



The Abdus Salam
International Centre for Theoretical Physics



2139-1

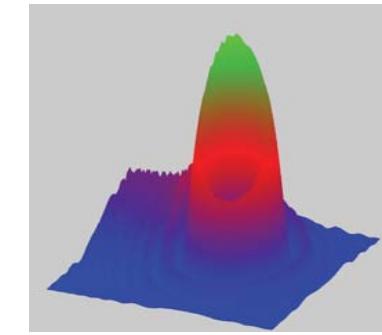
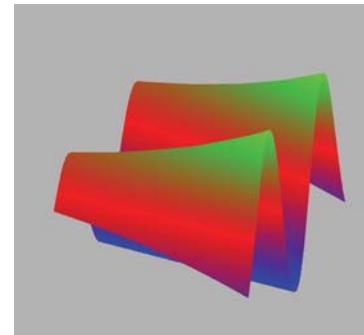
**School on Synchrotron and Free-Electron-Laser Sources and their
Multidisciplinary Applications**

26 April - 7 May, 2010

Synchrotron Infrared Emission: From Basic Principles to Applications

Paul Dumas

*SOLEIL Synchrotron-France
France*

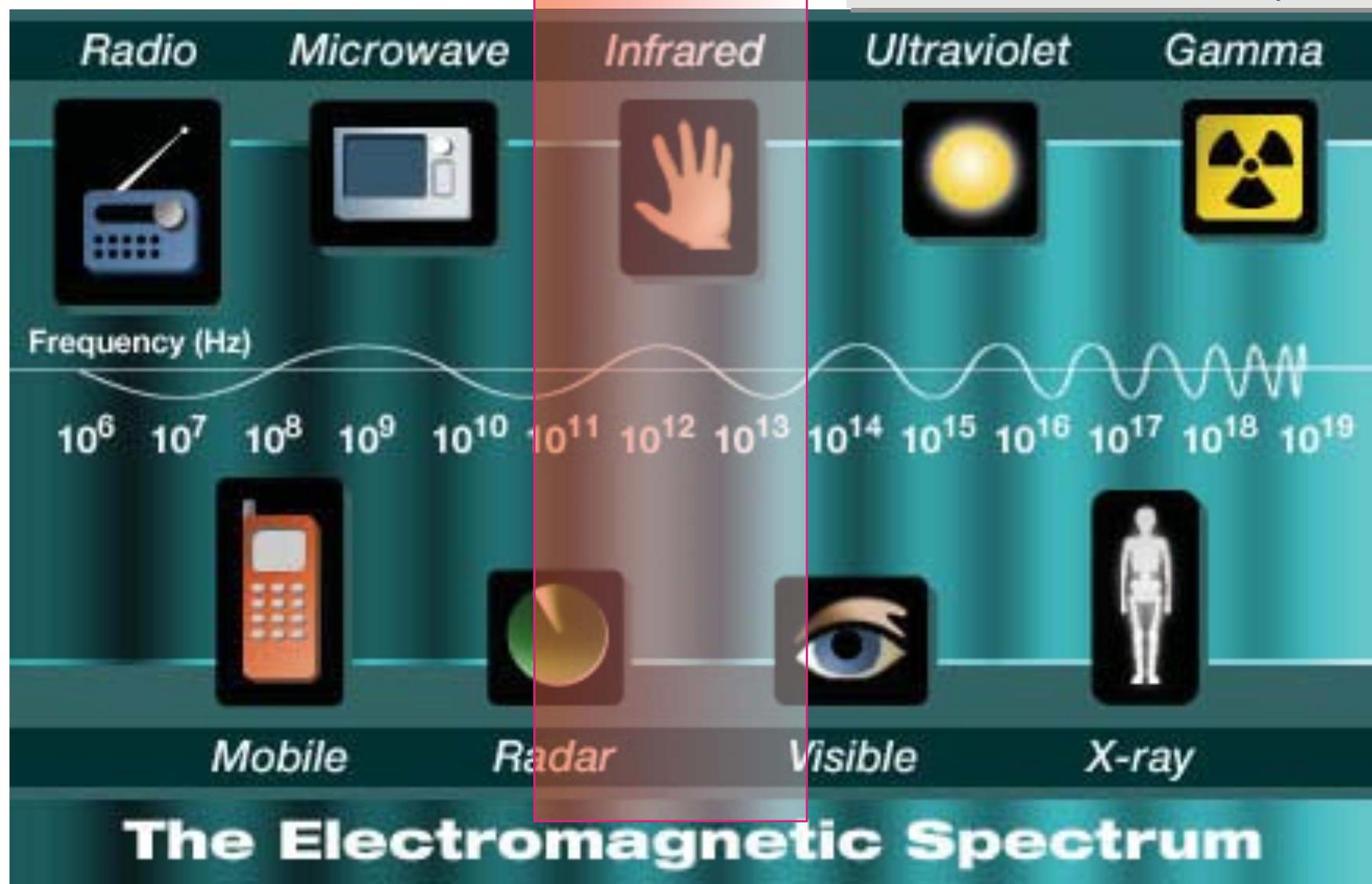


SYNCHROTRON INFRARED EMISSION: FROM BASIC PRINCIPLES TO APPLICATIONS

Paul Dumas
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paul.dumas@synchrotron-soleil.fr

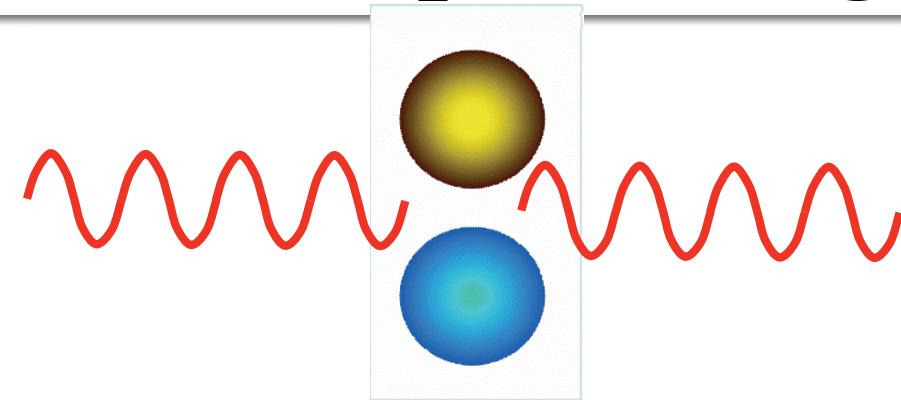
THE ELECTROMAGNETIC SPECTRUM

$$E \text{ (keV)} = 12.3985/\lambda \text{ (\AA)}$$

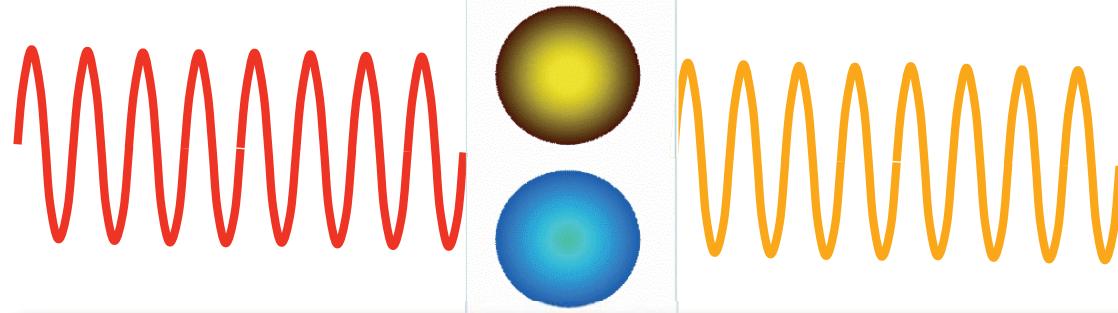


All matters, atoms, molecules and all kind of substances vibrate . Only at absolute zero temperature (-273.15 °C or -459.67°F), that all stop vibrating.

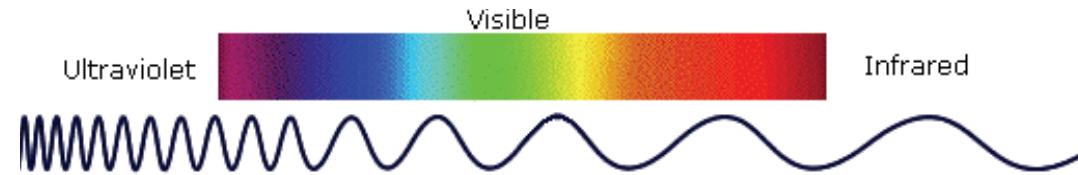
No resonance



Resonance



IT IS AN ABSORPTION PROCESS

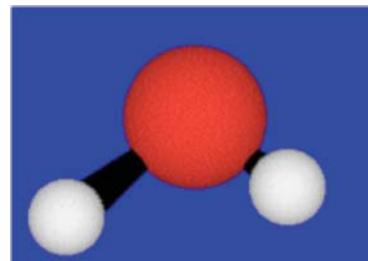


✓ Energy range: 1 to ~500 μm
(10000 to 20 cm⁻¹ or 1.23 to 0.0025 eV)

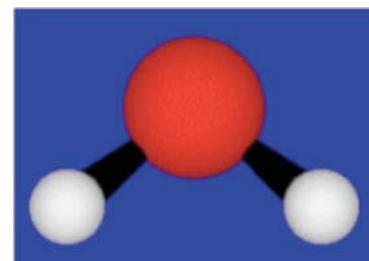
- ✓ ~1 to ~2.5 μm (10000-4000 cm⁻¹) Near IR
- ✓ ~2.5 à 20 μm (4000-500 cm⁻¹) Mid- IR
- ✓ ~20 à ~2500 μm (500-50 cm⁻¹) Far IR

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

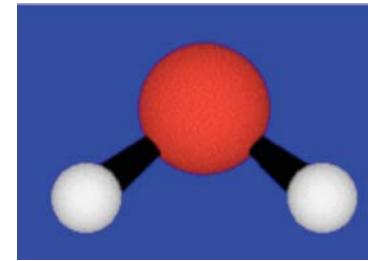
$\sim 3.3 \mu\text{m}$



3756 cm^{-1}

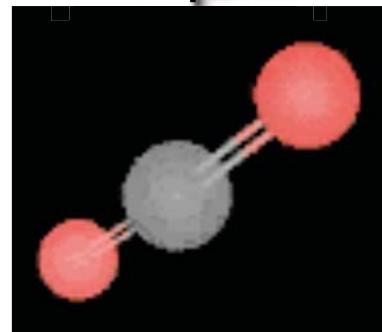


3652 cm^{-1}

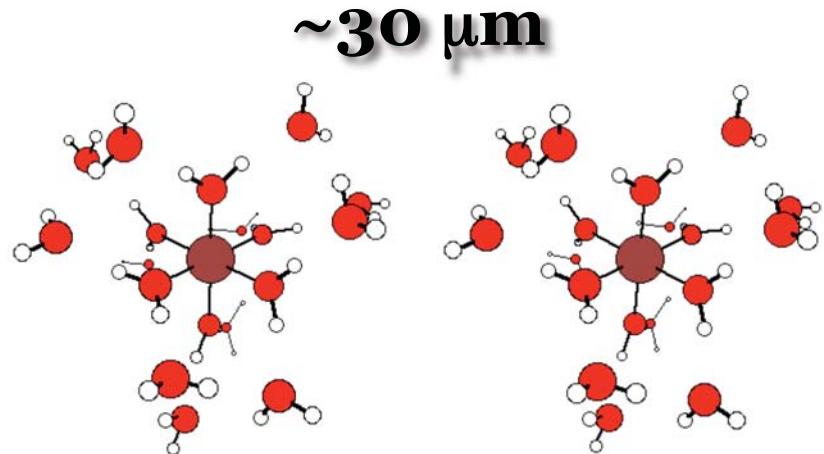
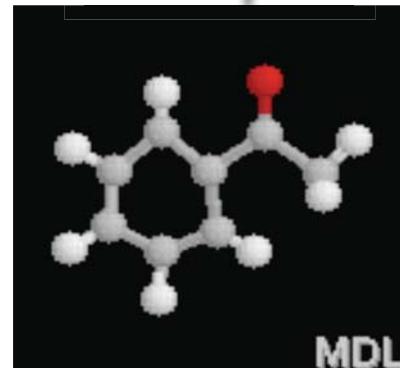


1595 cm^{-1}

$\sim 6 \mu\text{m}$



$\sim 10 \mu\text{m}$



$\sim 30 \mu\text{m}$

But also IR reflectivity and conductivity
(broadband change)

I- Infrared Spectroscopy , Infrared micro-spectroscopy

II- Infrared Emission from synchrotron radiation:

- Source of emission
- properties: flux, brightness, polarisation , time structure

III- Infrared Beamlne at synchrotron facilities:

Specificities, design and end stations

IV- Application in the Far-Infrared: Solid State Physics, High resolution gas phase, surface science

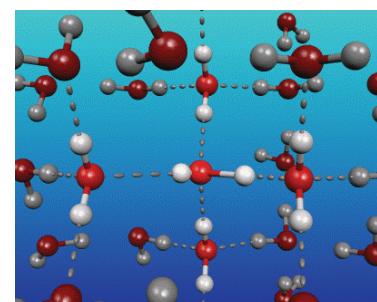
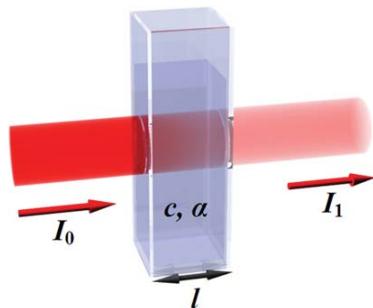
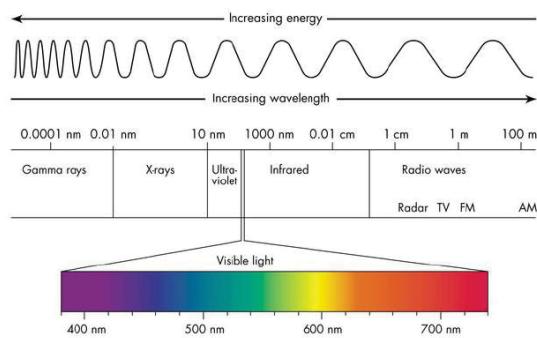
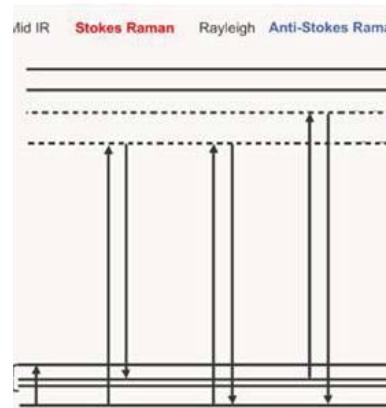
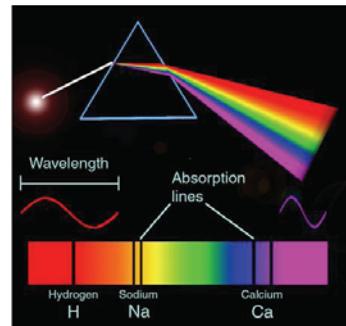
V- Application in Micro-spectroscopy:

- V-1. Polymer
- V-2. Astrophysique
- V-3. Cultural Heritage
- V-4. Earth Science
- V-5. Very High Pressure
- V-6. Biology

INFRARED SPECTROSCOPY

INFRARED MICRO-SPECTROSCOPY

INFRARED SPECTROSCOPY: BASICS



INFRARED (IR) SPECTROSCOPY

○ OPTICAL SPECTROSCOPY

- **MID-IR l: 2,5-25 μm**
- **NEAR-IR l: 0,8-2,5 μm**
- **FAR IR l: 25-200 μm**

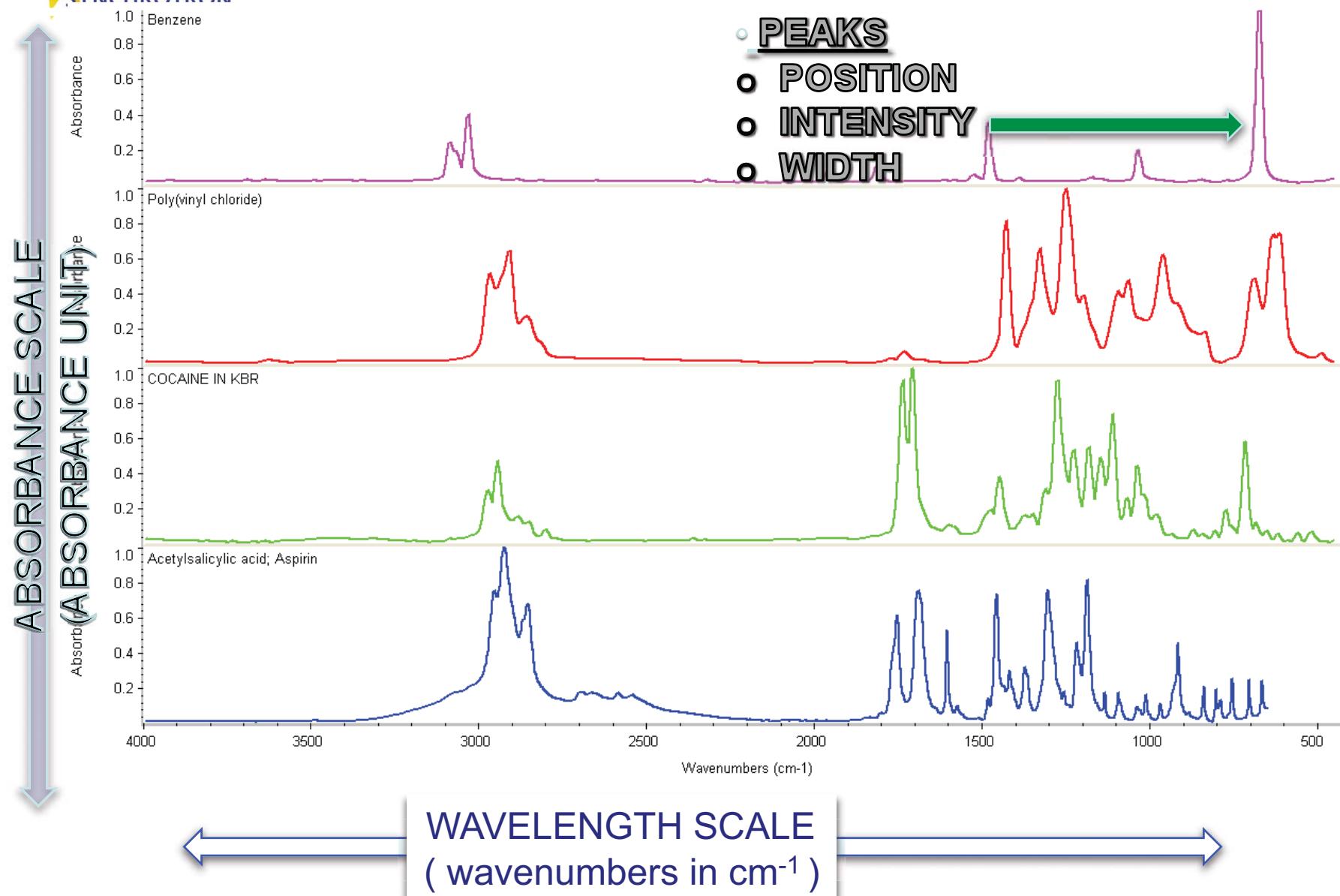
○ ABSORPTION SPECTROSCOPY

- $A=\alpha c l$
- $A=-\log(I/I_0)$

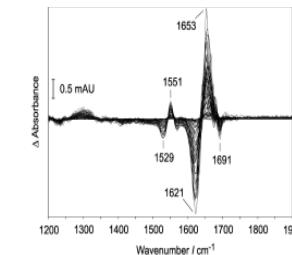
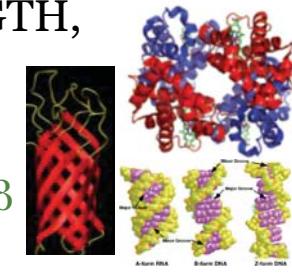
○ VIBRATIONAL SPECTROSCOPY

