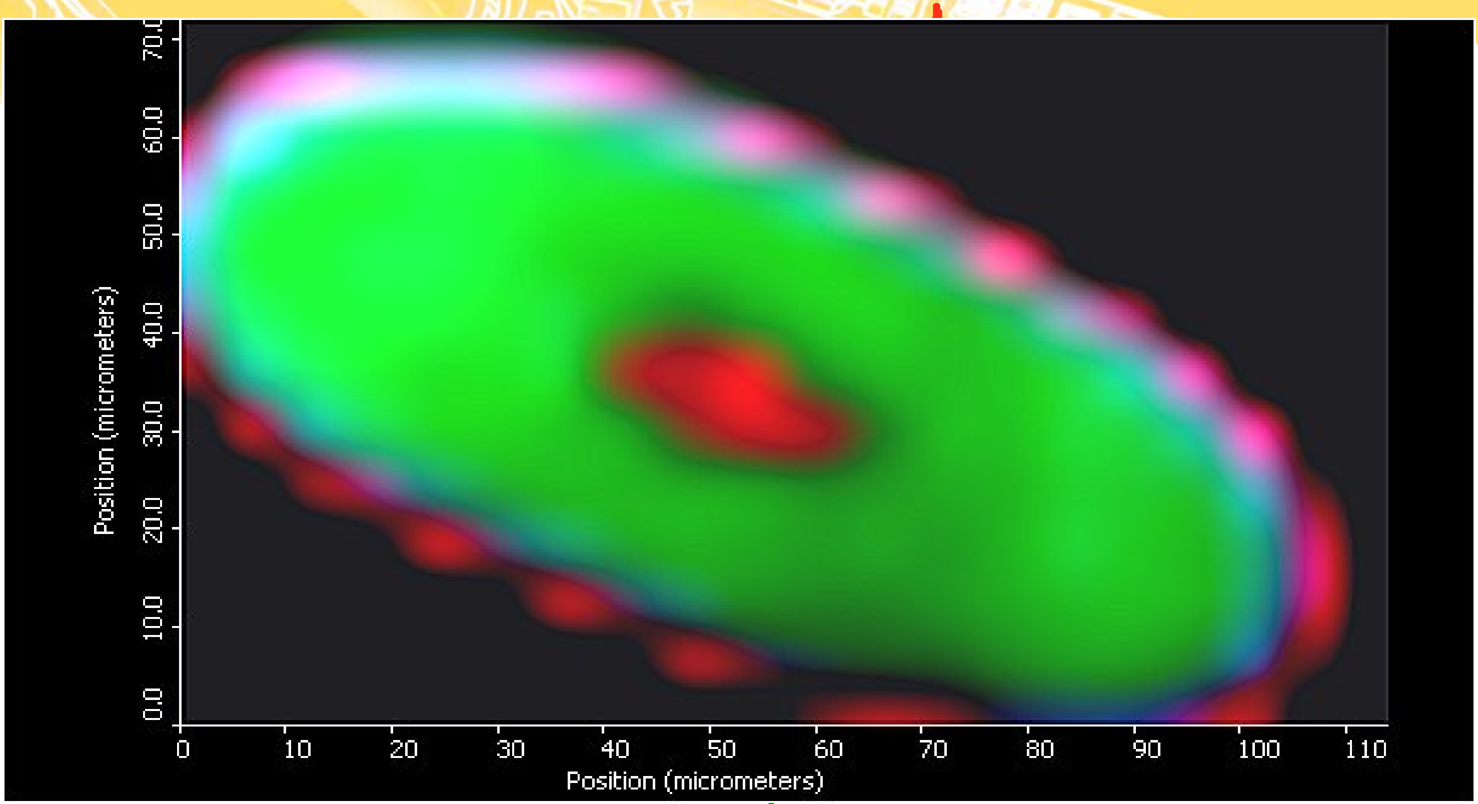
Polymer laminate

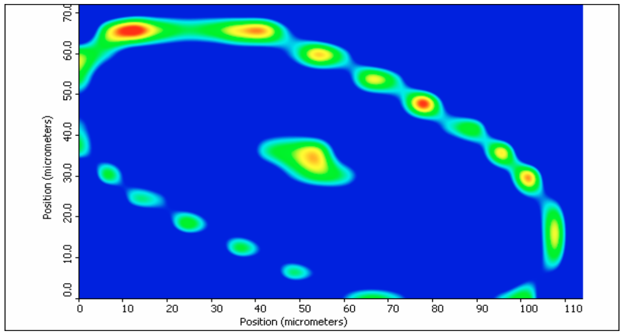


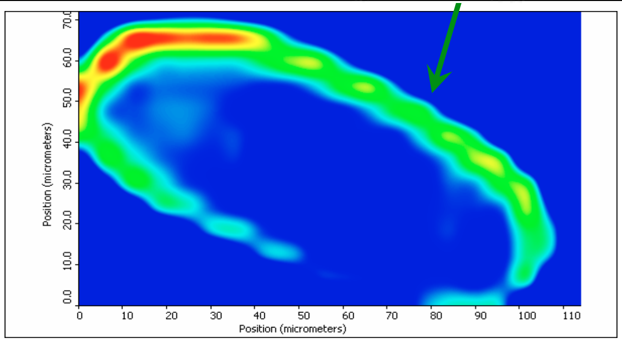
lipids

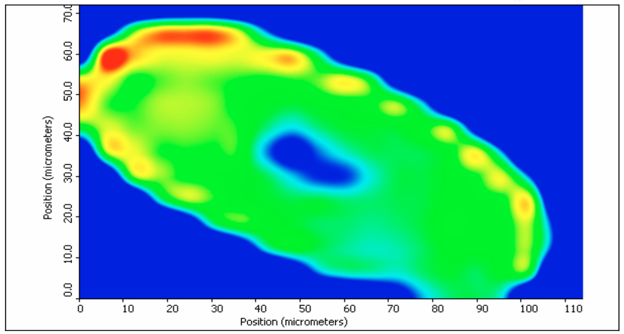
proteins

β sheets

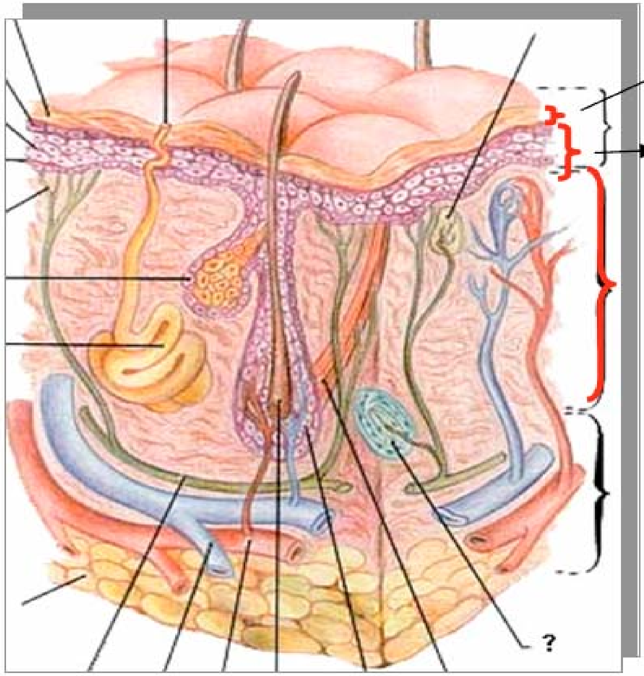








Biological applications: human tissues

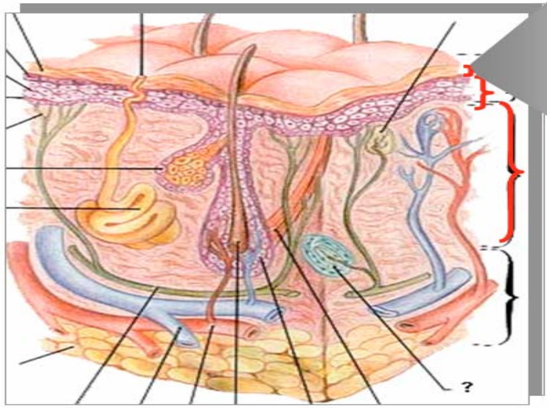


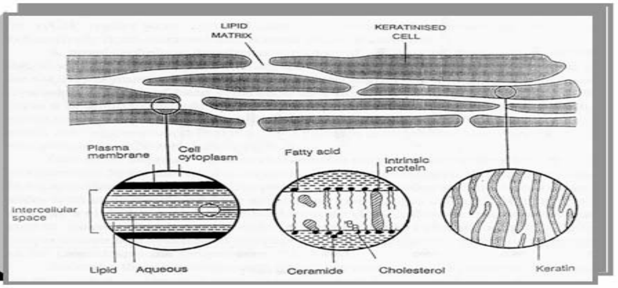
Stratum Corneum