- **PROBES the VIBRATIONS of INTER-ATOMIC BONDS**

INFRARED SPECTRA: EXAMPLES

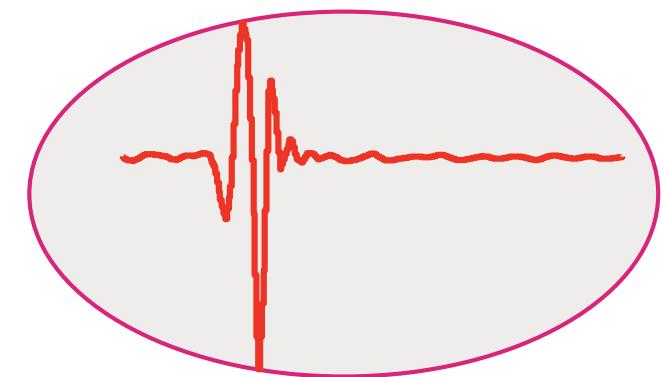
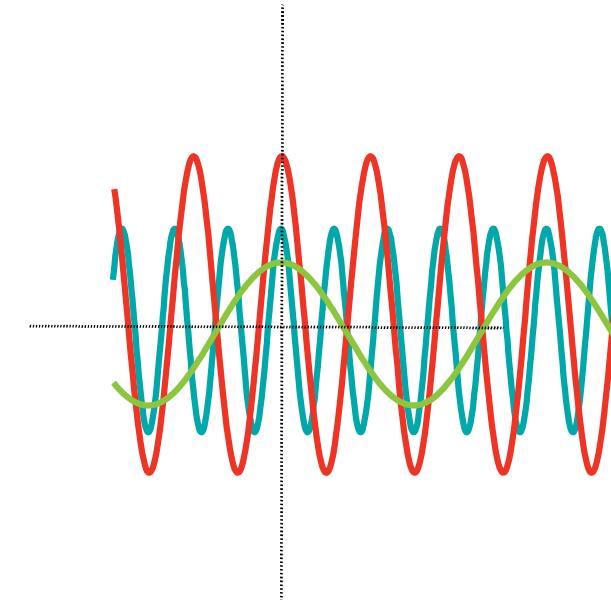
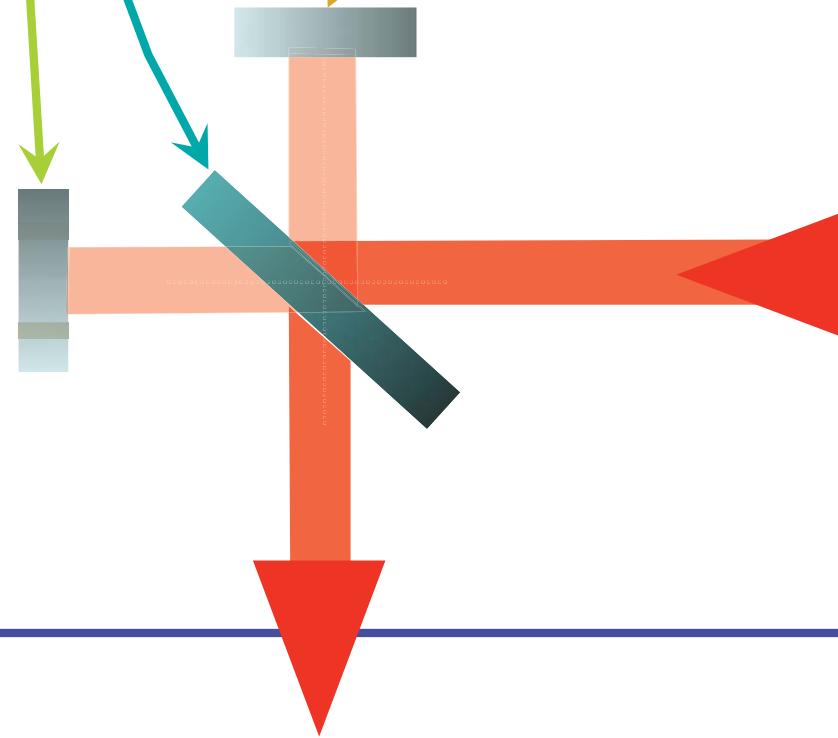
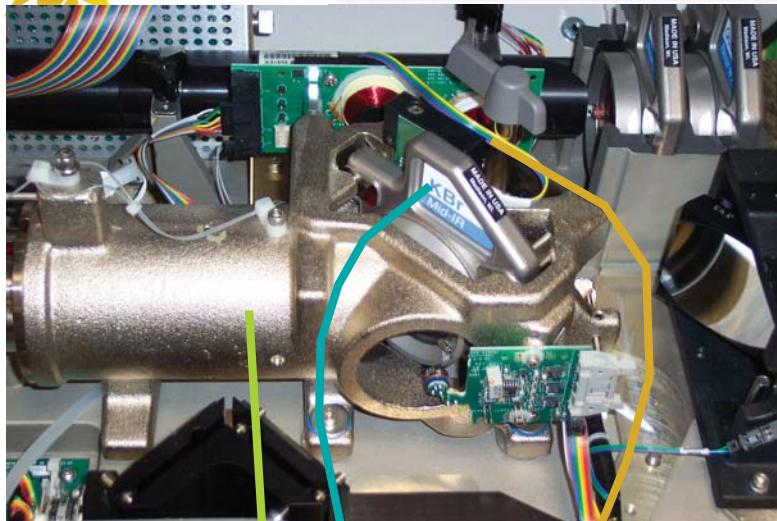


- FROM PEAK POSITION, INTENSITY AND WIDTH
 - NATURE OF THE ATOMIC BOND
 - PARAMETERS OF THE ATOMIC BOND : BOND STRENGTH, LENGTH, VIBRATION FREQUENCY
 - CHEMICAL ENVIRONMENT, CHEMICAL MOIETY
 - BOND CONFORMATION: C=C CIS/TRANS, PROTEINS α HELIX / β SHEET, A, B, Z DNA ...
- FROM WHOLE SPECTRUM
 - NATURE OF THE MOLECULE: SPECTRAL FINGERPRINT=> IDENTIFICATION IN SPECTRAL DATABASE
 - SAMPLE INTERACTIONS: FREE/BOUNDED WATER ...
 - SAMPLE EVOLUTION: REACTION KINETIC, AGING, PHYSICO CHEMICAL TREATMENT, CONSTRAINTS (PRESSURE, STRETCHING, TEMPERATURE, pH) ...
 - ATOMIC BOND ORIENTATION: POLARIZATION MEASUREMENT
- QUANTITATIVE or SEMI-QUANTITATIVE ANALYSIS
 - SIMPLE MIXTURES: BEER LAMBERT BOUGUER LAW
 - COMPLEX MIXTURE : PLS, CLS, ALS, MCR, PCR ...

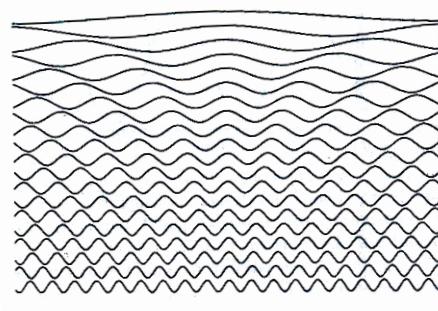
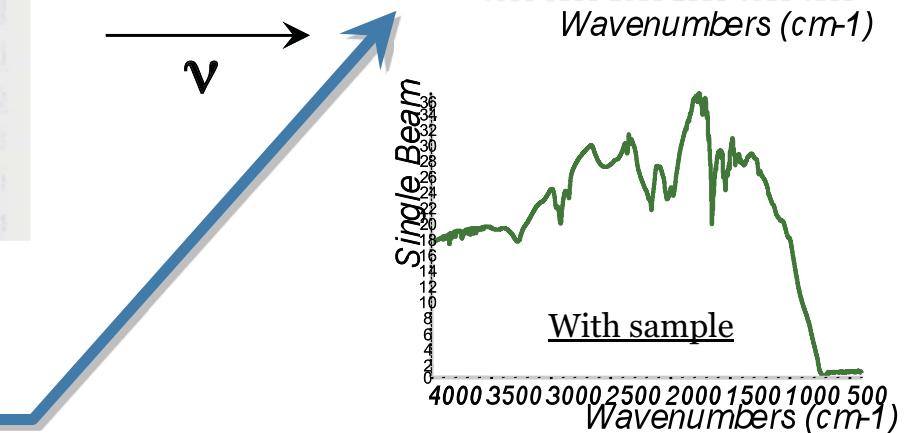
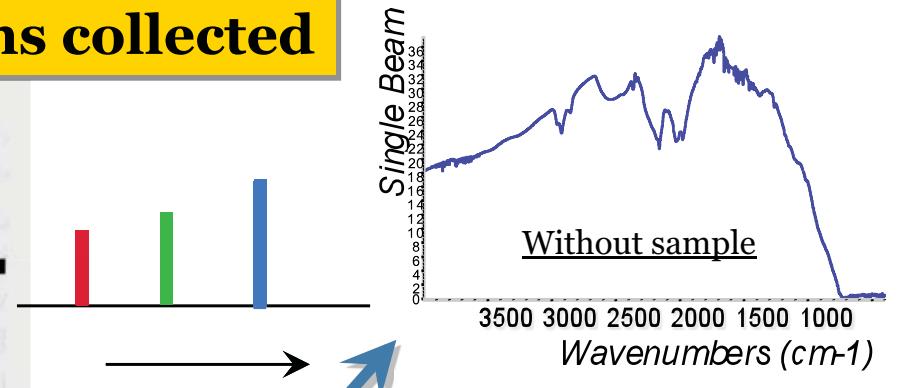
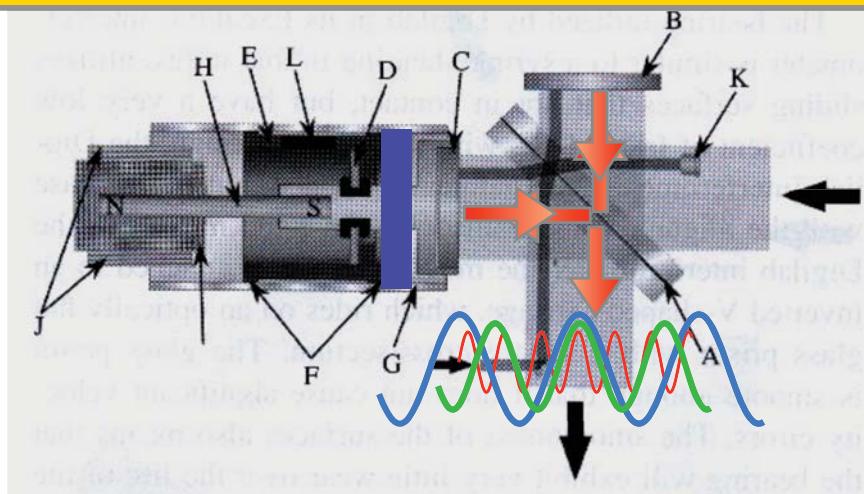




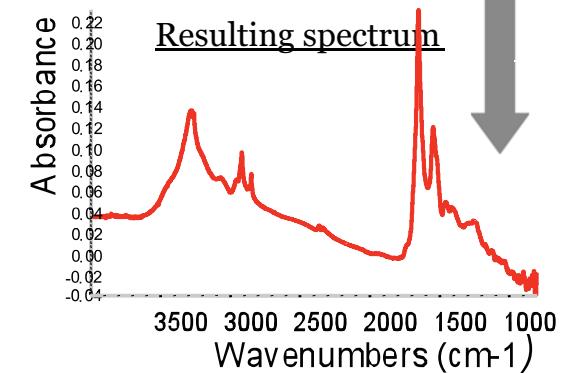
FOURIER TRANSFORM INFRARED SPECTROSCOPY



No monochromator, all wavelengths collected



Fast Fourier Transform



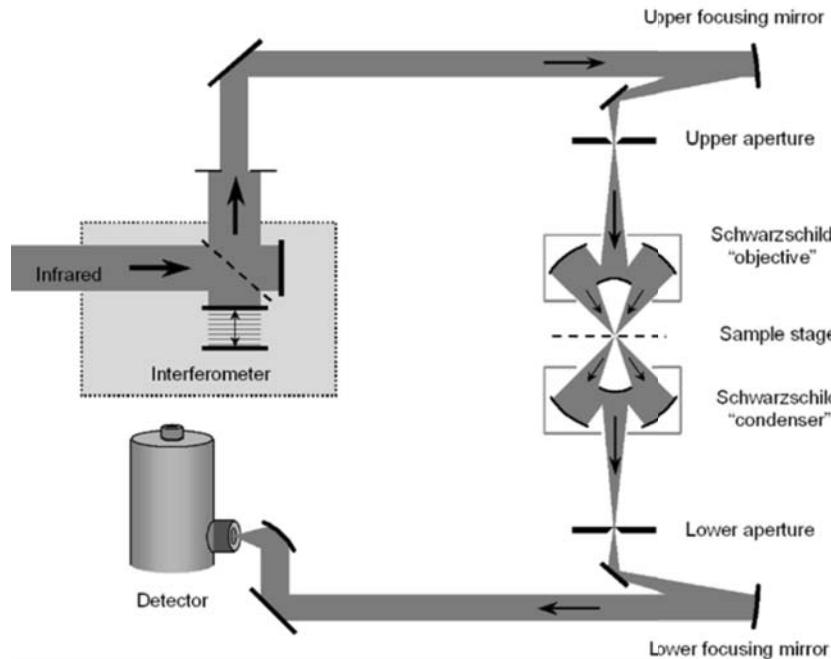
ADVANTAGES

- SIMPLE
- CHEAP
- NON-DESTRUCTIVE
- COUPLING WITH OTHER TECHNIQUES
- QUICK
- SENSITIVE
- FLEXIBLE: SOLIDS, LIQUIDS, POWDERS, THIN FILMS, GAZ ...

APPLICATIONS

- ASTROPHYSICS
- BIOLOGY
- PLANT BIOLOGY
- CHEMISTRY
- GEOLOGY
- HERITAGE SCIENCE
- PHARMACEUTICS
- PHYSICS
- POLYMERS
- SURFACE SCIENCES
- ...

- MICROSCOPE COUPLED TO IR SPECTROMETER

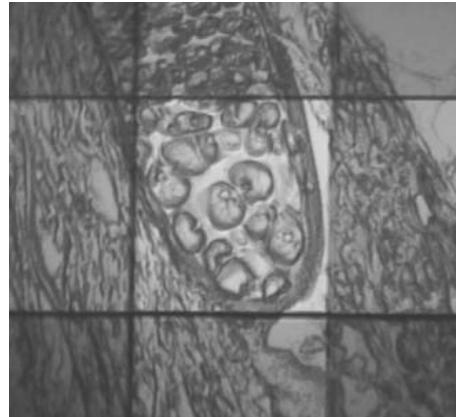


- SMALL SAMPLE ANALYSIS ($<500 \mu\text{m}$, even $< 5 \mu\text{m}$ with synchrotron)
- ANALYSIS OF INCLUSION IN A MATRIX
- DISTRIBUTION OF COMPONENTS : CHEMICAL MAPS

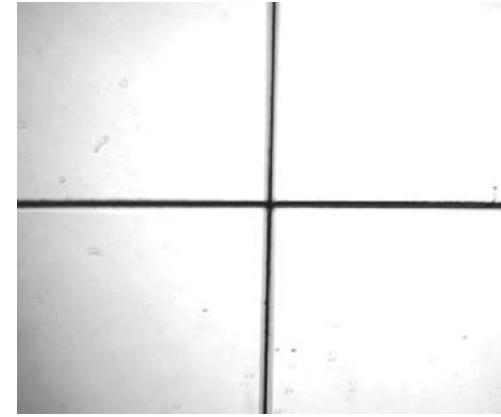
INFRARED MICRO-SPECTROSCOPY AND SPATIAL RESOLUTION

- Set by aperture

KNIFE EDGE APERTURE



open



close

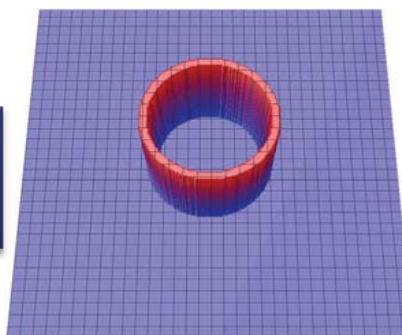
- Dual aperturing improves resolution...

INFRARED MICRO-SPECTROSCOPY AND SPATIAL RESOLUTION

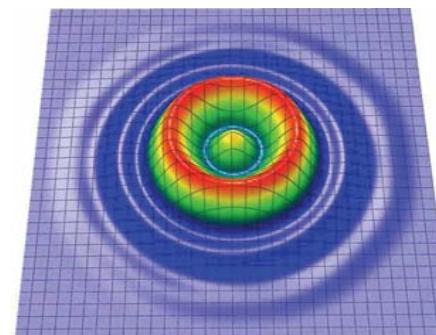
- MINIMUM DISTANCE BETWEEN TWO INDEPENDENTLY MEASURED OBJECTS THAT CAN BE DISTINGUISHED BY THE SPECTRA
- CLASSICAL SOURCE:
 - LIMITED BY SOURCE BRIGHTNESS: 20-500 μm
- SYNCHROTRON SOURCE:
 - DIFFRACTION LIMITED: 2-12 μm

SIMULATION FOR ANNULAR DISK

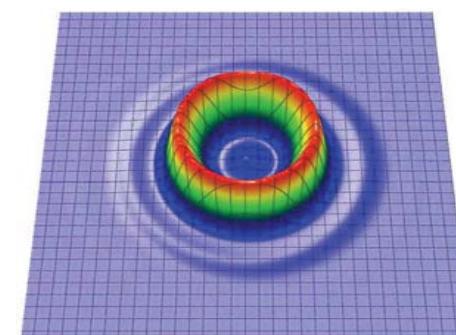
FOR
 $\lambda = 6 \mu\text{m}$



REAL OBJECT
 \varnothing int. 13 μm
 \varnothing ext. 17 μm



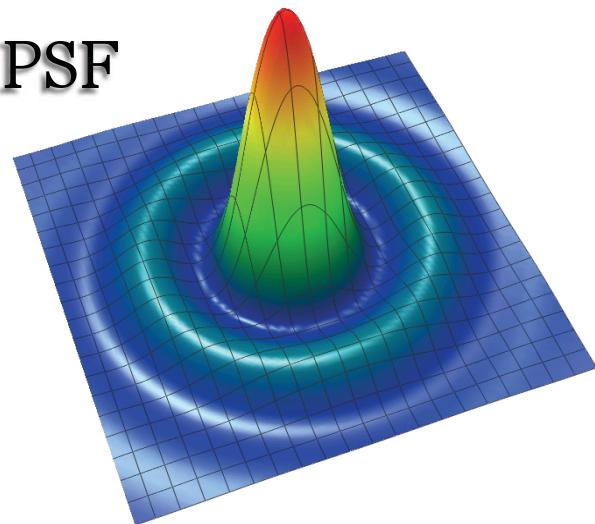
SINGLE APERTURE



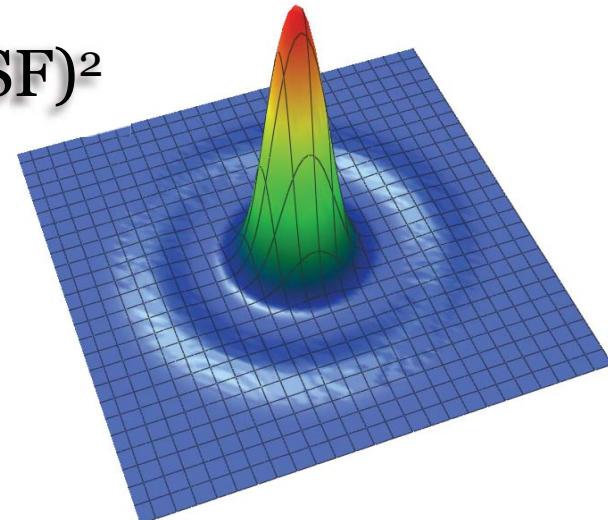
DOUBLE APERTURE

SPATIAL RESOLUTION: CONFOCAL versus NON-CONFOCAL

PSF

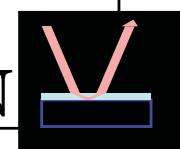
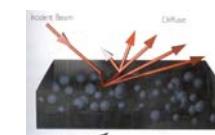


$(PSF)^2$

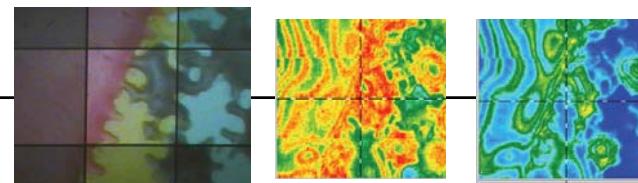
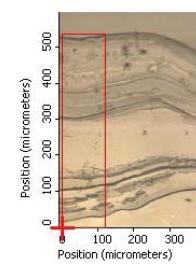
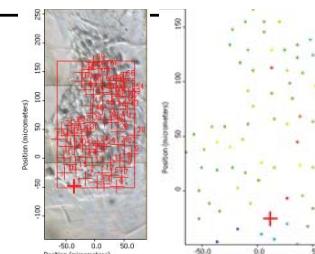


Confocal results in narrower central peaks, and also reduces effect of 1st order diffraction ring.