10-20 µm

Epidermus
60-80 µm

Dermus
>100 µm

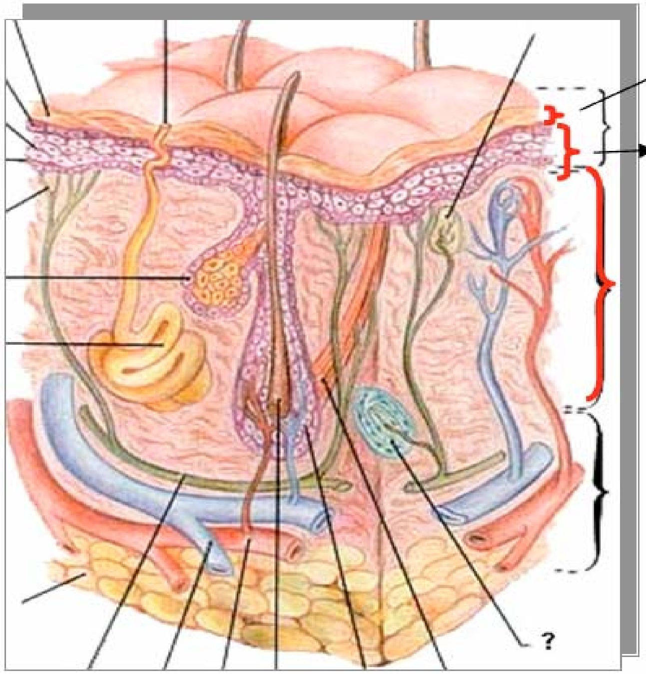
Biological applications: human tissues





Derm
>100 µm

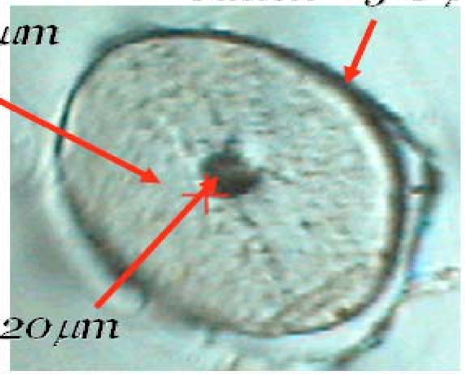
Biological applications: human tissues

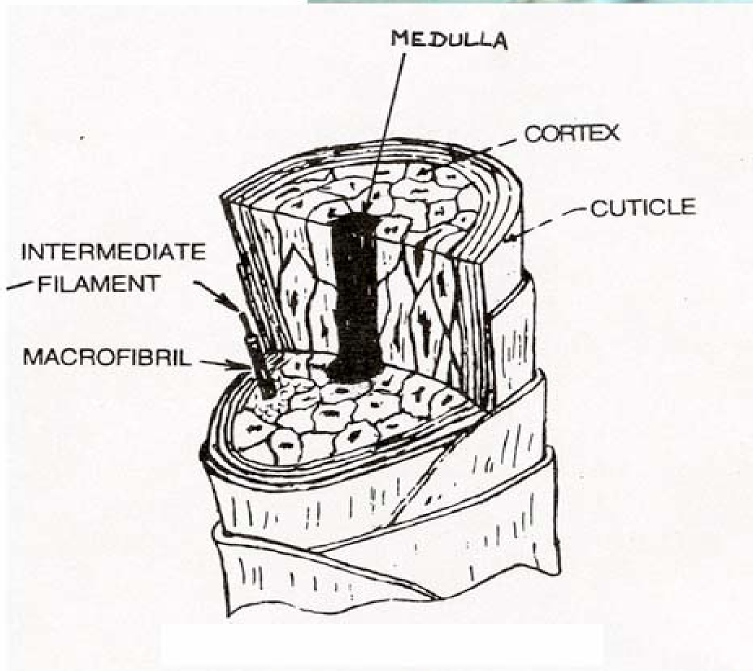


Stratum Corneum
10-20 μm

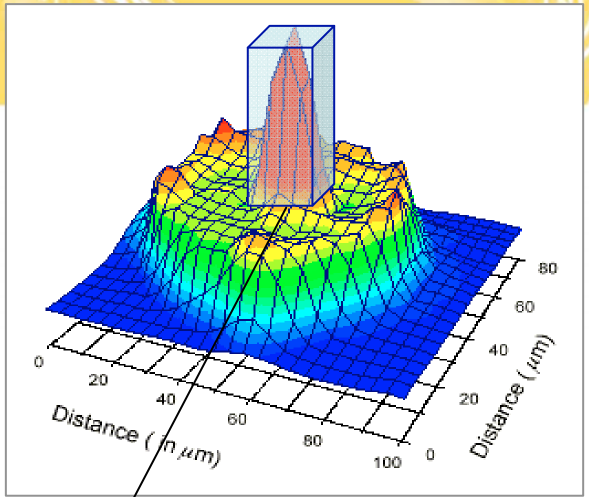
Epidermus
60-80 μm

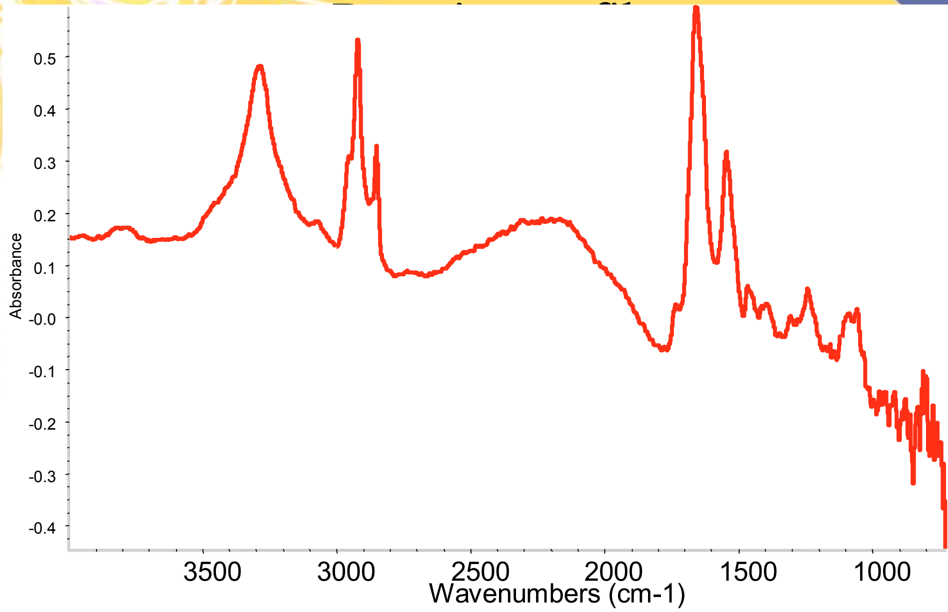
Dermus