- TRANSMISSION
- REFLEXION
 - SPECULAR
 - DIFFUSE
 - TOTAL
 - GRAZING INCIDENCE
 - TRANSREFLECTION

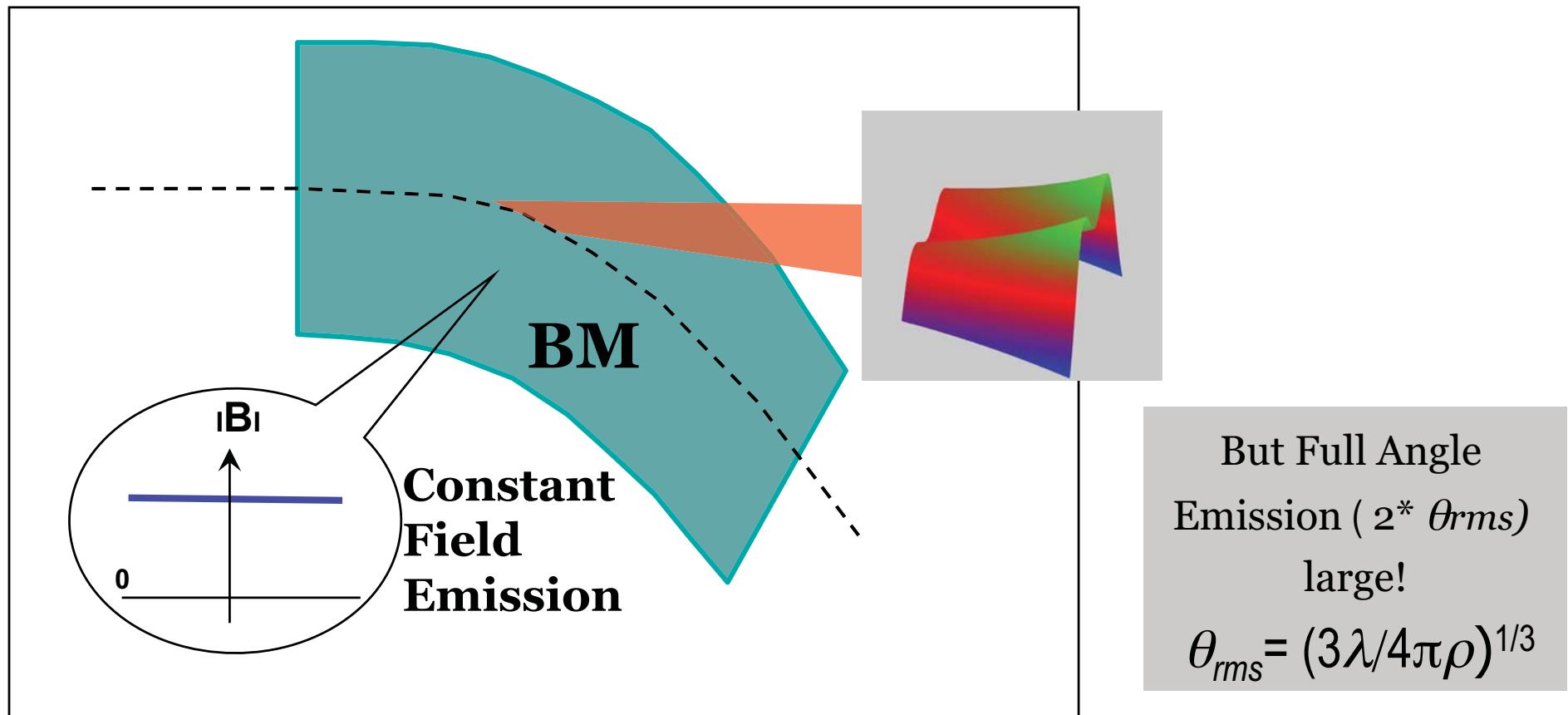


- MAPPING
 - CONFOCAL
 - POINT MAP
 - AREA MAP
- IMAGING
 - SIMULTANEOUS ACQUISITION
 - NO CONFOCALITE



SYNCHROTRON INFRARED EMISSION

The most conventional is a Bending Magnet emission



SRW: Chubar O, Elleaume P. Accurate And Efficient Computation Of Synchrotron Radiation In The Near Field Region. 1998; EPAC98 Conference p. 1177-9.

VERTICAL OPENING ANGLE DEPENDS ON ELECTRON ENERGY

INDUS

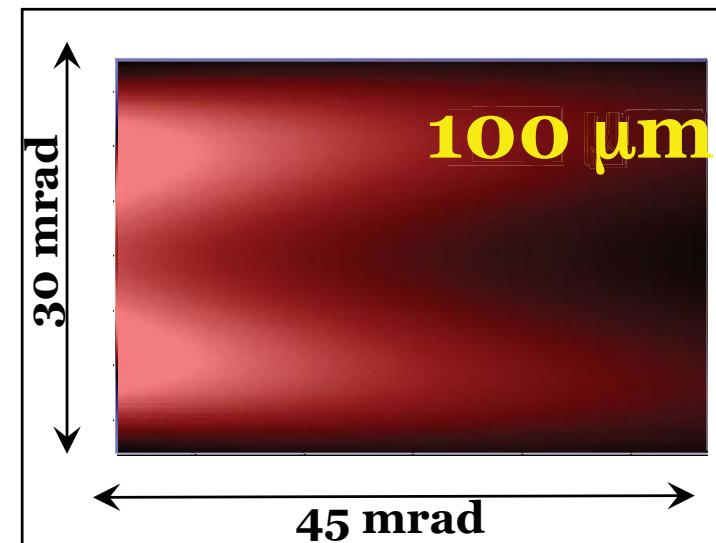
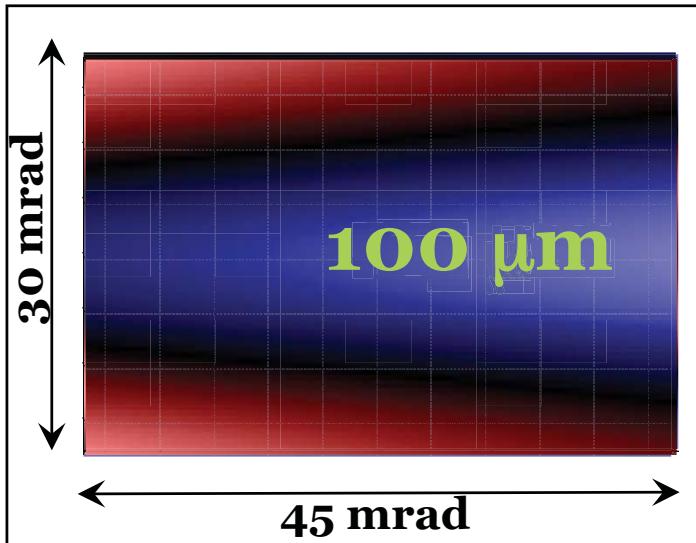
0.45 GeV

**45 mrad H X 30 mrad V
BM**

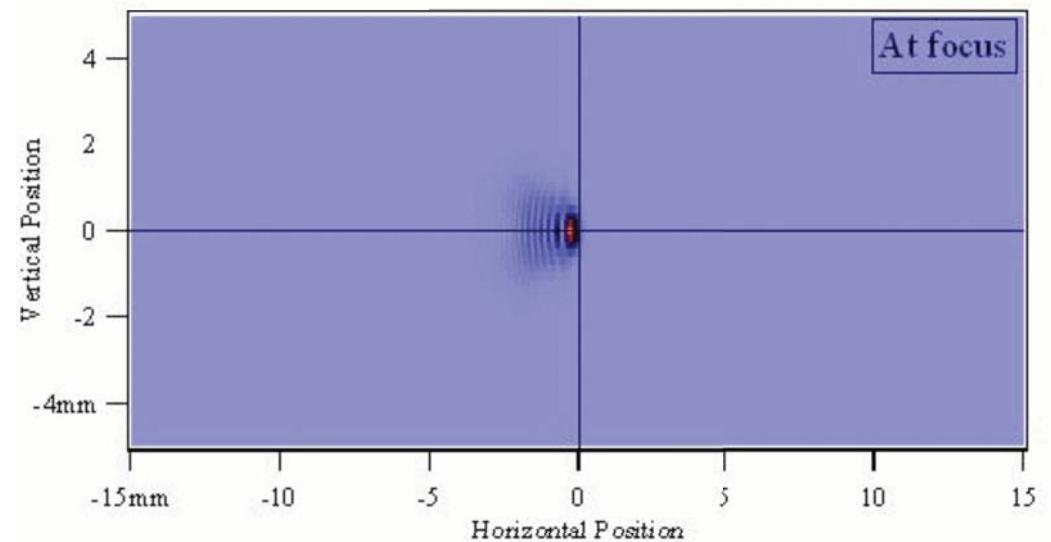
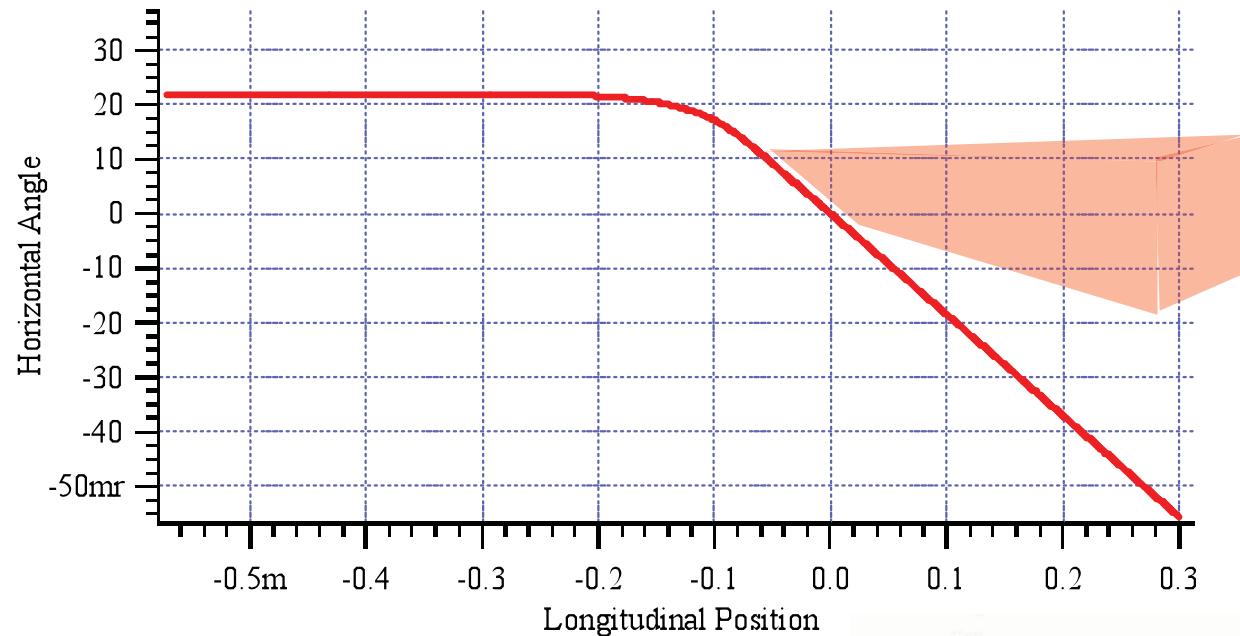
DIAMOND

3.0 GeV

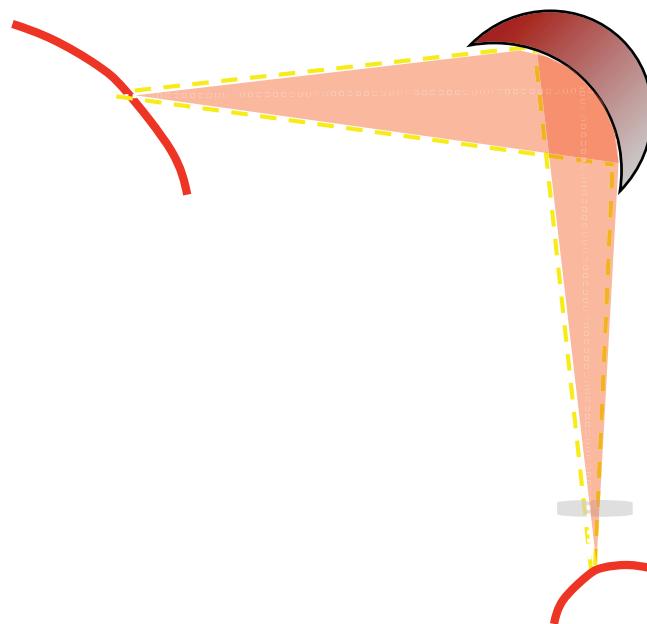
**45 mrad H X 30 mrad V
BM**



BM EMISSION AND SOURCE DEPTH



Most existing options use either an ellipsoid or toroid



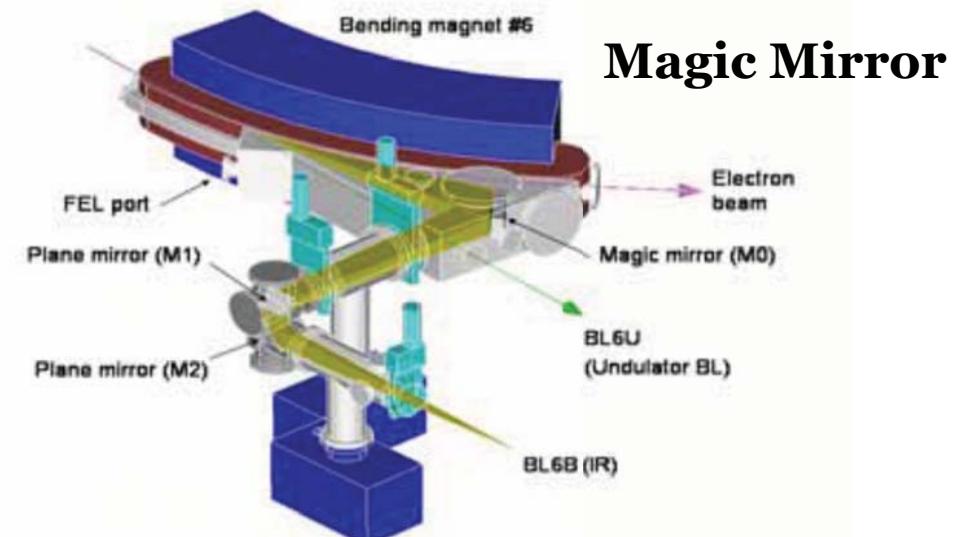
Most traditional optical set up

Front end and optics of infrared beamline at SPring-8

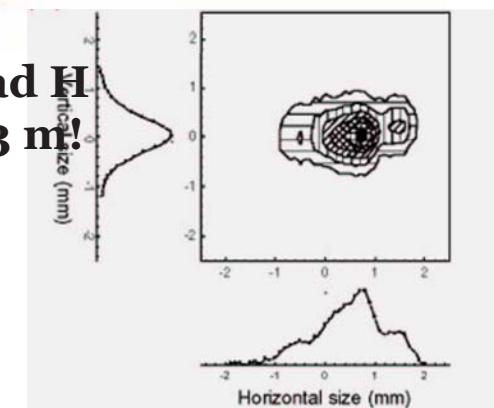
S. Kimura, et al.

NIM in Physics Research A: volume 467-468, part1, 21 July 2001, Pages 437-440

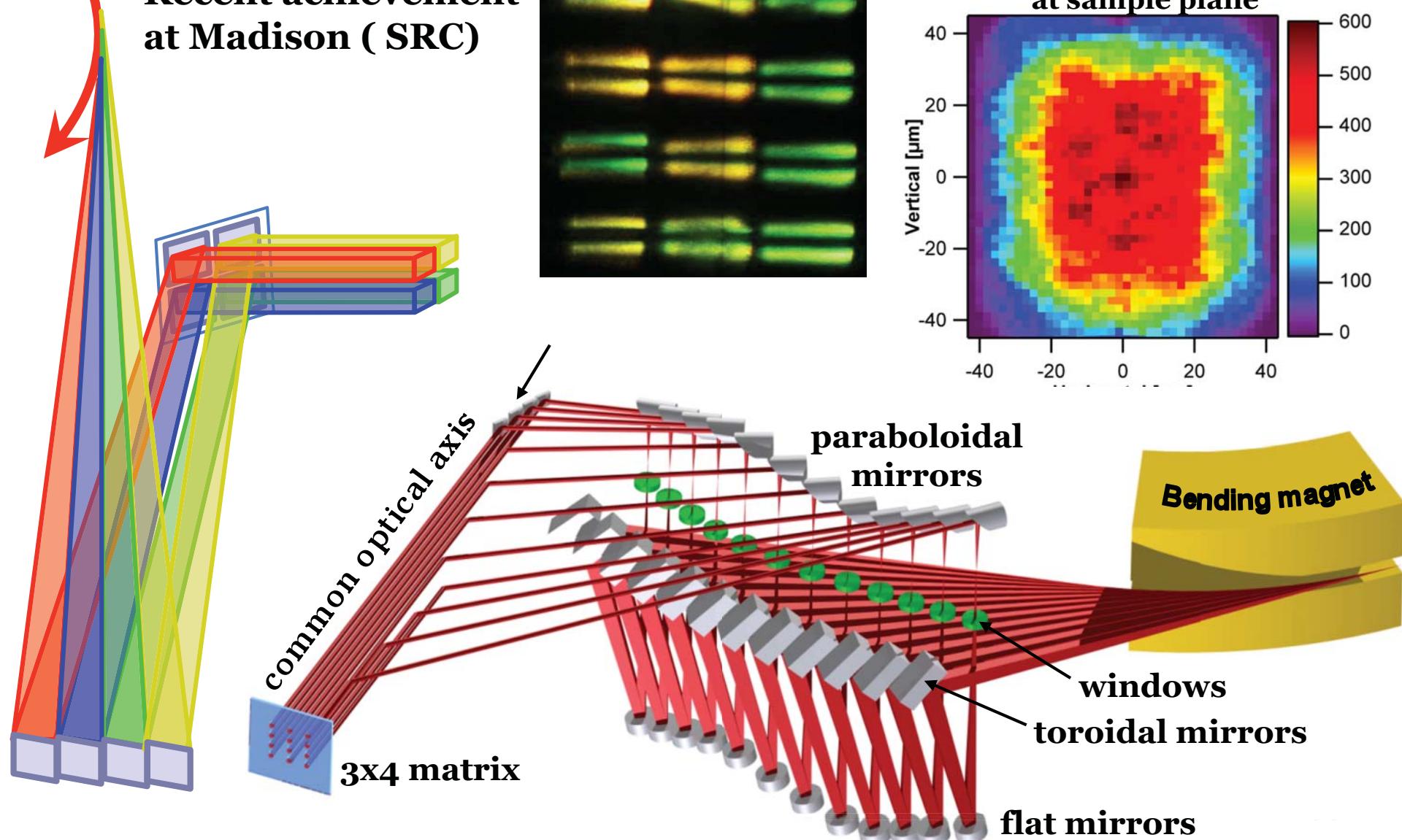
@ Spring-8 and UVSOR



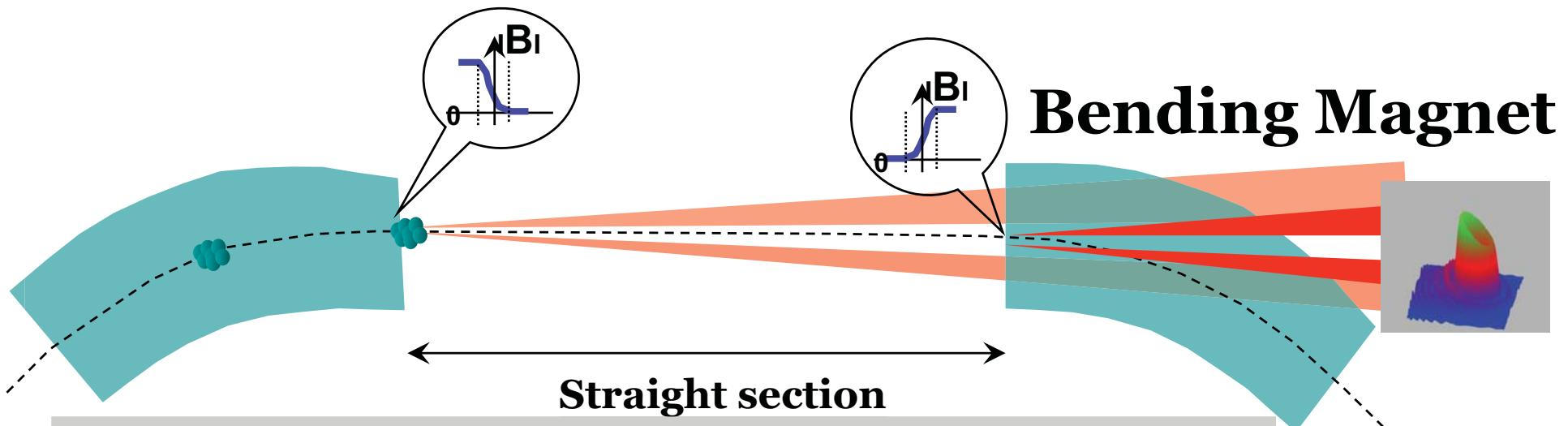
Spring-8=36.5 mrad H
Source depth= 1.43 m!



Recent achievement at Madison (SRC)



Edge radiation was identified as a real potential IR source



- Edge radiation emitted at transitions entering/exiting dipole magnets (two-edge interference, cancellation on-axis).
- Intrinsically bright.
- Radial polarization .
- It is not an extended source!!!

EDGE RADIATION EMISSION IN A NARROWER CONE

SOLEIL

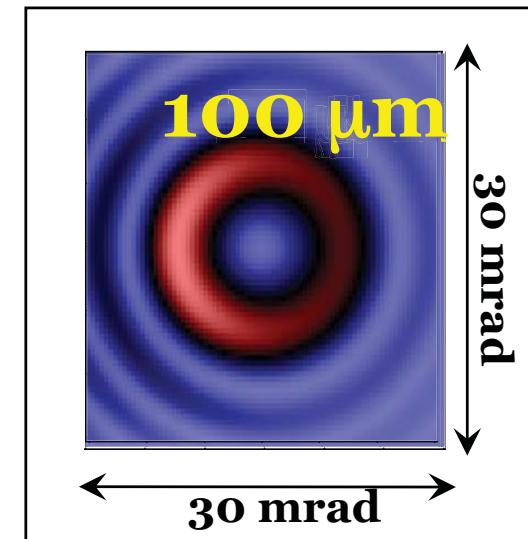
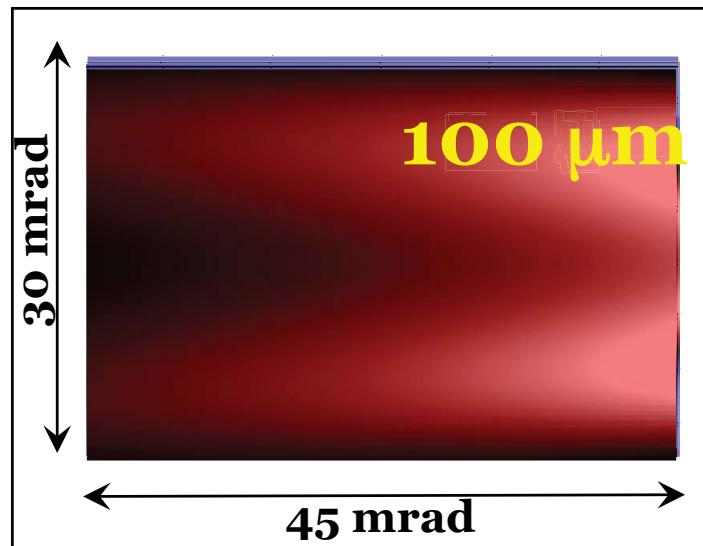
2.75 GeV

**45 mrad H X 30 mrad V
BM**

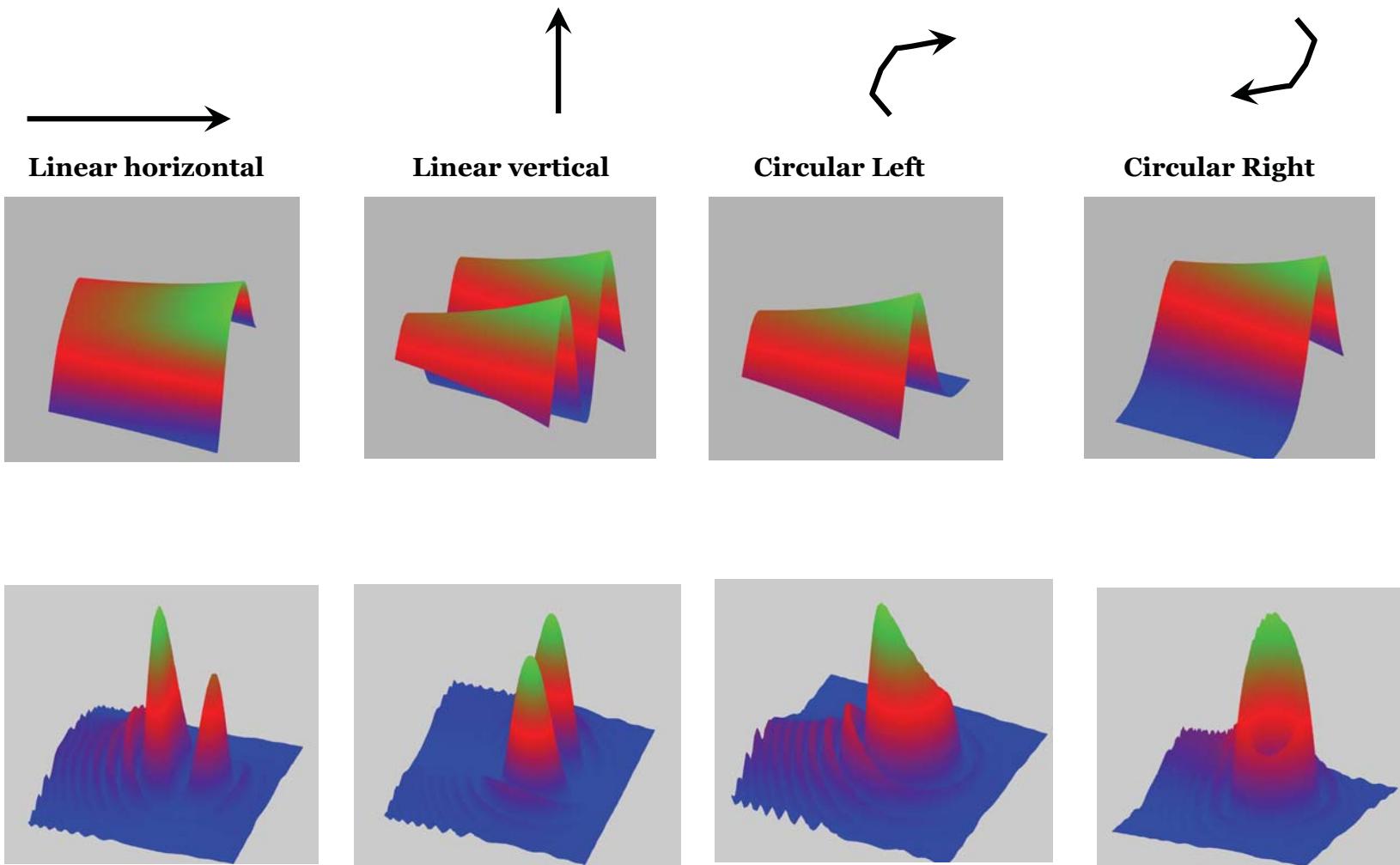
SOLEIL

2.75 GeV

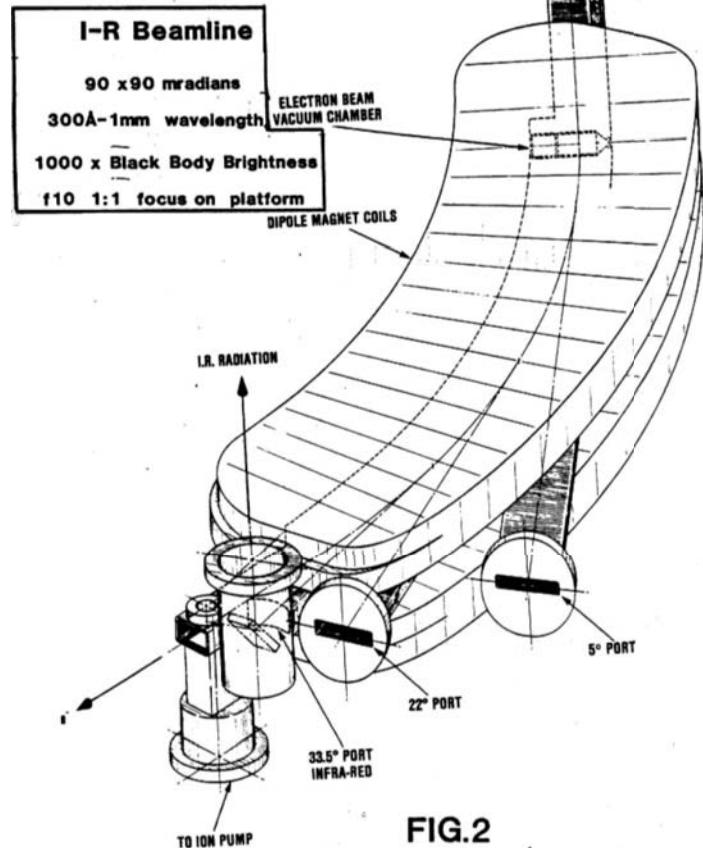
**30 mrad H X 30 mrad V
BM**



ER and BM EMISSION HAVE DIFFERENT POLARISATION PROPERTIES



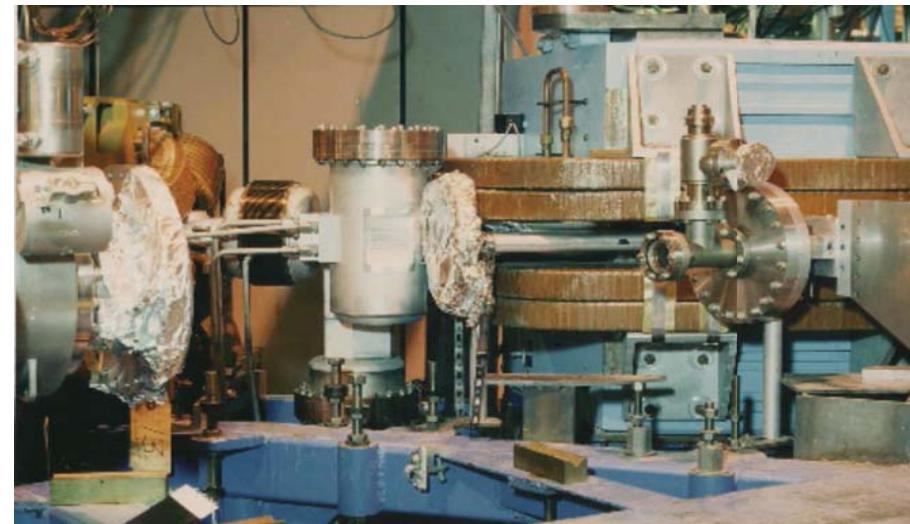
MECHANICAL CHALLENGES: DIPOLE CHAMBERS HAVE TO BE LARGELY MODIFIED



NSLS Phase2 Infra-Red Beam Extraction

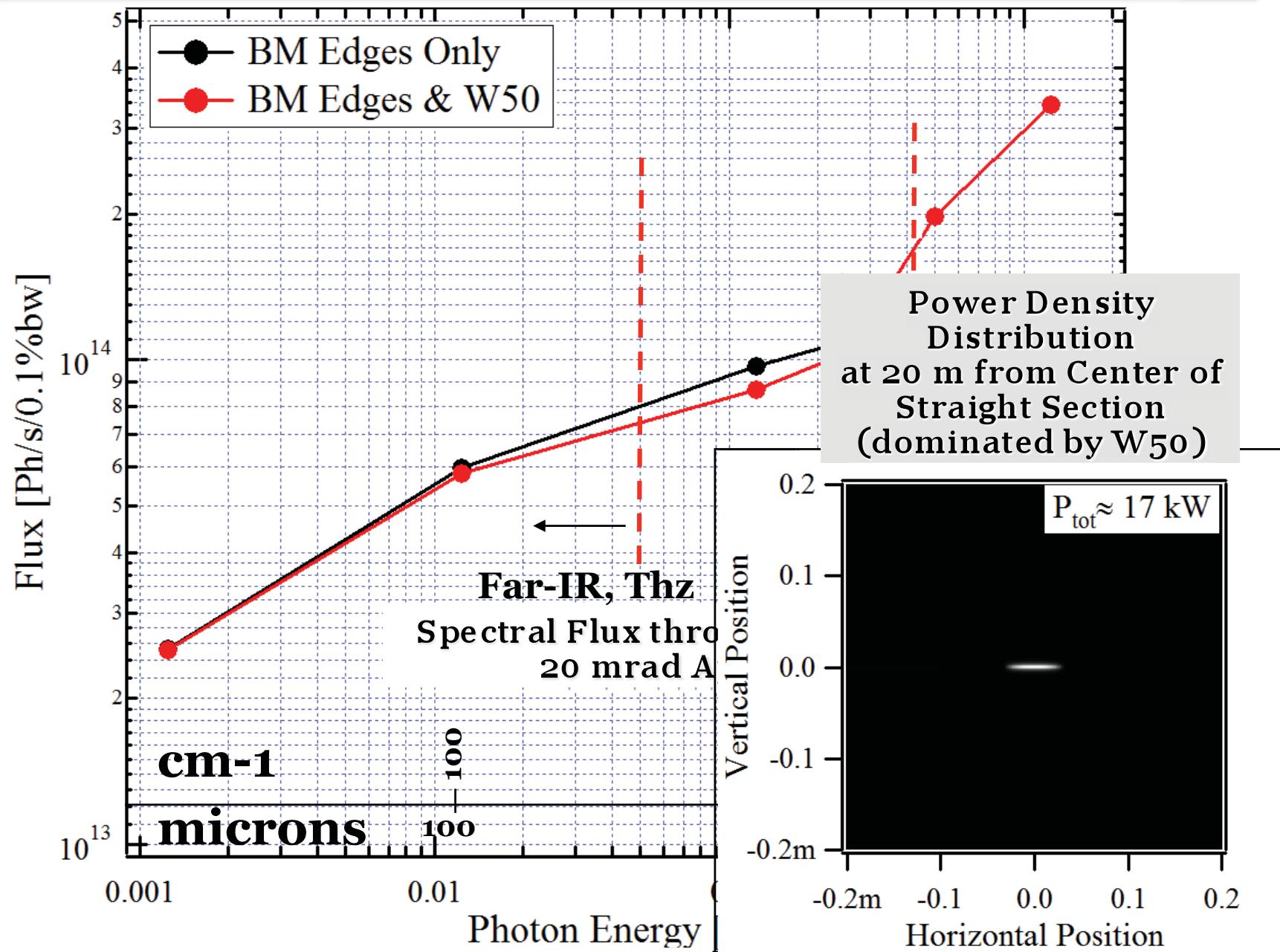
NSLS 90x90 mrad, 1986

E= 0.808 GeV



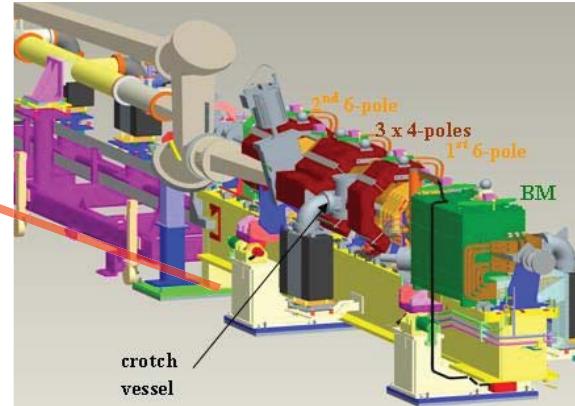


ARE INSERTION DEVICES CANDIDATES FOR HIGHER INFRARED PHOTON PRODUCTION?