>100 μm



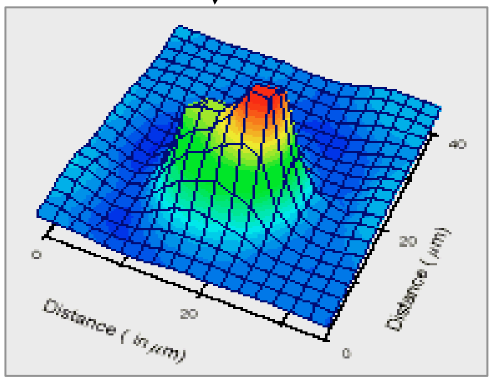


Lipid profile

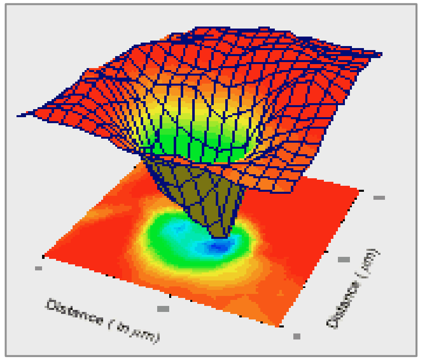




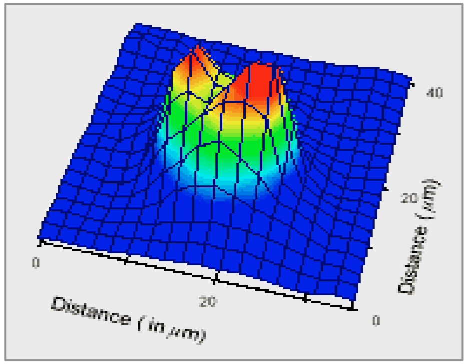
3x3 μm^2 aperture
1 µm step



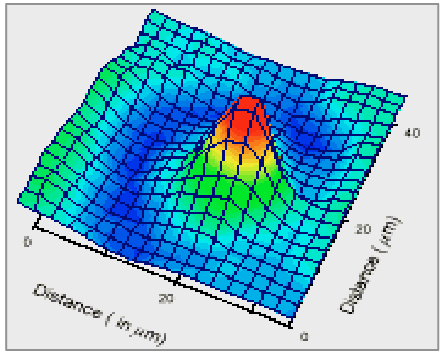
CH_2



Amide I



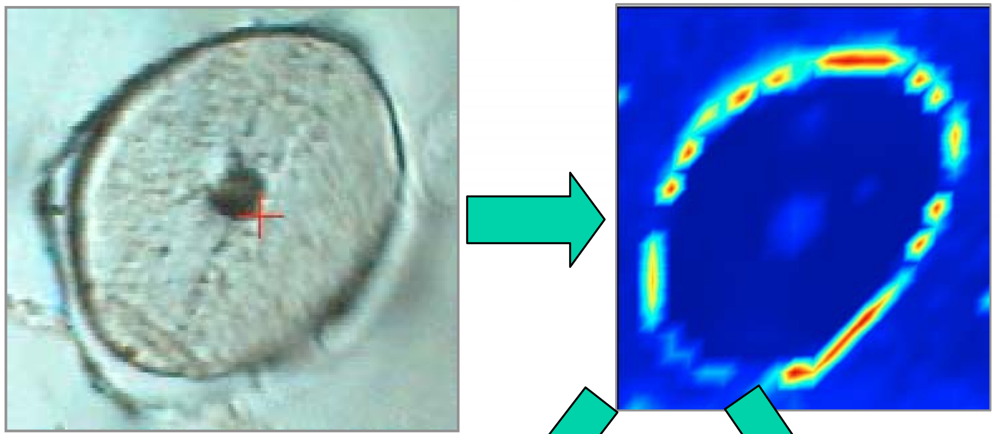
C=0



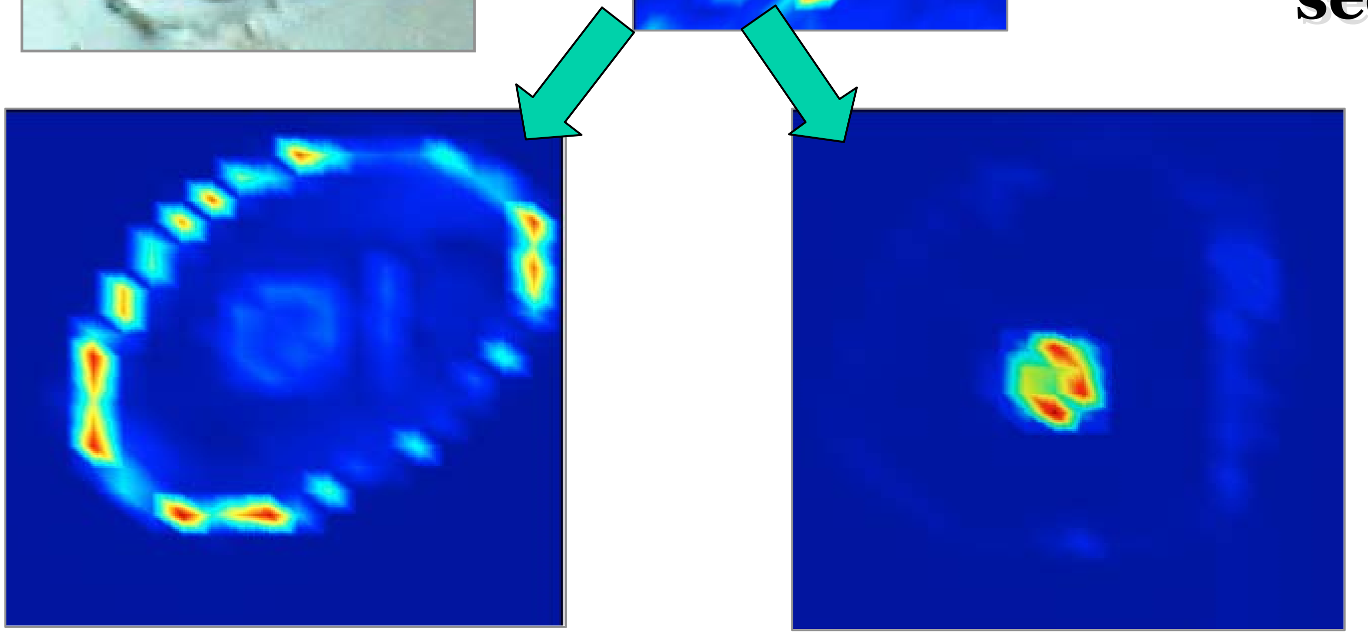
carboxylate

Intern.J. of Cosmetics Science. **23** *1-6* (2001) 369-374