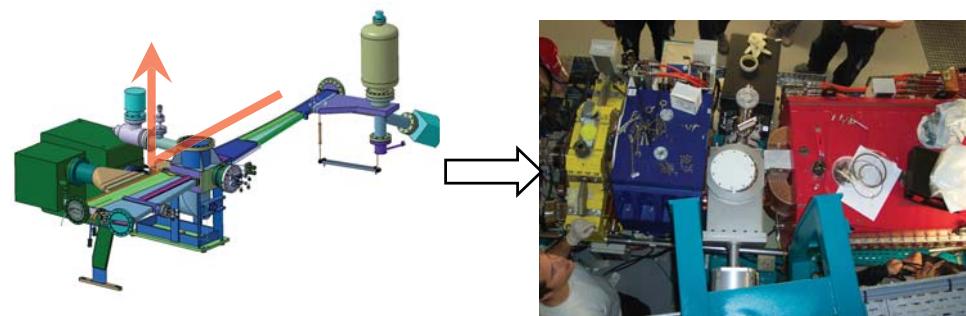


EXTRACTING INFRARED BEAM AT SYNCHROTRON STORAGE RINGS

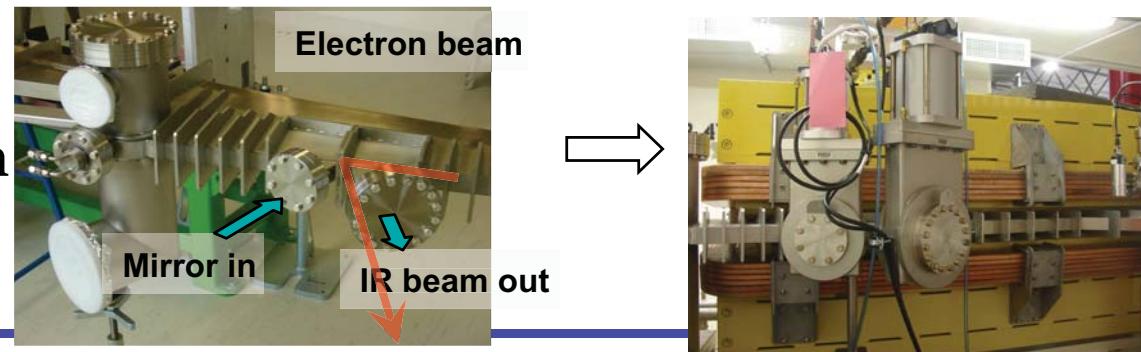
Horizontal extraction
(e.g. DIAMOND)



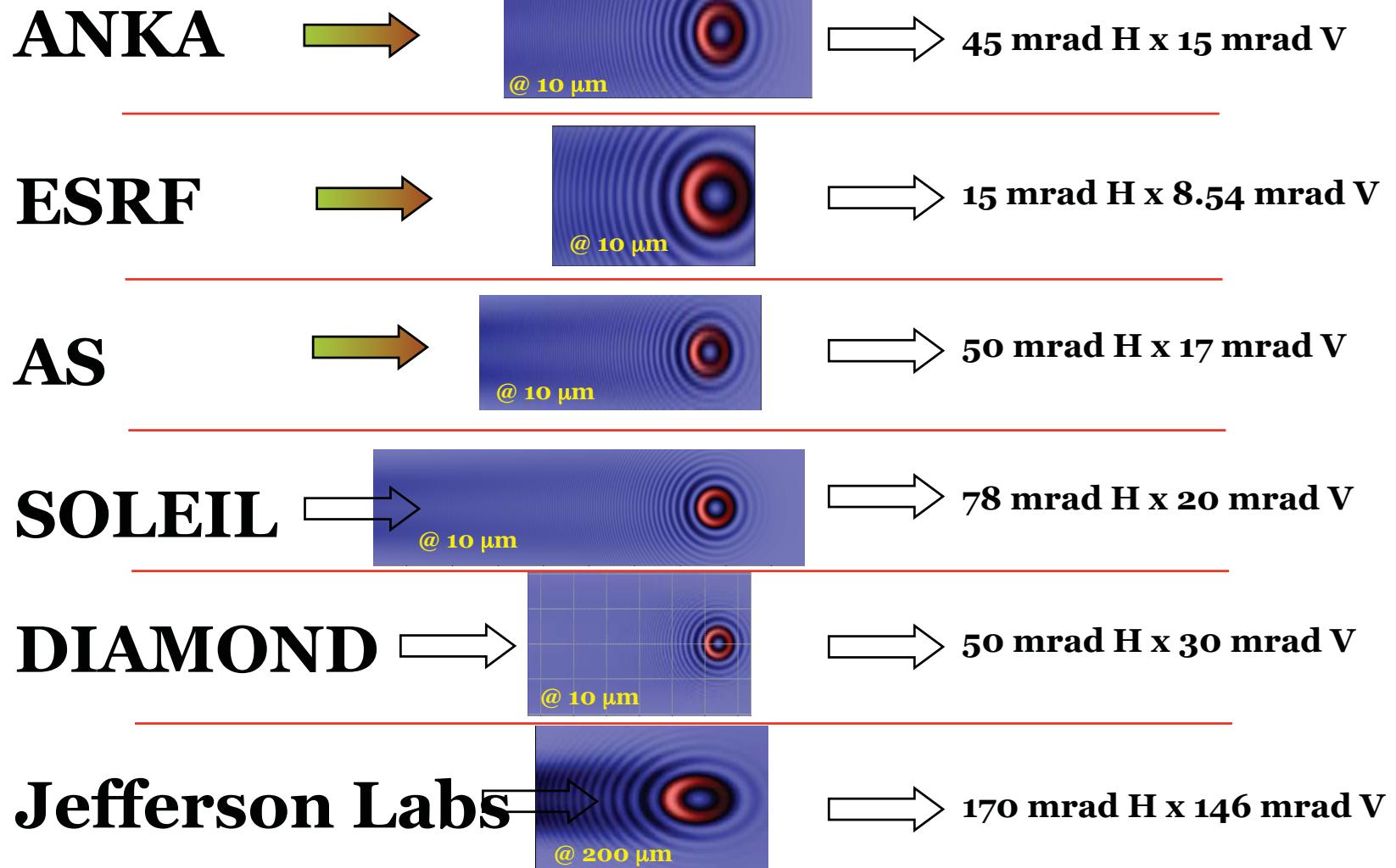
Vertical extraction
(e.g. SOLEIL)



Horizontal extraction
(e.g. AS, ALBA)



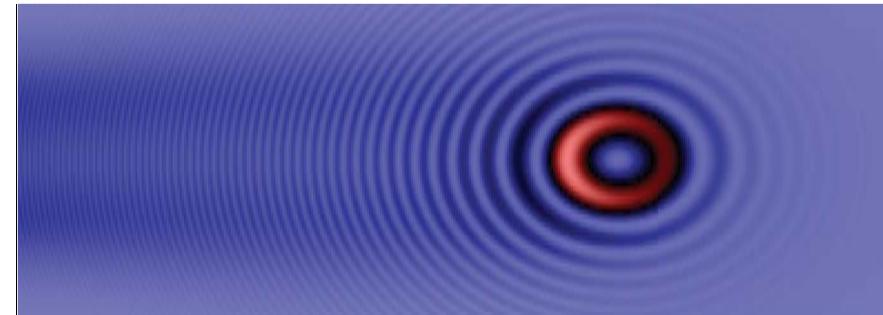
RECENT IR BEAMLINES EXPLOIT BOTH ER and BM



AS WELL AS ONES IN DESIGN STAGE

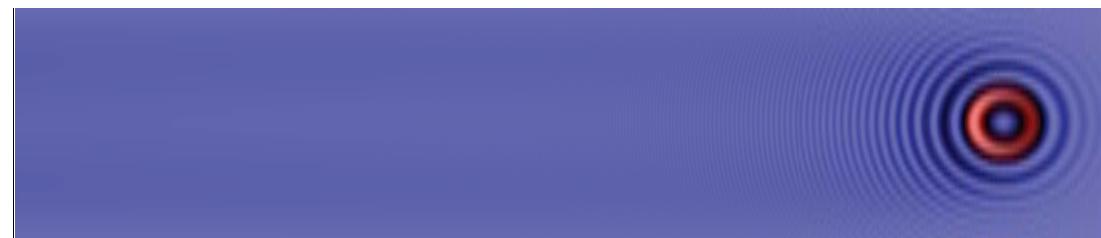
*Facility
(GeV)*

ALBA(3)



43 mrad (H) x 25.17 mrad (V)

SRLI(1.2)

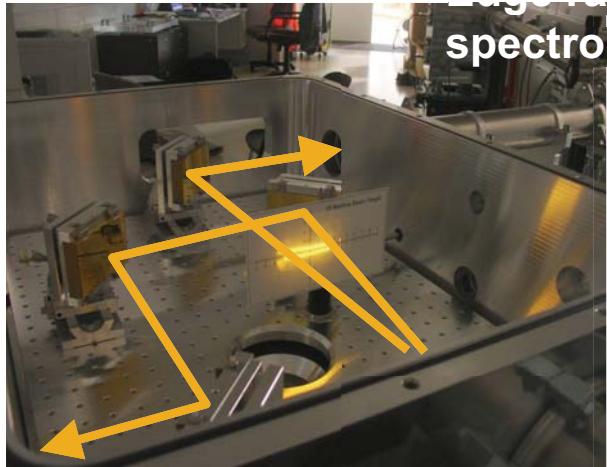


92 mrad (H) x 20 mrad (V)

SESAME (2.5)



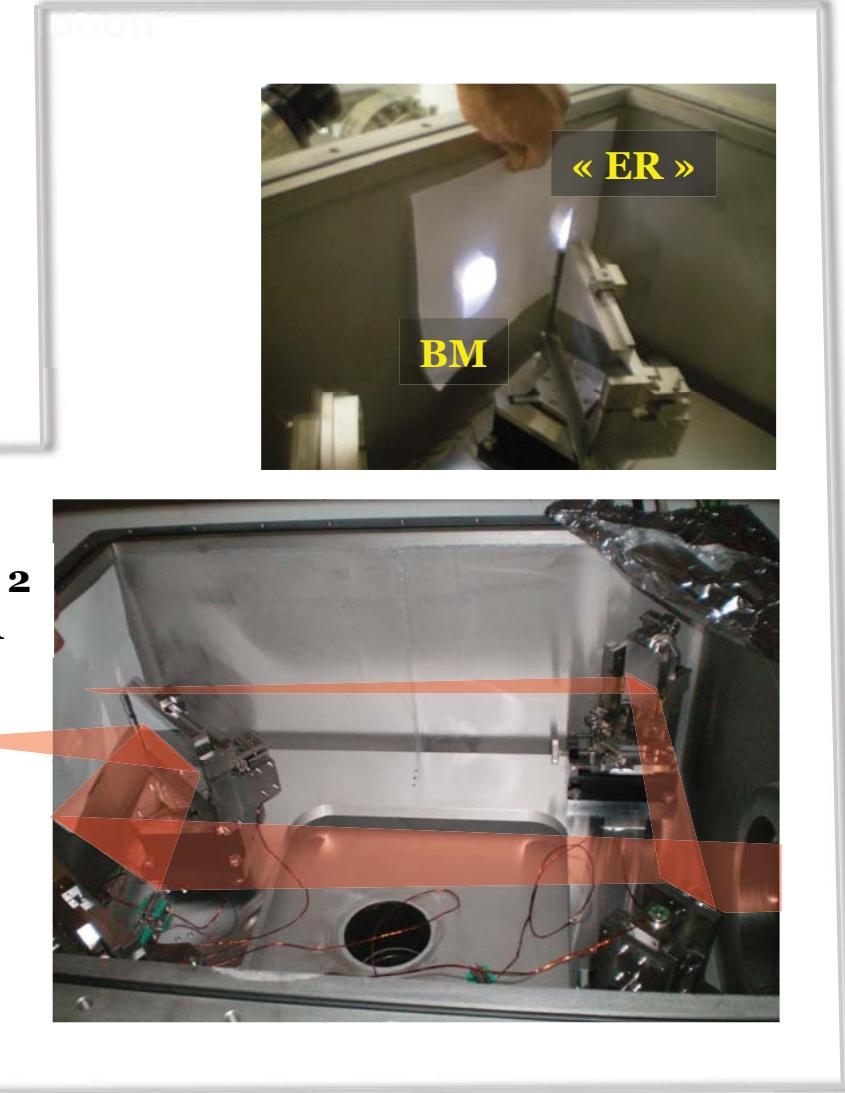
40 mrad (H) x 18 mrad (V)



@ AS

Microscope 2
Branche ER

Microscope 1
Branche BM



@ SOLEIL

CRUCIAL: THE FIRST EXTRACTION MIRROR

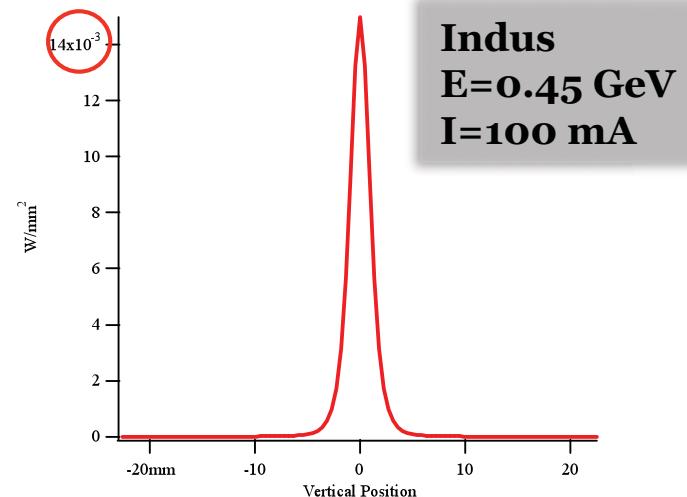
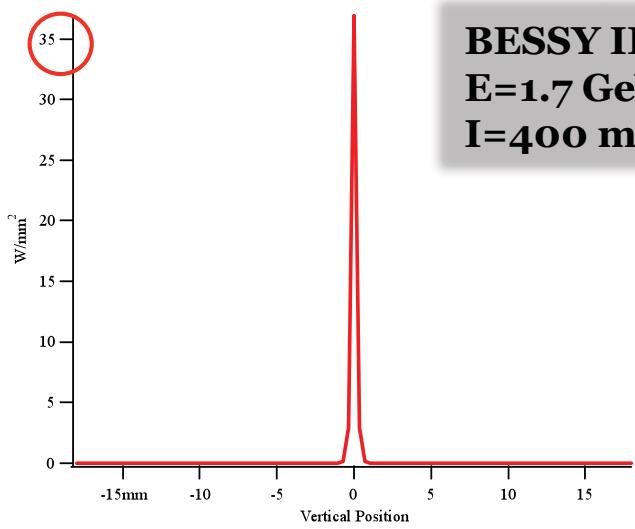
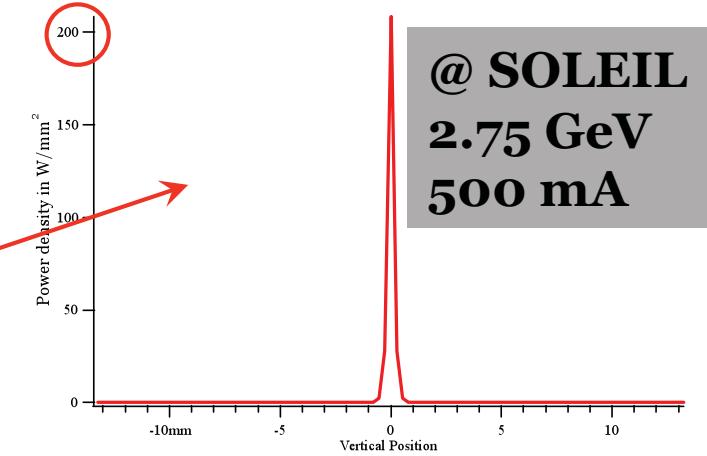
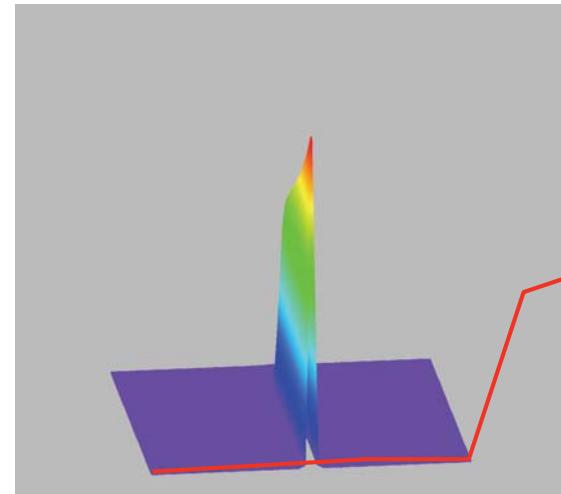
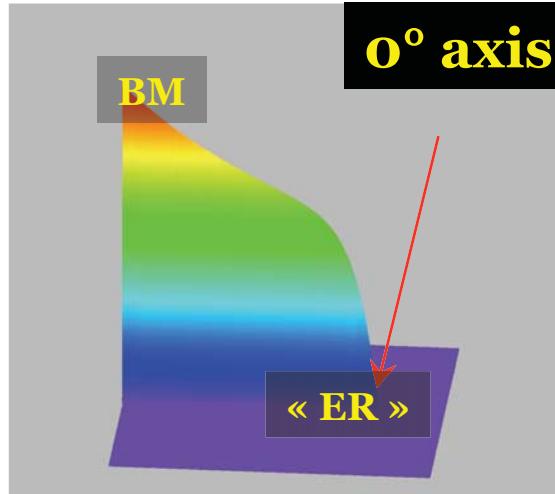


Heat load and cooling issues

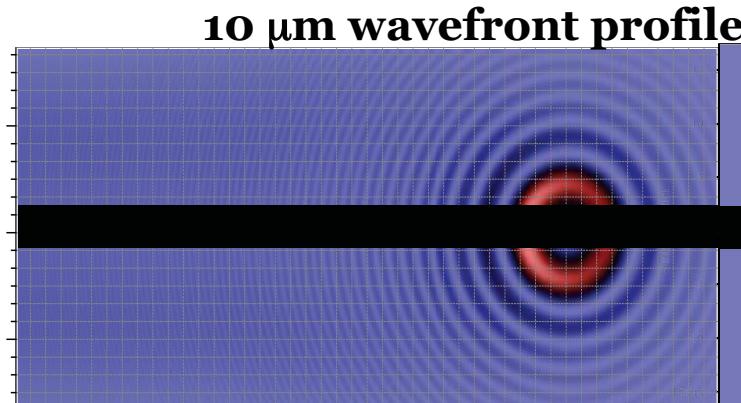
**Precise positioning issues
(and often retraction)**

Blackening issues

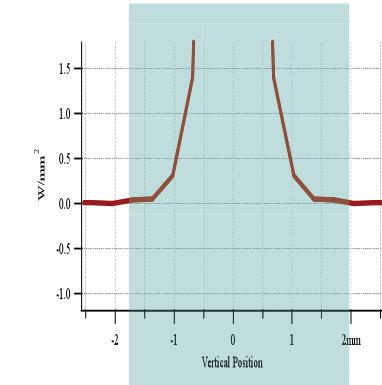
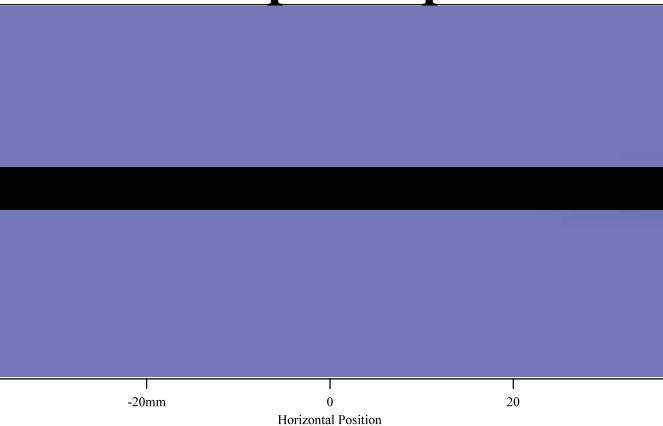
HEAT LOAD AT FIRST EXTRACTION MIRROR



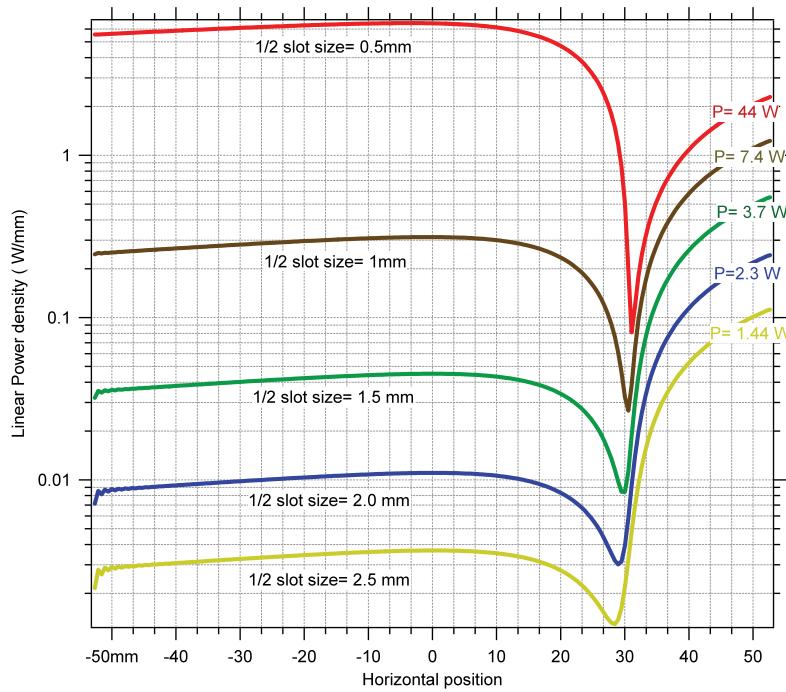
SLOTTED MIRROR



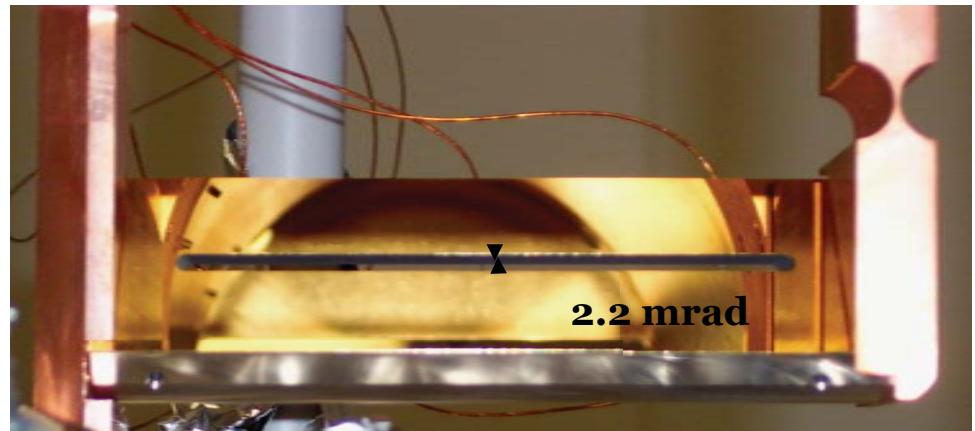
Heat power profile



Heat load on first extracting mirror:

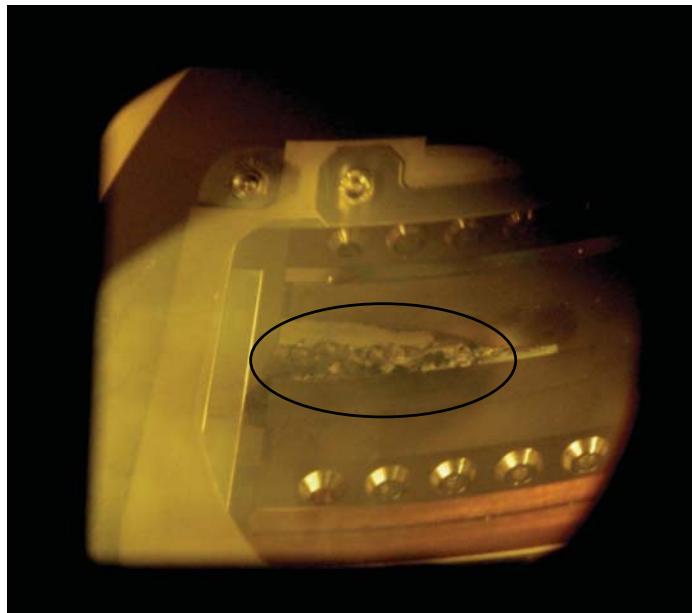


Case at SOLEIL



MIRROR POSITIONNING MUST BE PRECISE AND REPRODUCIBLE

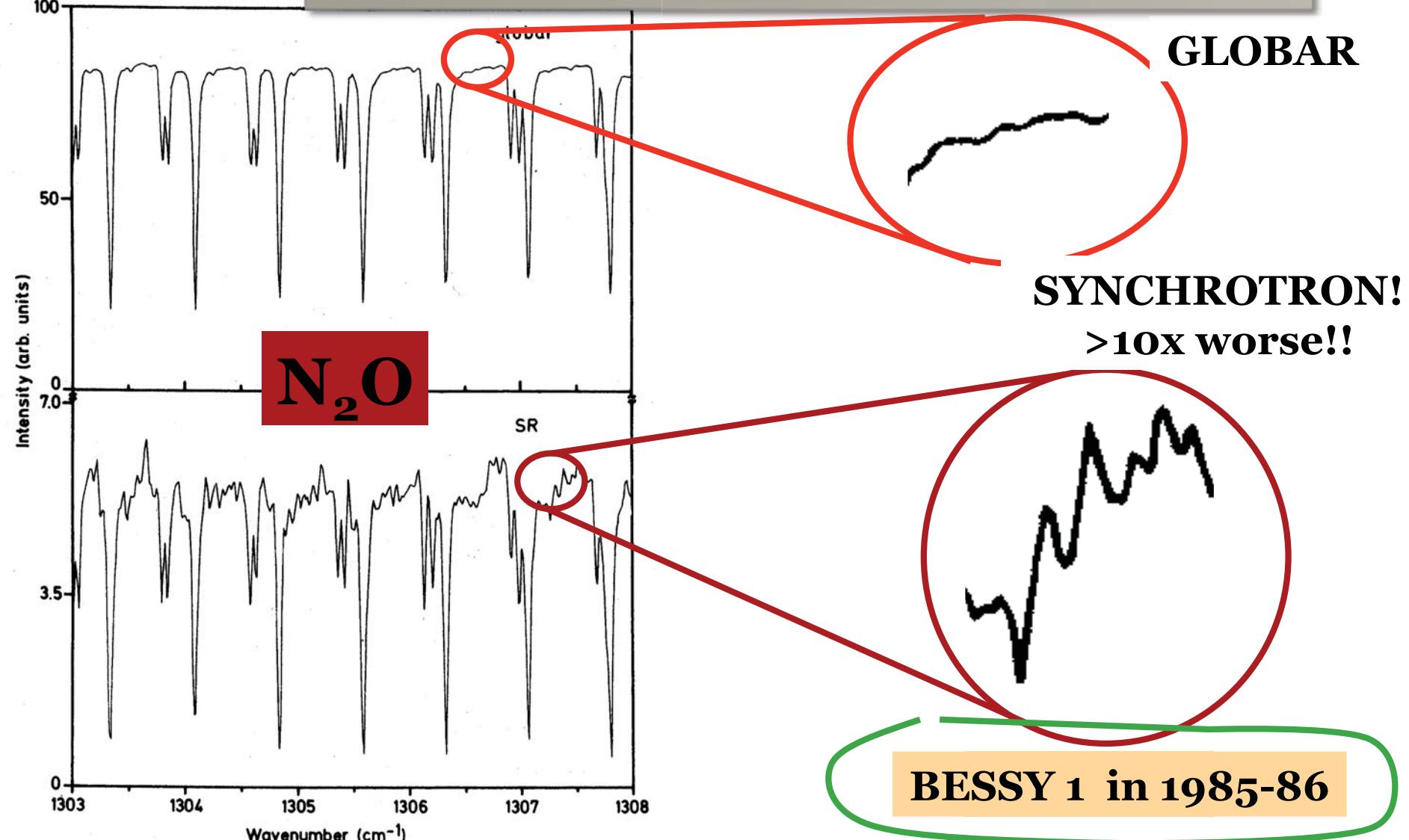
@ SLS



@ SPRING-8

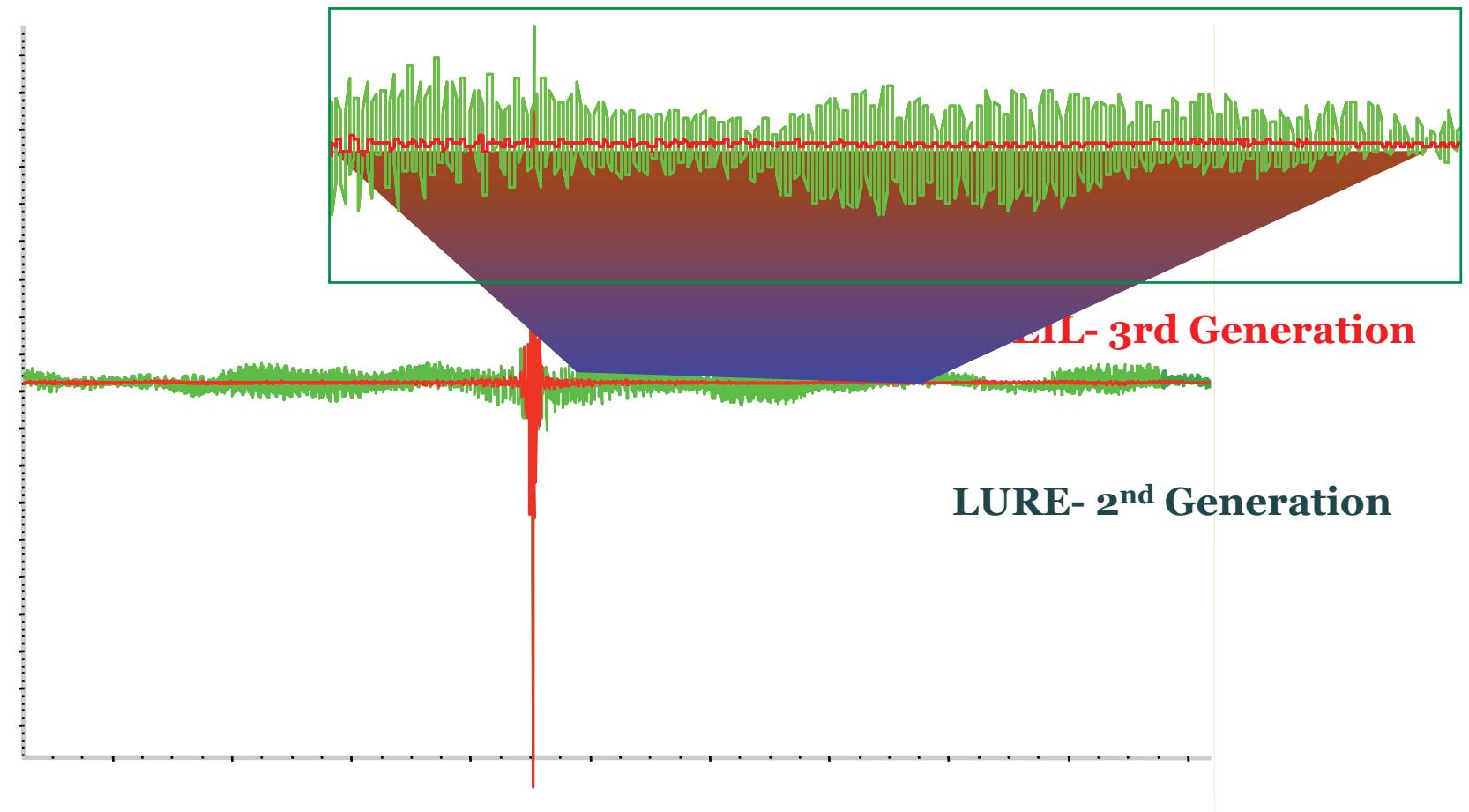


INFRARED EMISSION AND BEAM INSTABILITIES

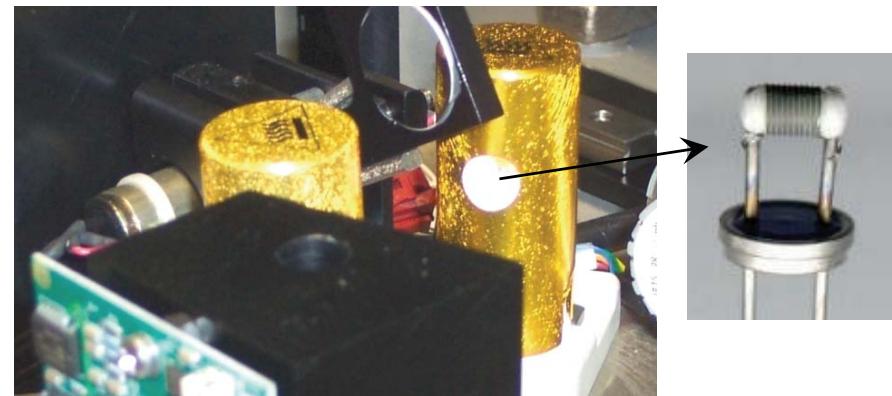


Schweitzer, Nagel, Brain, Lippert and Bradshaw Nucl. Instr. &
Methods A246 163 (1986)

IMPORTANT IMPROVEMENTS WITH THIRD GENERATION SYNCHROTRON FACILITIES



Blackbody radiation



S_{src} The spectral flux emitted by isotropic black-body source into a solid angle $\Omega = 2\pi \sin \theta_r$ (where θ_r is the angular radius of the first optical element of the spectrometer), is:

$$\left(\frac{dW}{d(1/\lambda)} \right)_{BB} \approx \frac{2\pi h c^2 S_{src} \sin \theta_r}{\lambda^3} \left[\exp\left(\frac{hc}{\lambda k_B T}\right) - 1 \right]^{-1}$$

h =Planck constant

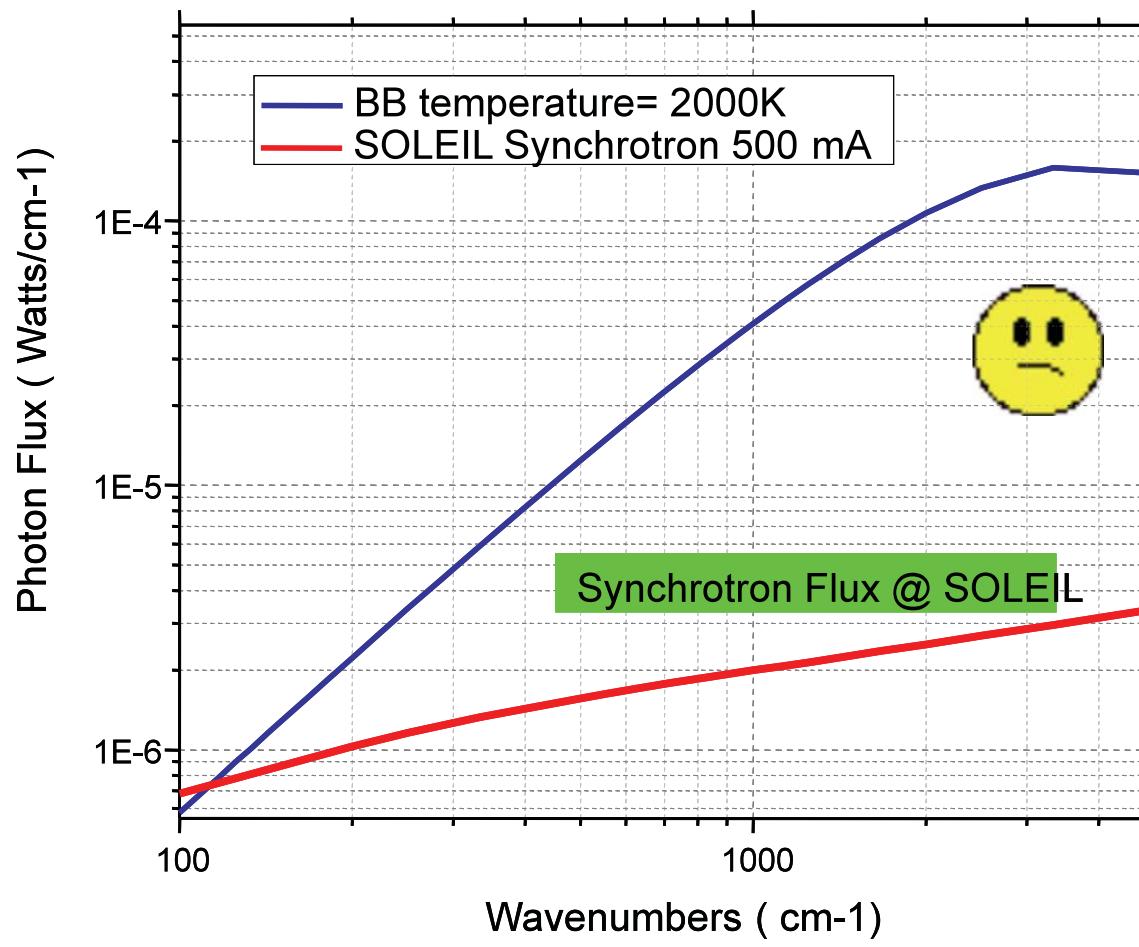
λ =Radiation wavelength

S_{src} =Source area

c =Speed of light

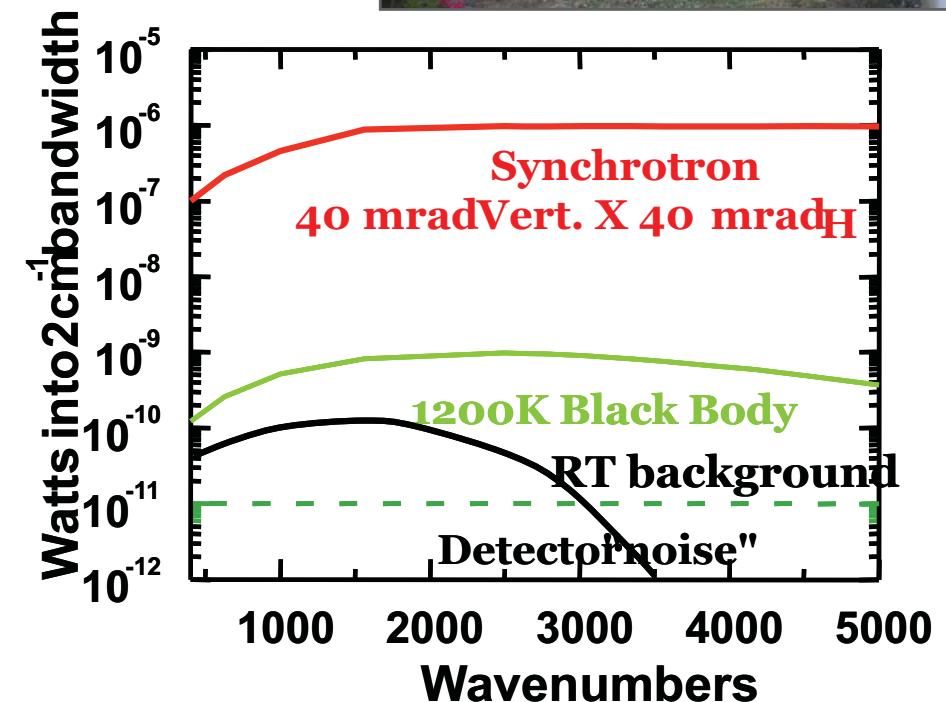
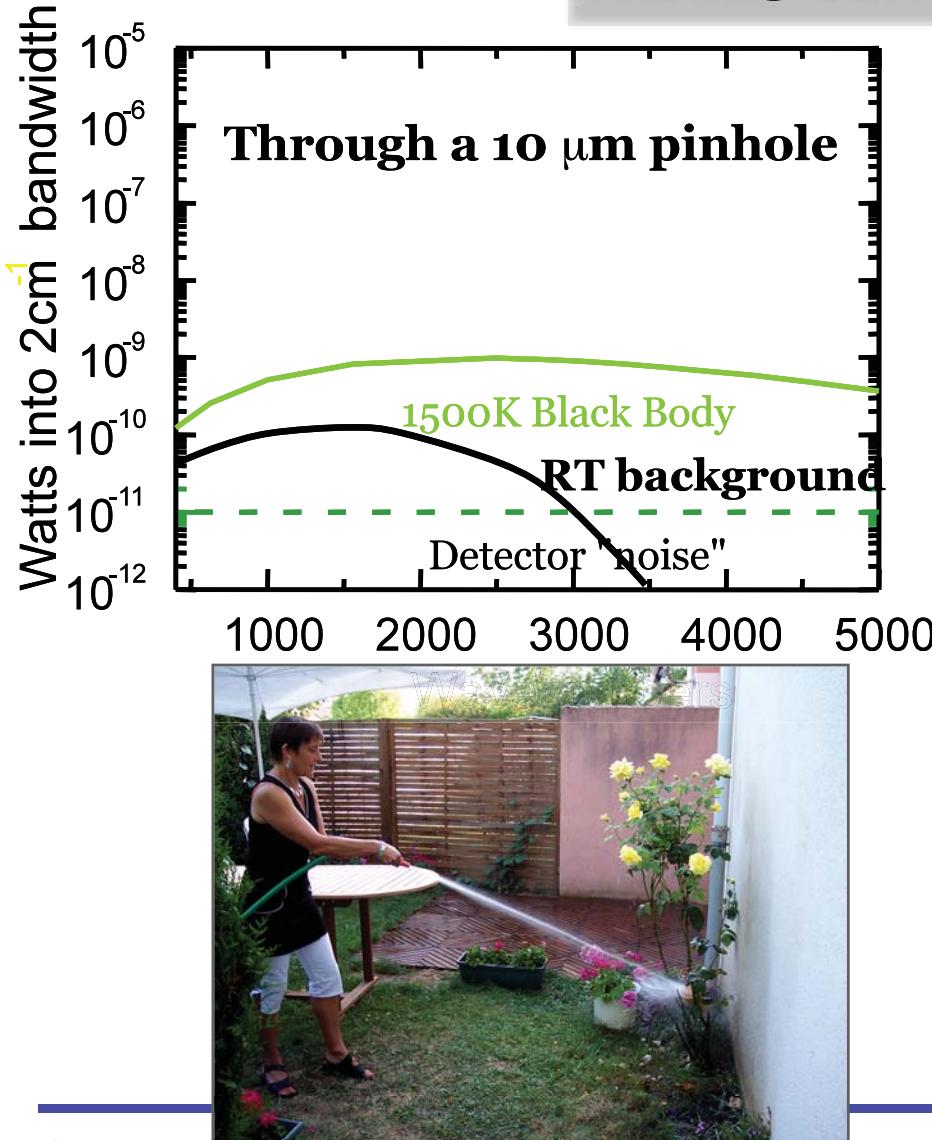
k_B =Boltzmann constant