Beside chemical imaging: multivariate…

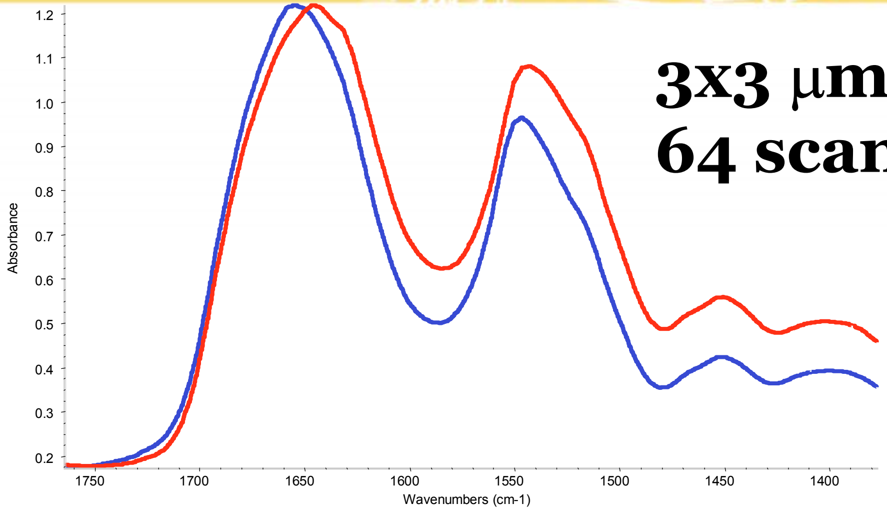


Two types of lipids identified across hair section

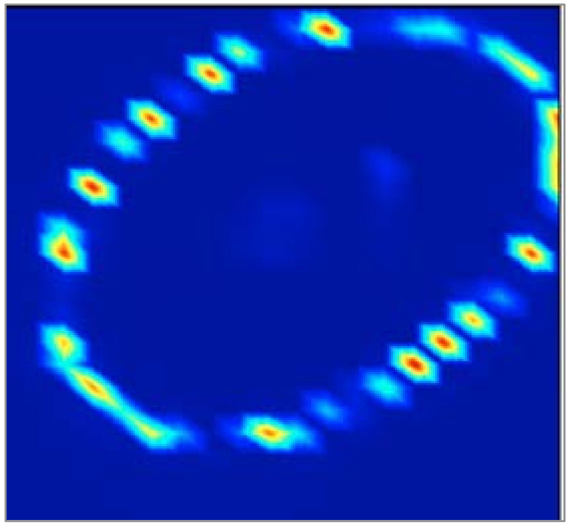


Two types of lipids identified by HCA (Hierarchical Cluster Analysis)

Secondary structure of proteins

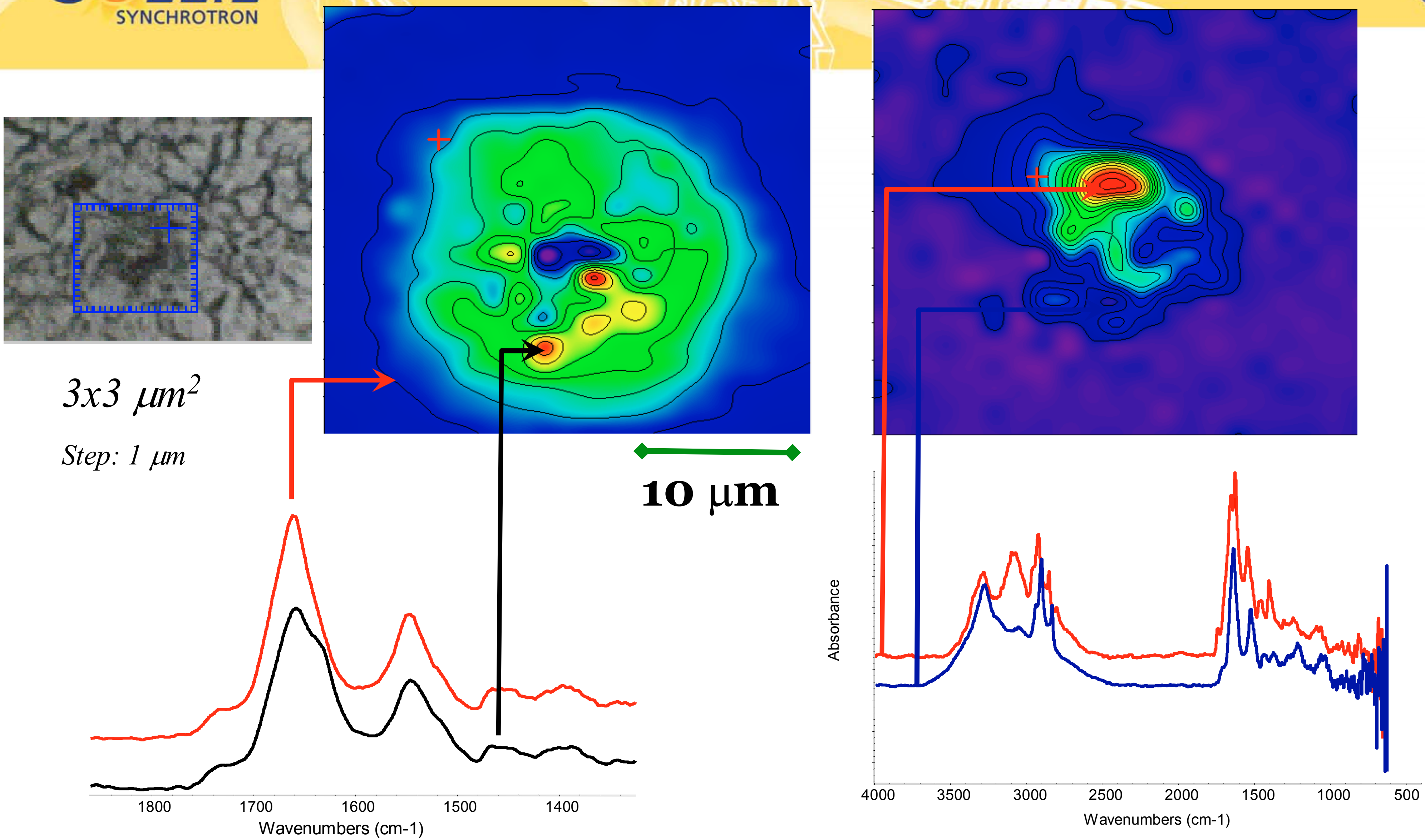


3x3 µm²
64 scans



Higher concentration in β Sheets in the cuticle.