FLUX:

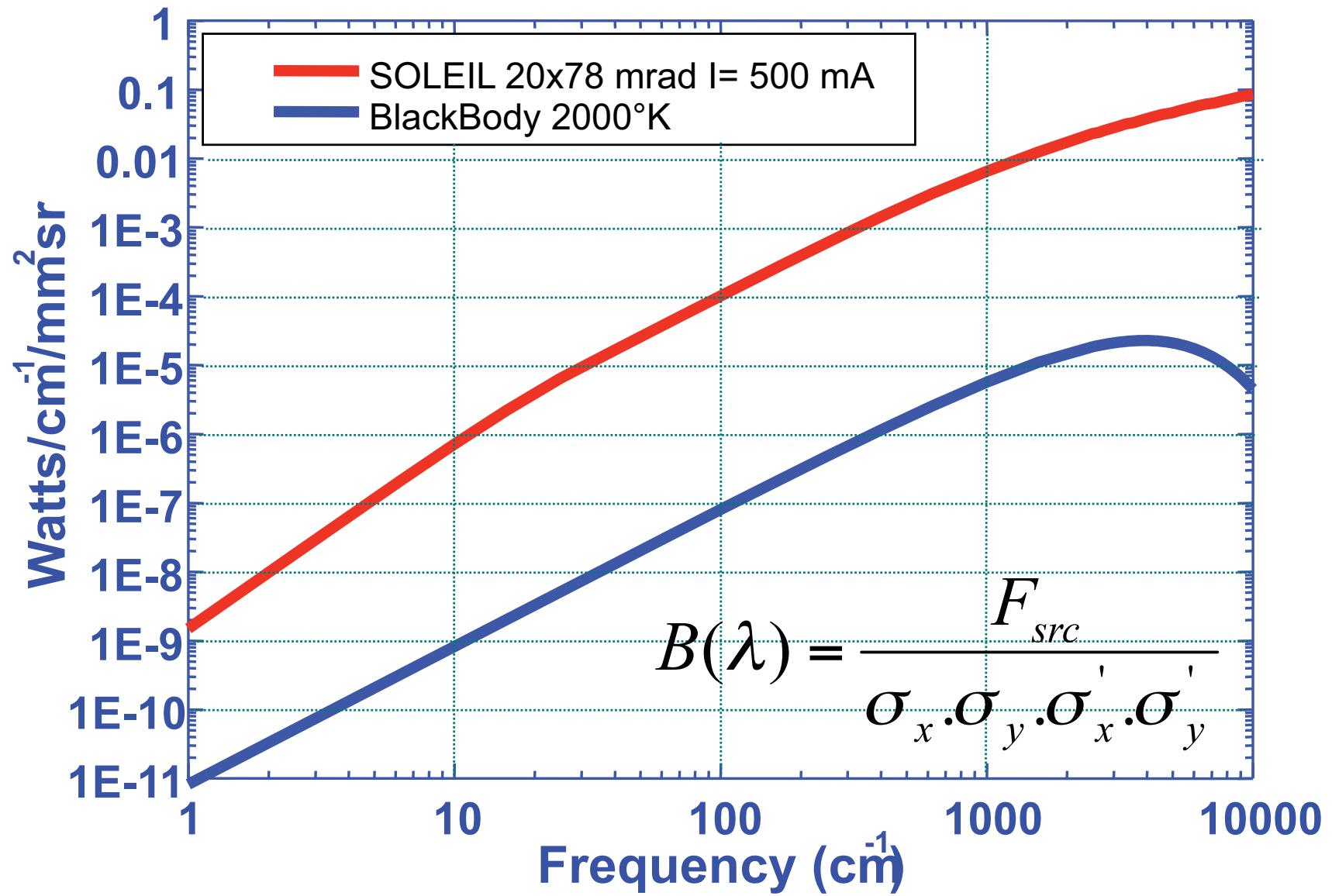


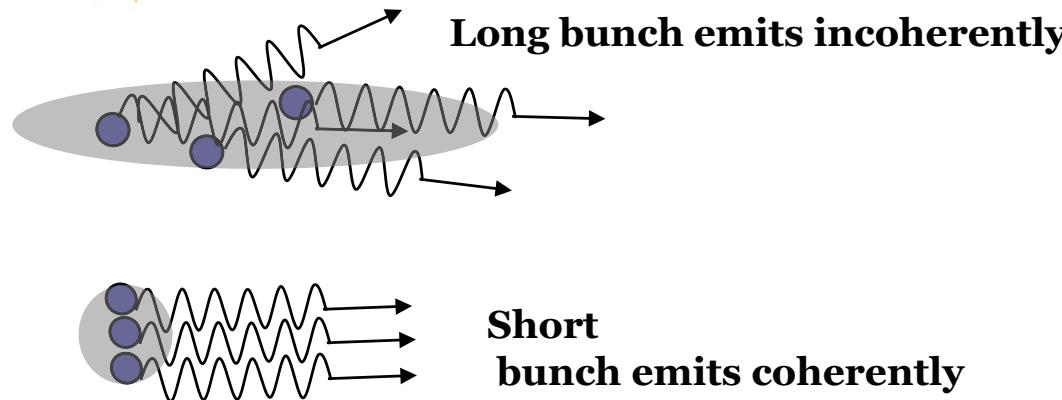
**Synchrotron IR
is much
brighter !**

BRIGHTNESS:

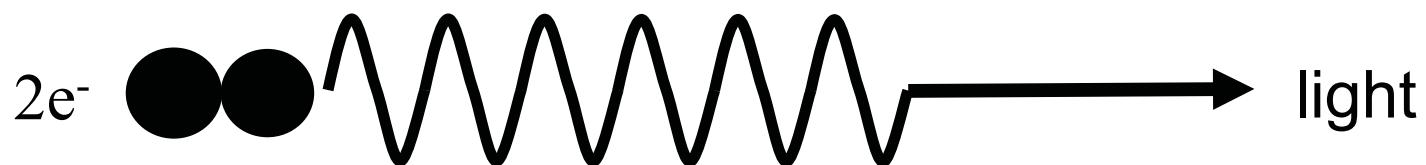


BRIGHTNESS CURVE





A source optimized for
Coherent THz
 $10^6 - 10^{10}$ more flux
 than other
 broadband sources

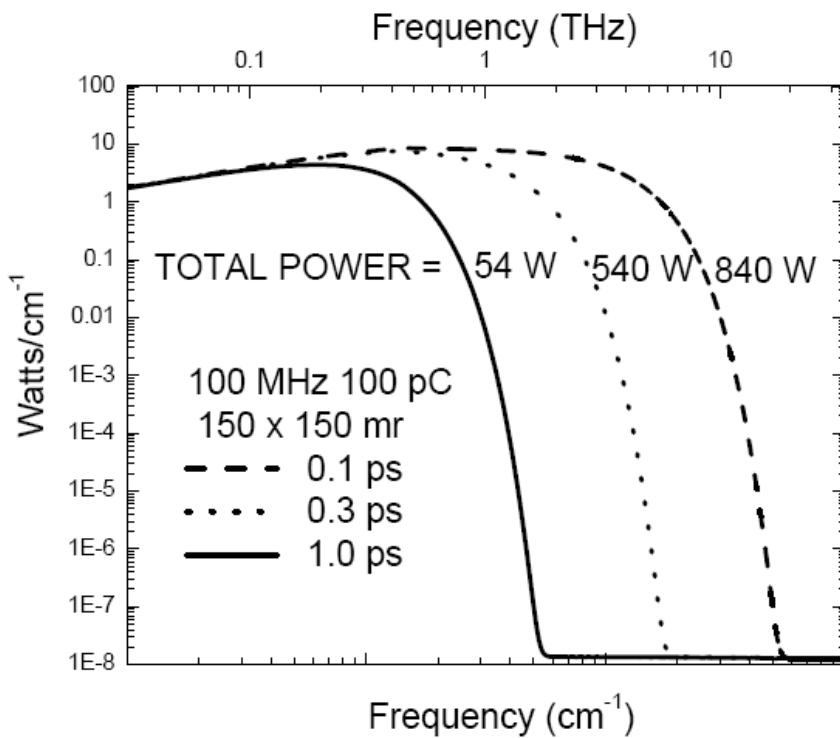


Larmor's formula:

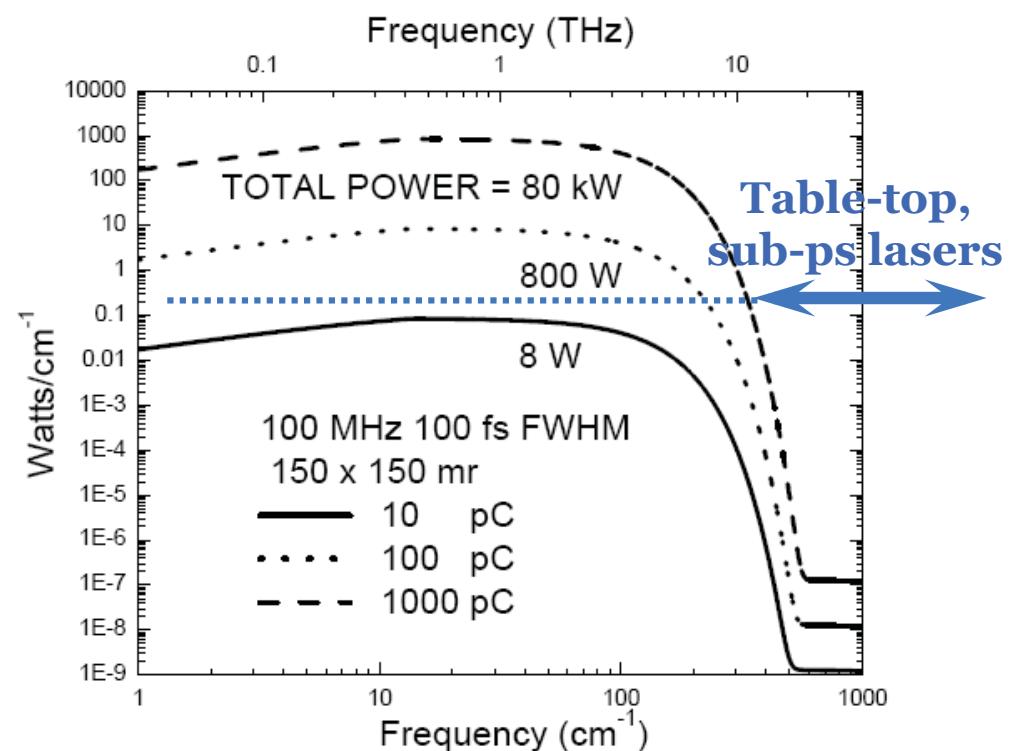
$$\text{Power} = \frac{2(Ne)^2 a^2}{3c^3} \gamma^4 \text{ (in cgs units)}$$

$P \propto N^2$
Can be huge!

CALCULATED THz EMISSION FROM A COHERENT SYNCHROTRON RADIATION SOURCE



For 100 pC bunch, 100 MHz,
versus bunch lengths



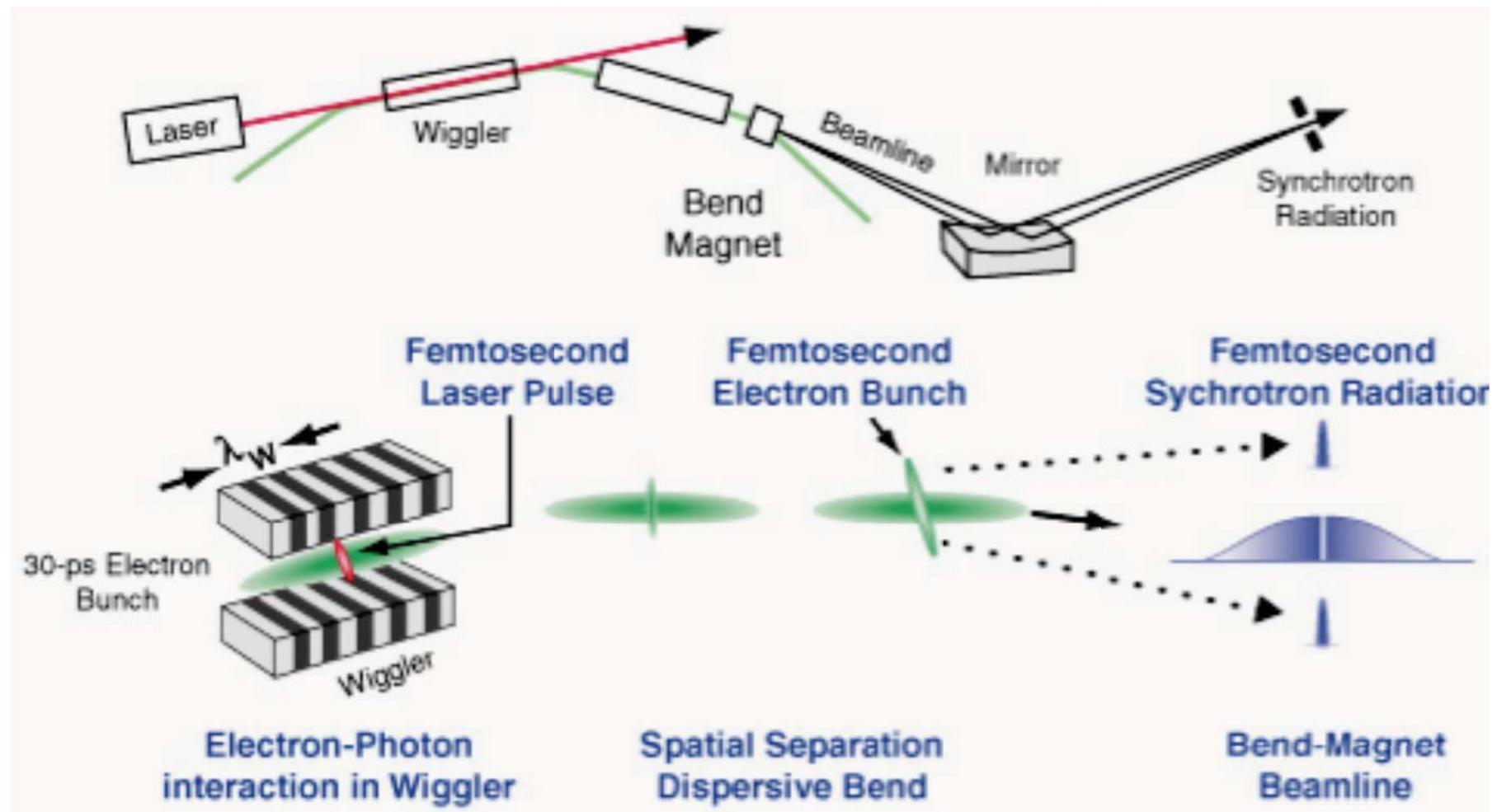
For 100 fs FWHM pulses , 100
MHz, versus bunch charge

From G.P. Williams « *Filling the THz gap-High Power sources and applications* » Report on Progress in Physics and Applications (2005) in print

- 1) Generating short pulses < 10ps (*with significant photon flux*) in storage ring is not that easy .**

- 2) In general, the natural pulse length is ~ 20ps rms (6mm) :(energy dispersion , RF voltage,Touschek, ...).**

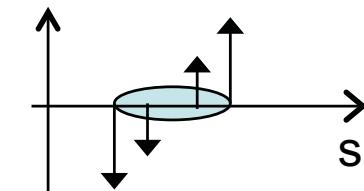
- 3) Increasing the current per bunch increases the bunch length(impedance)**