Plaque in brain tissue



MIRAGE beamline LURE

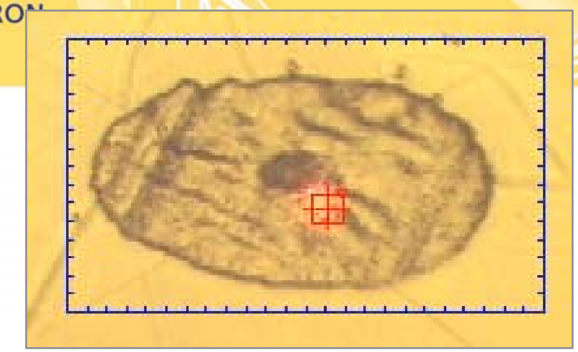
From K. Gough , P. Dumas unpublished

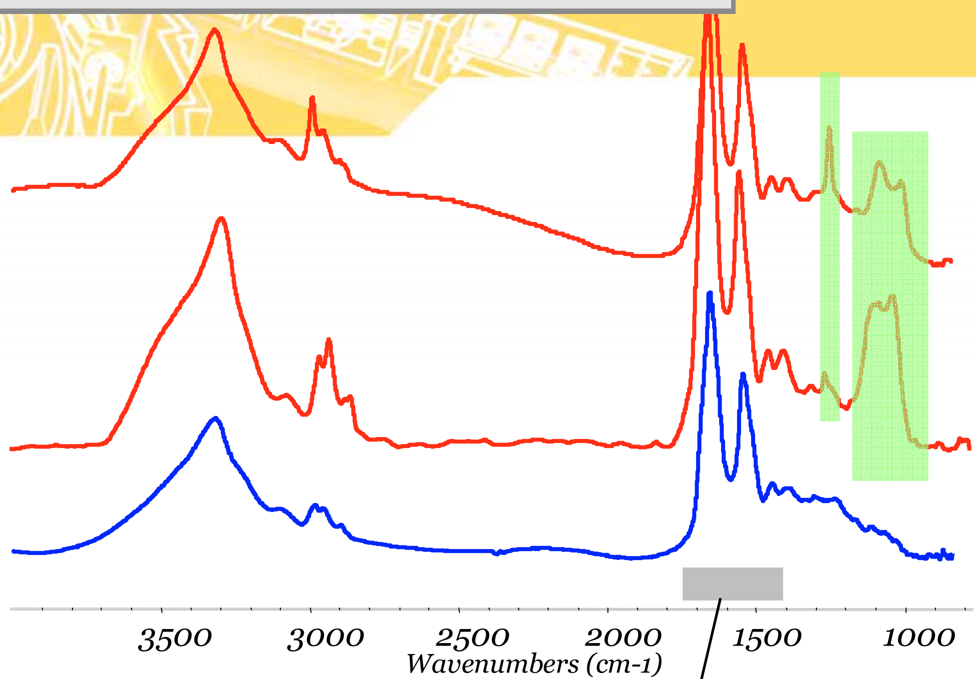
Human tissues from mummy

Mummy from Taklamakan desert

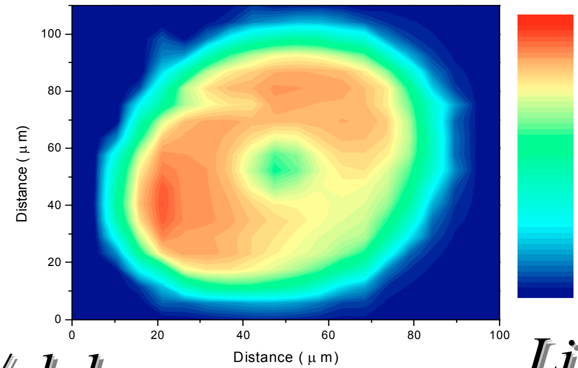
M. Cotte, Ph. Walter and P. Dumas

Mummy from Taklamakan desert: hair

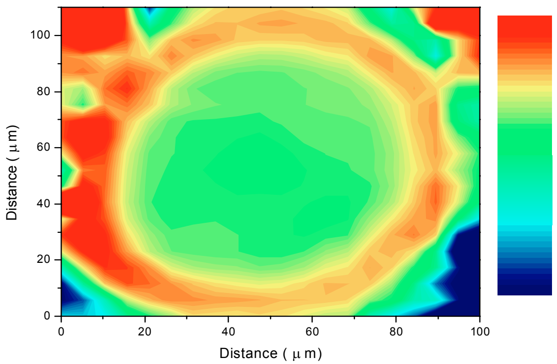




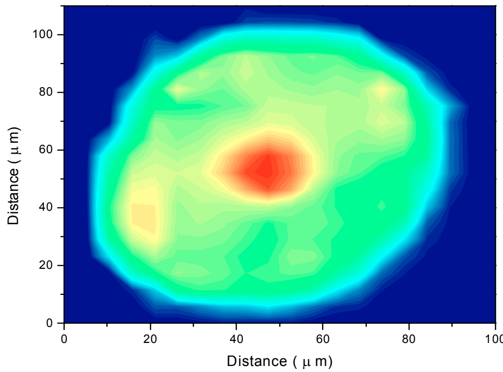
Proteins

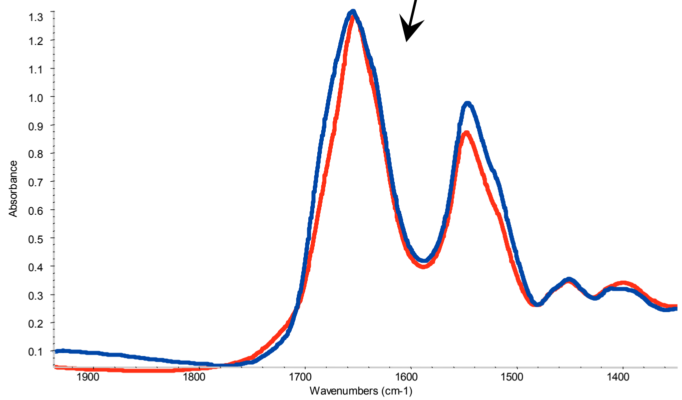


Beta/alpha

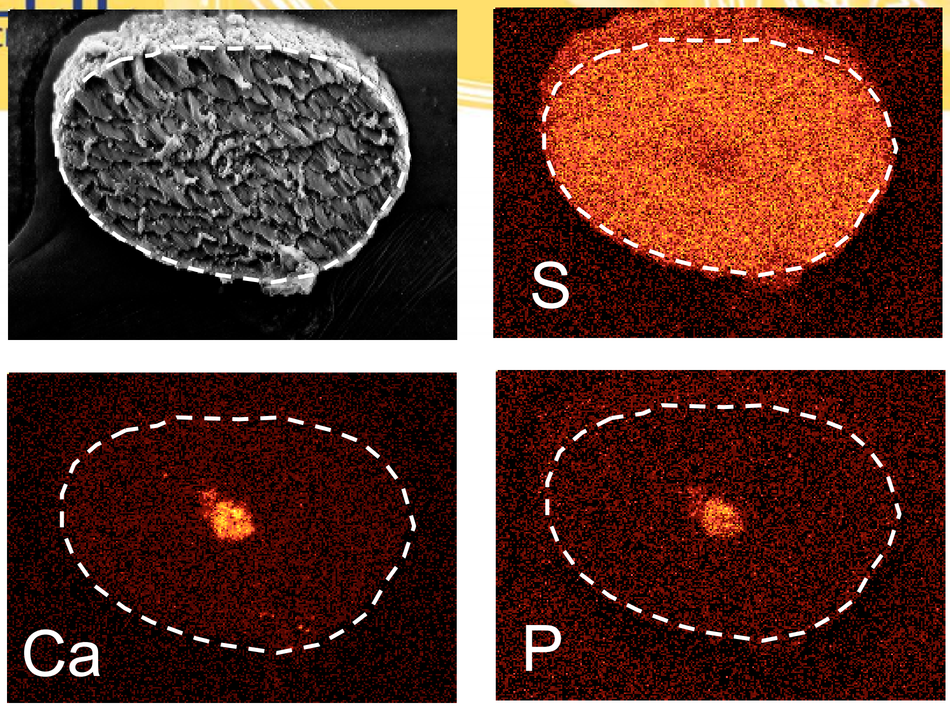


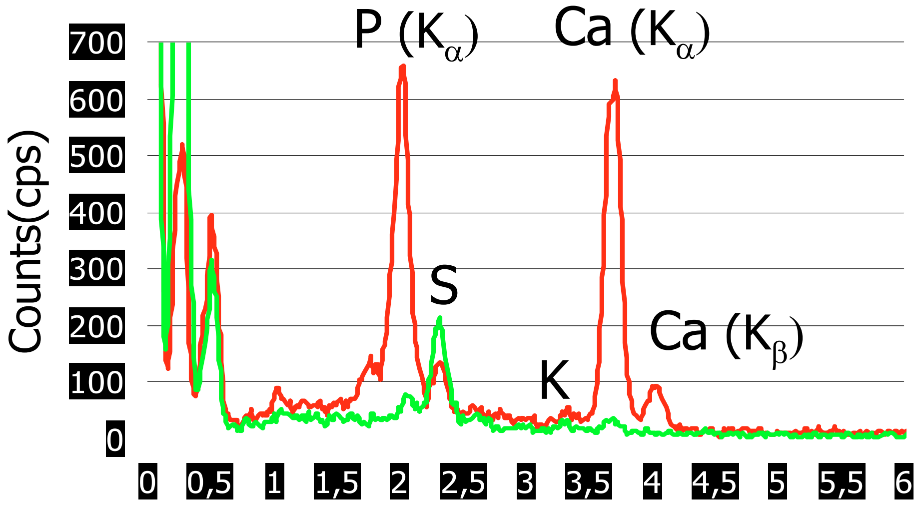
Lipids



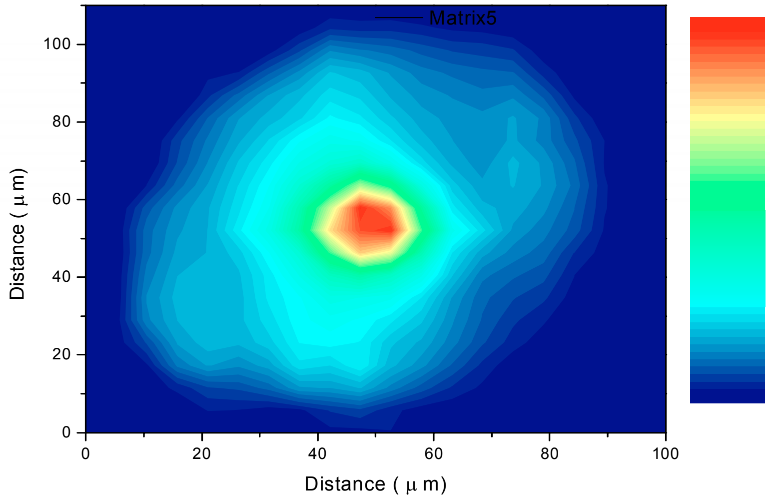


Mummie from Taklamakan desert:hair

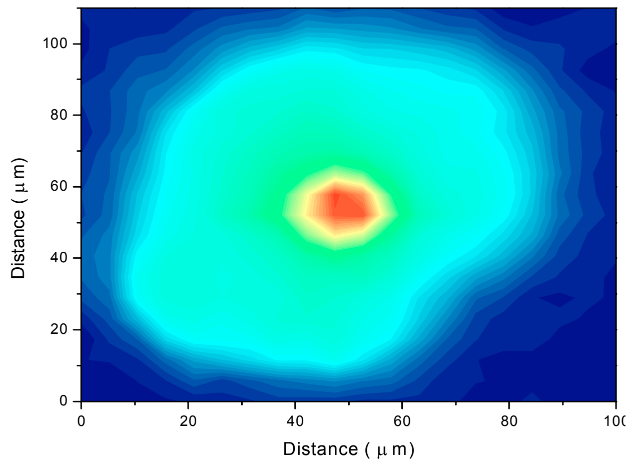




« Phosphate » band at 1250 cm-1

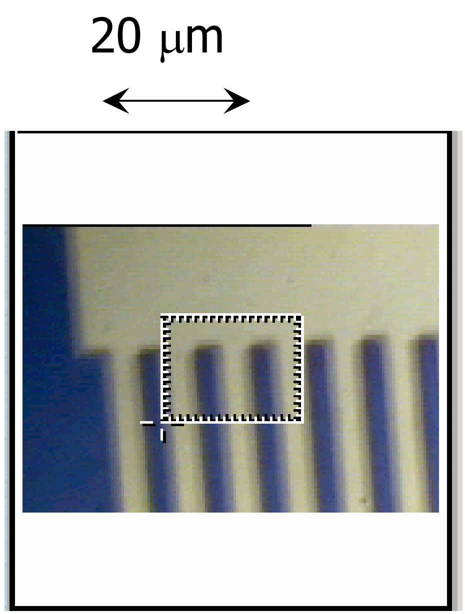


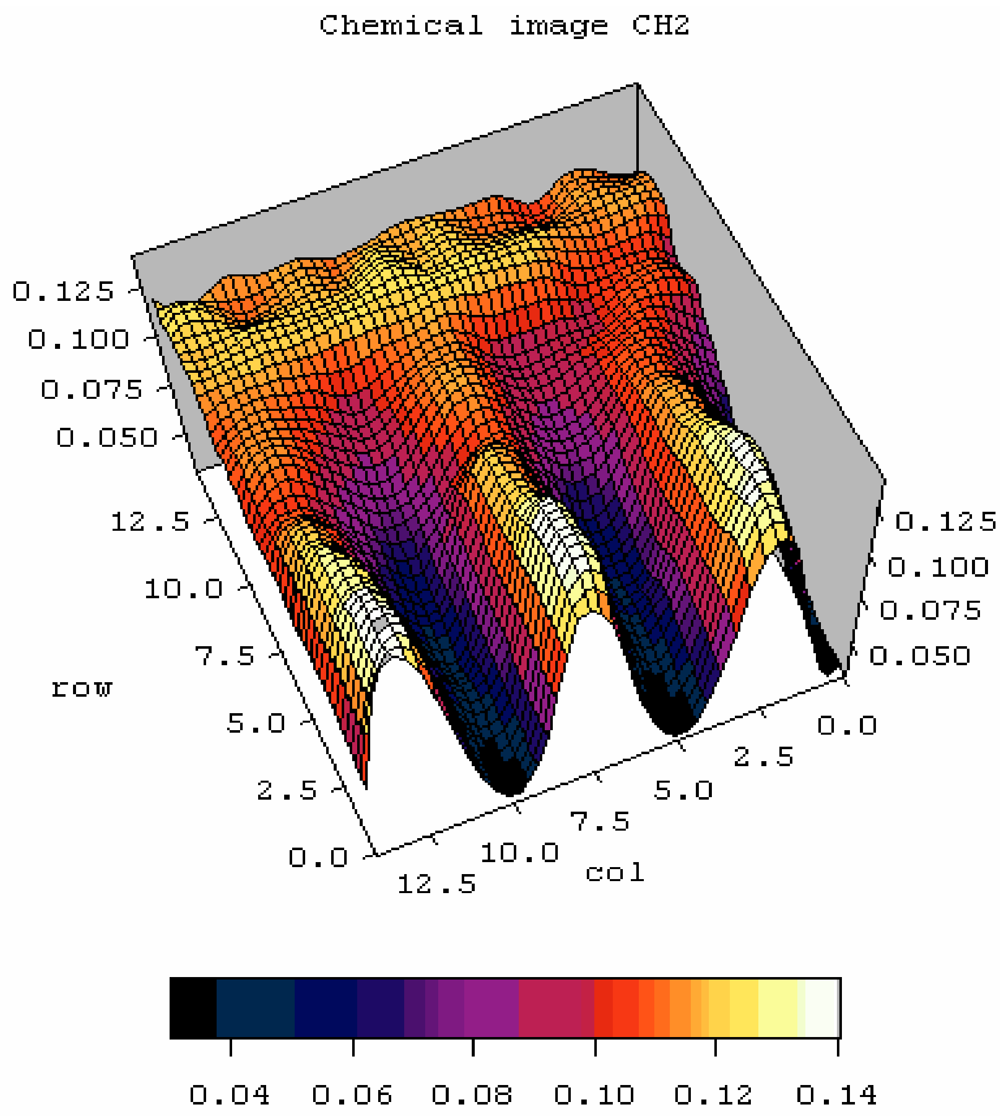
«Hydroxyapatite » band 1000-1100 cm-1



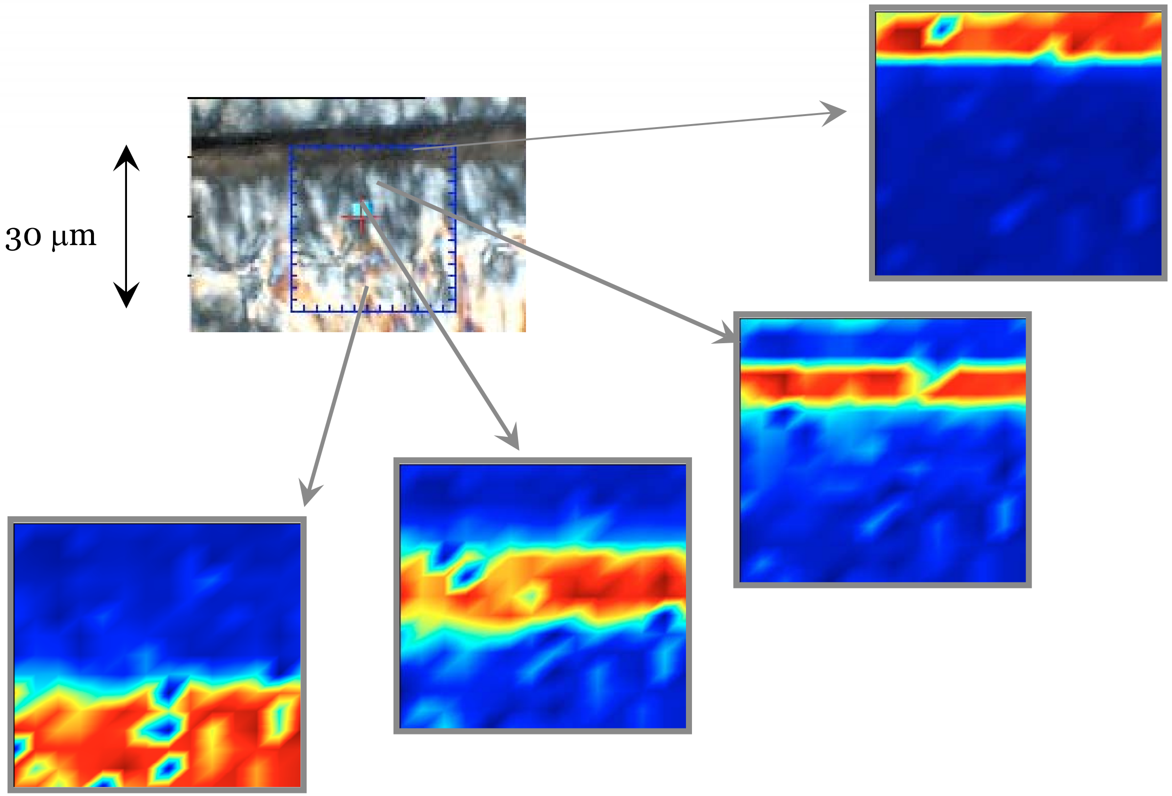
Gold grid deposited on silicon wafer

imaging the protective layer on top of the gold grid

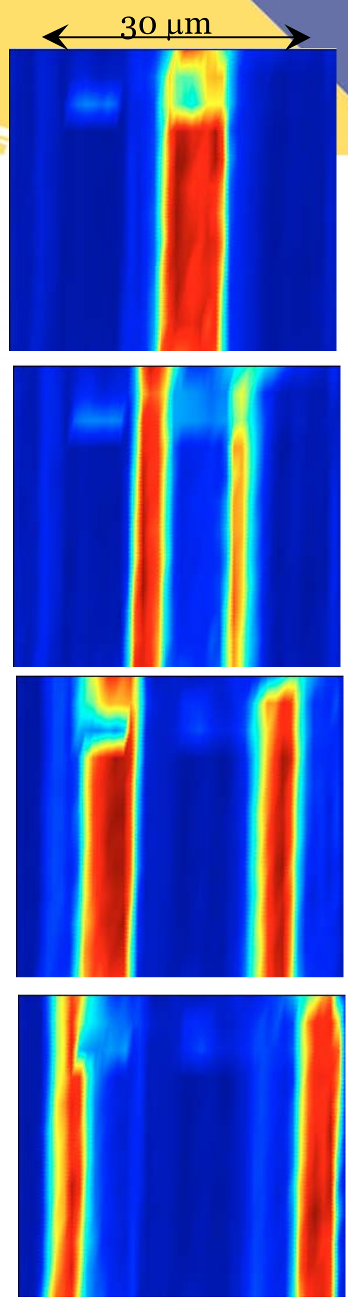




Polymer films

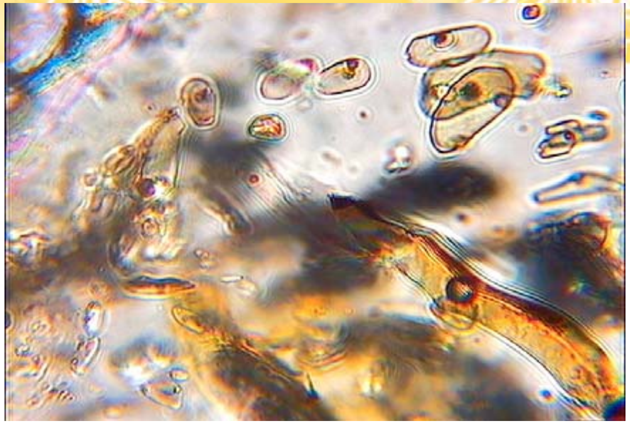


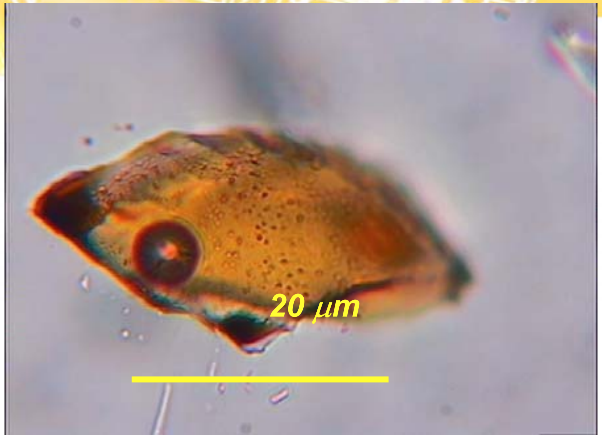
Isotactic polypropylene (iPP) polymorphism in a sheared film from a fibre

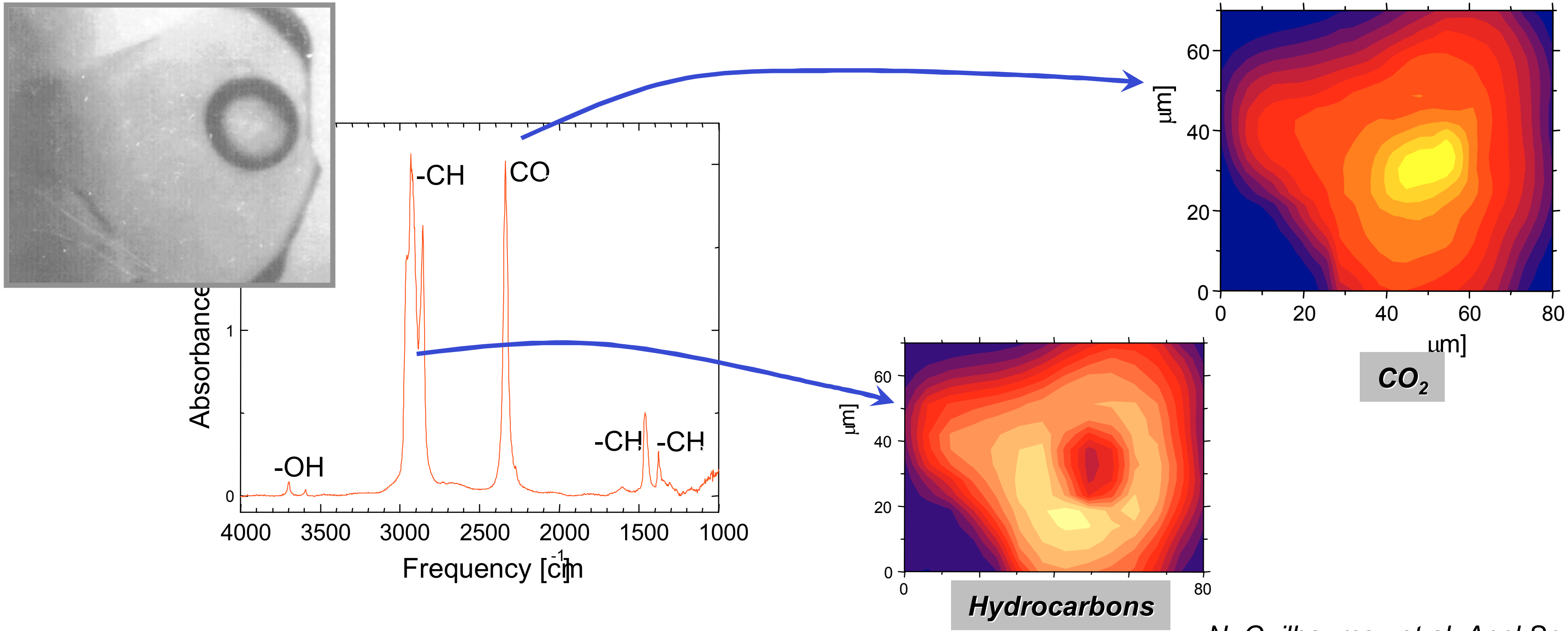


PE assembly

Inclusions in rocks







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Water in deep seated minerals (200-400 kms)

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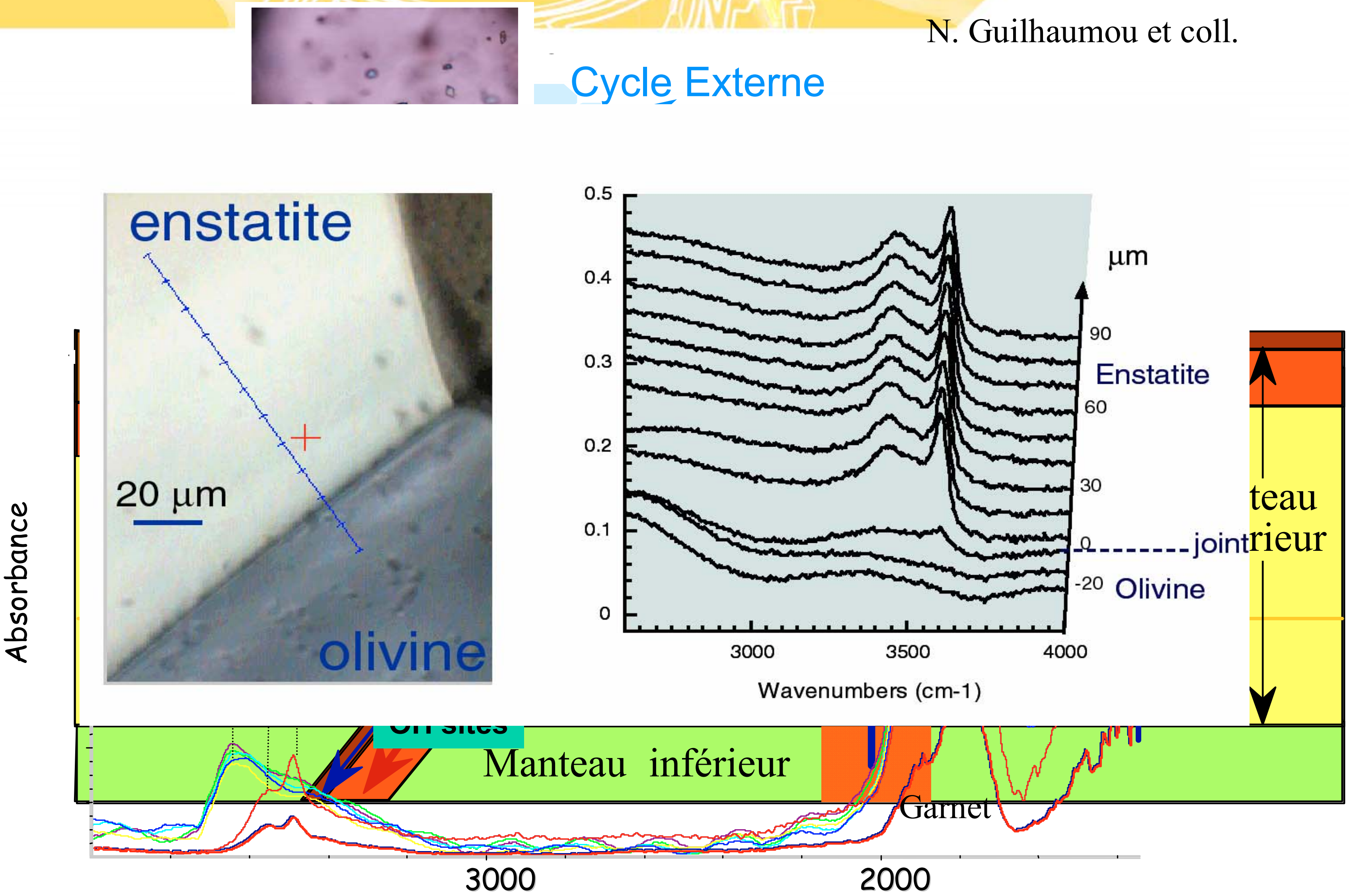
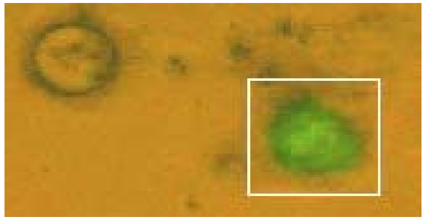


Summary

- Synchrotron IR microscopy has became an important analytical tool in synchrotron facilities
- Such facilities are of high ratio scientific/cost
- Association with fluorescence is desirable



- Good S/N and higher spatial resolution.... Statistical treatment (unsupervised or supervised)
- Complementarities with other synchrotron based techniques are very potential especially if combined studies are performed on the same sample.