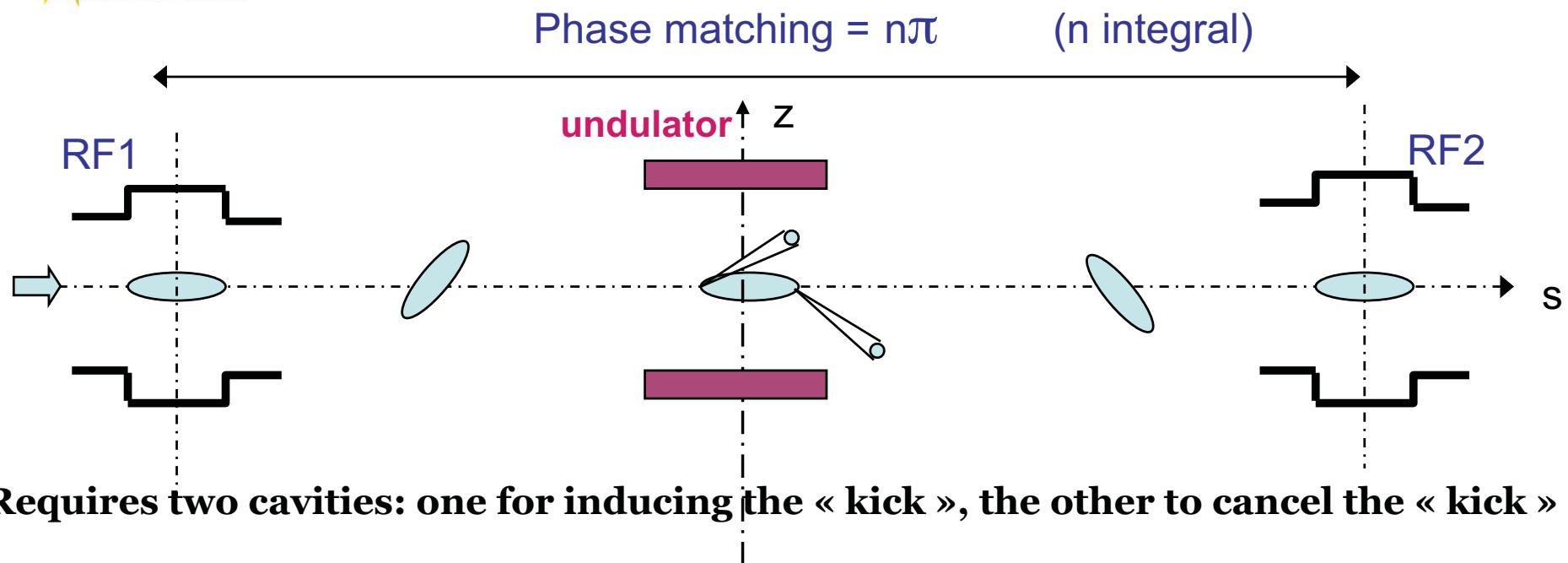
Weak photon flux, but doable

A. Zholents [NIM A425 385 (1999)]

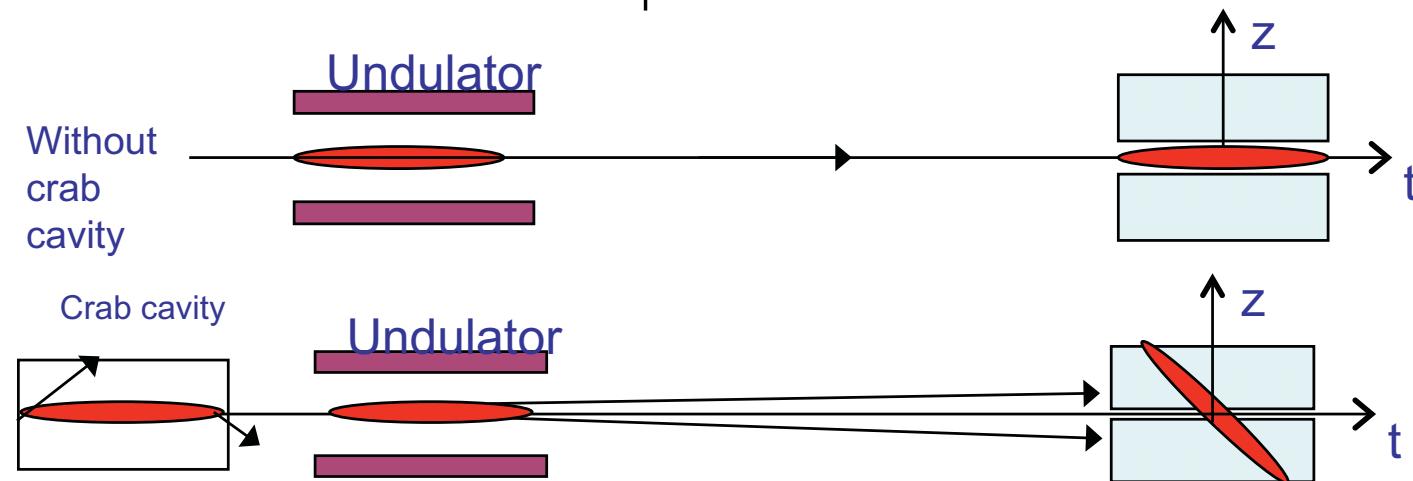
- RF cavities, named «Crab cavities», can provide transverse «kick» to an electron bunch where the force is proportional to the longitudinal distance for the bunch center



- One, then, creates a correlation between the longitudinal position of an electron in the bunch and its transverse angle (momentum)
- By passing through an undulator, photons are emitted with dispersion (correlation effect).. So the «head »photon are oriented upright , and tail photons downright



Requires two cavities: one for inducing the « kick », the other to cancel the « kick »



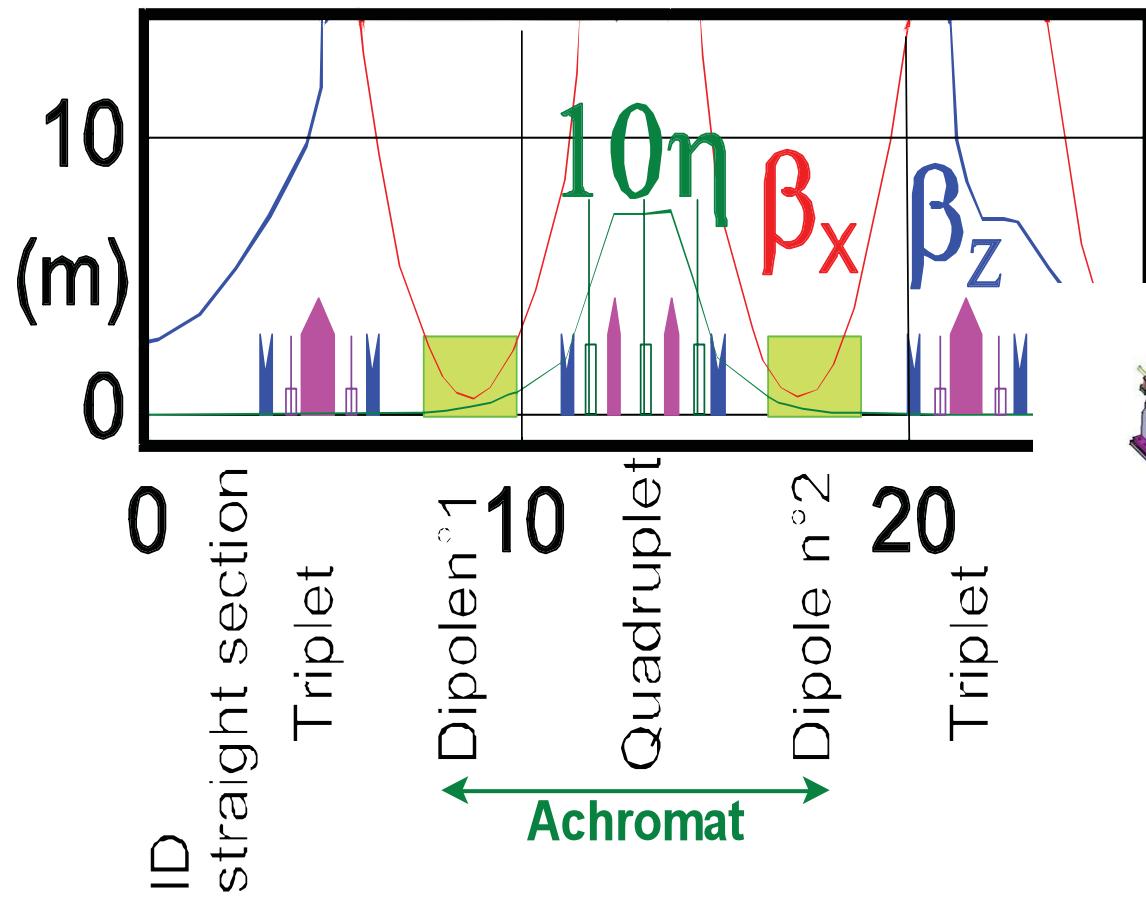
SHORT PULSES BY MOMENTUM COMPACTION

Typical storage ring lattice

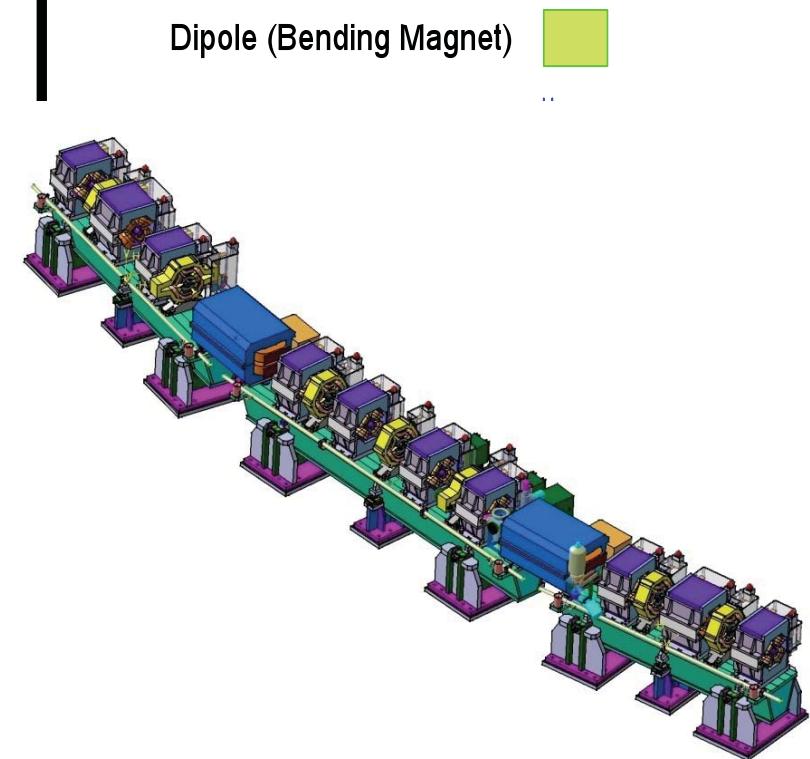
Dispersion η generated in the first dipole brought back to zero by the quadruplet

$$\text{Dipole n}^{\circ}1 + \text{Quadruplet} + \text{Dipole n}^{\circ}2 = \text{Achromat}$$

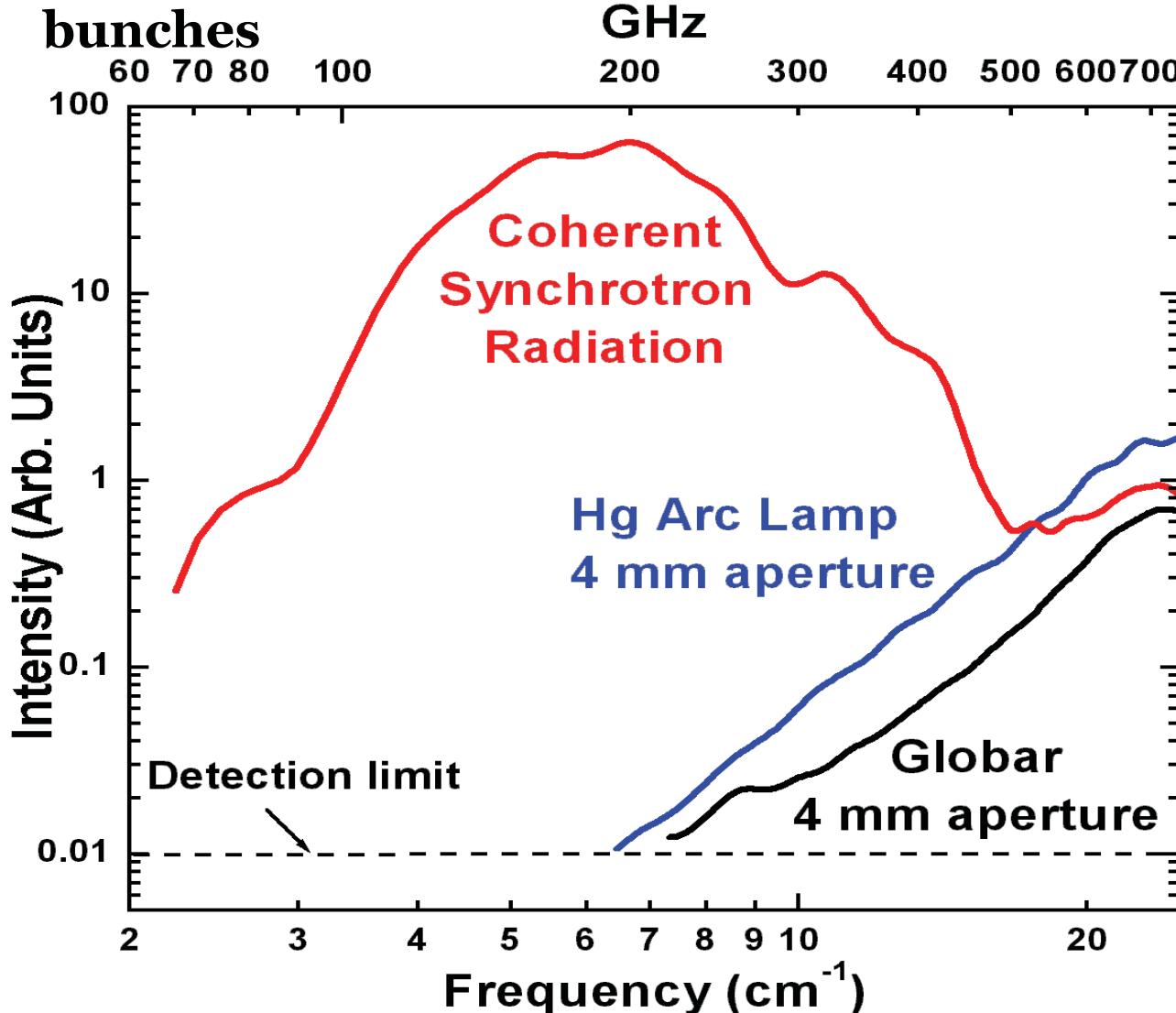
Triplets at both ends of the straight sections allow for a good match of the envelop in the ID



Dipole (Bending Magnet)



Used BESSY-II synchrotron to get low- α tune: short & shaped bunches



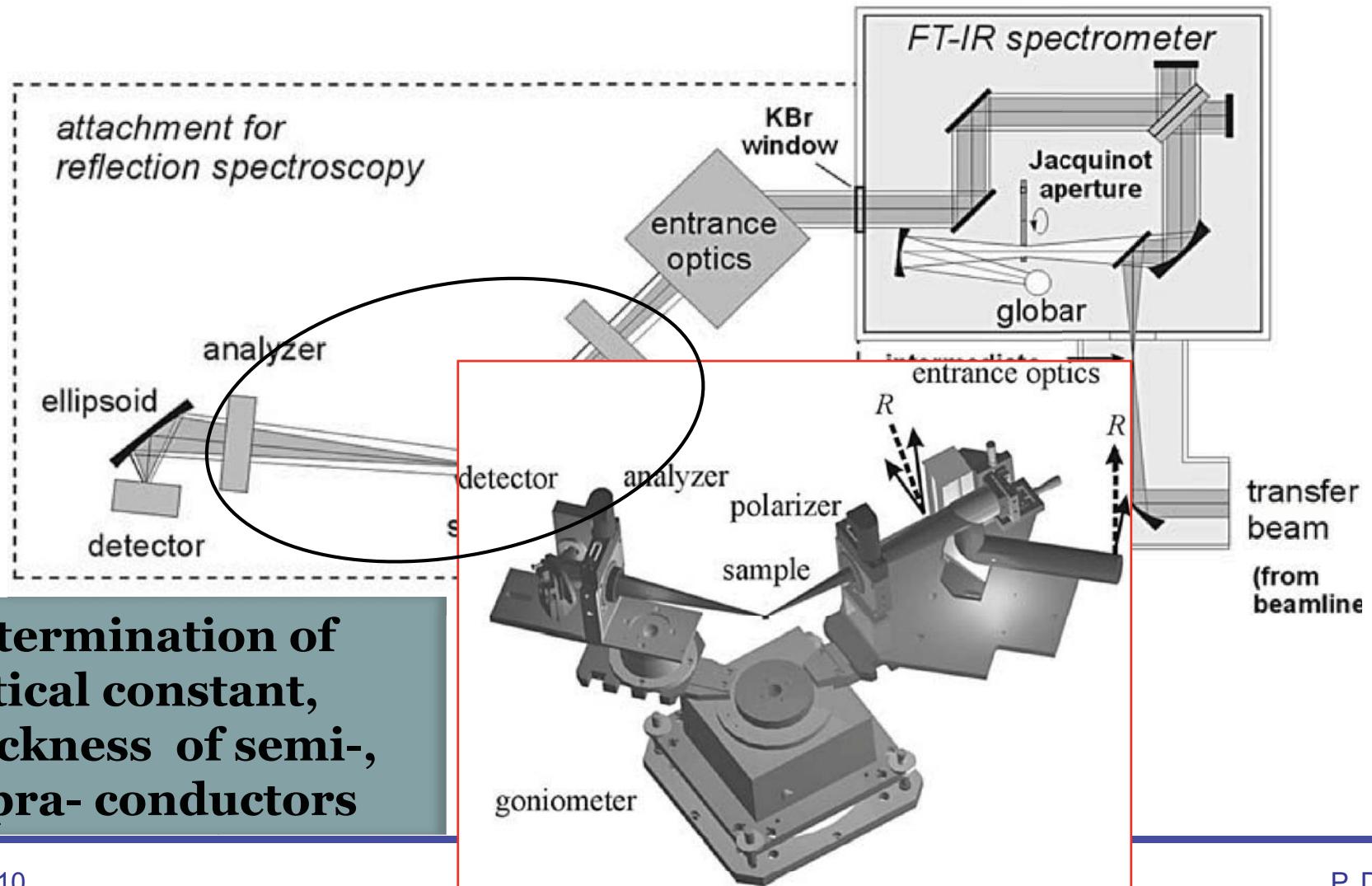
BESSY-II

Abo-Bakr *et al.*, PRL (2002) & (2003).
Singley *et al.*, PRB 69, 092512 (2004).

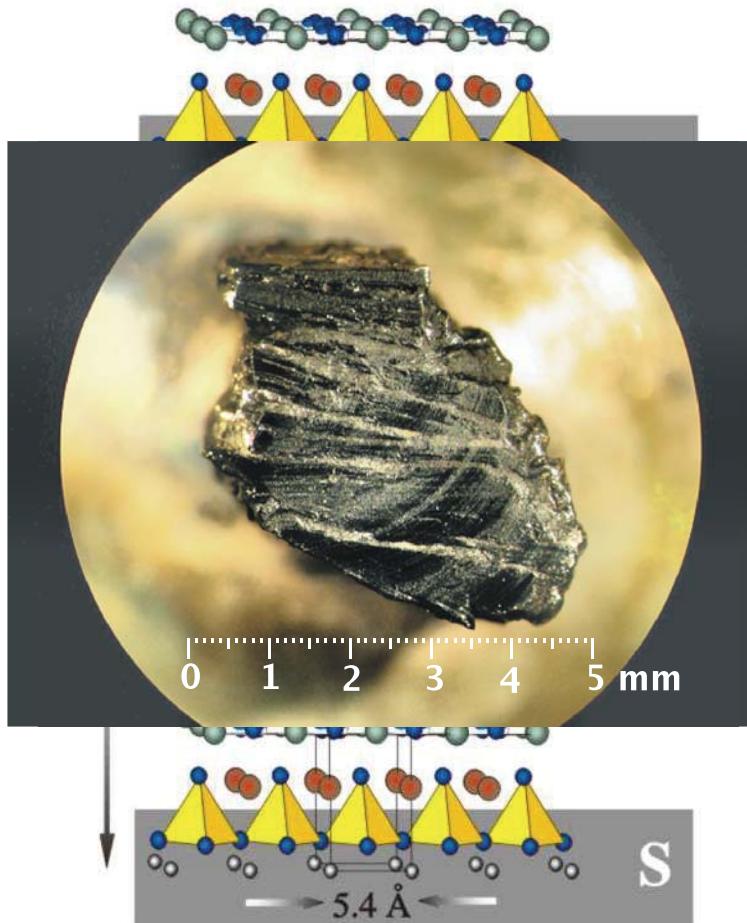
APPLICATIONS IN THE FAR-INFRARED (THz) DOMAIN

M. Gensch · K. Hinrichs · A. Roseler · E. H. Korte ·
U. Schade

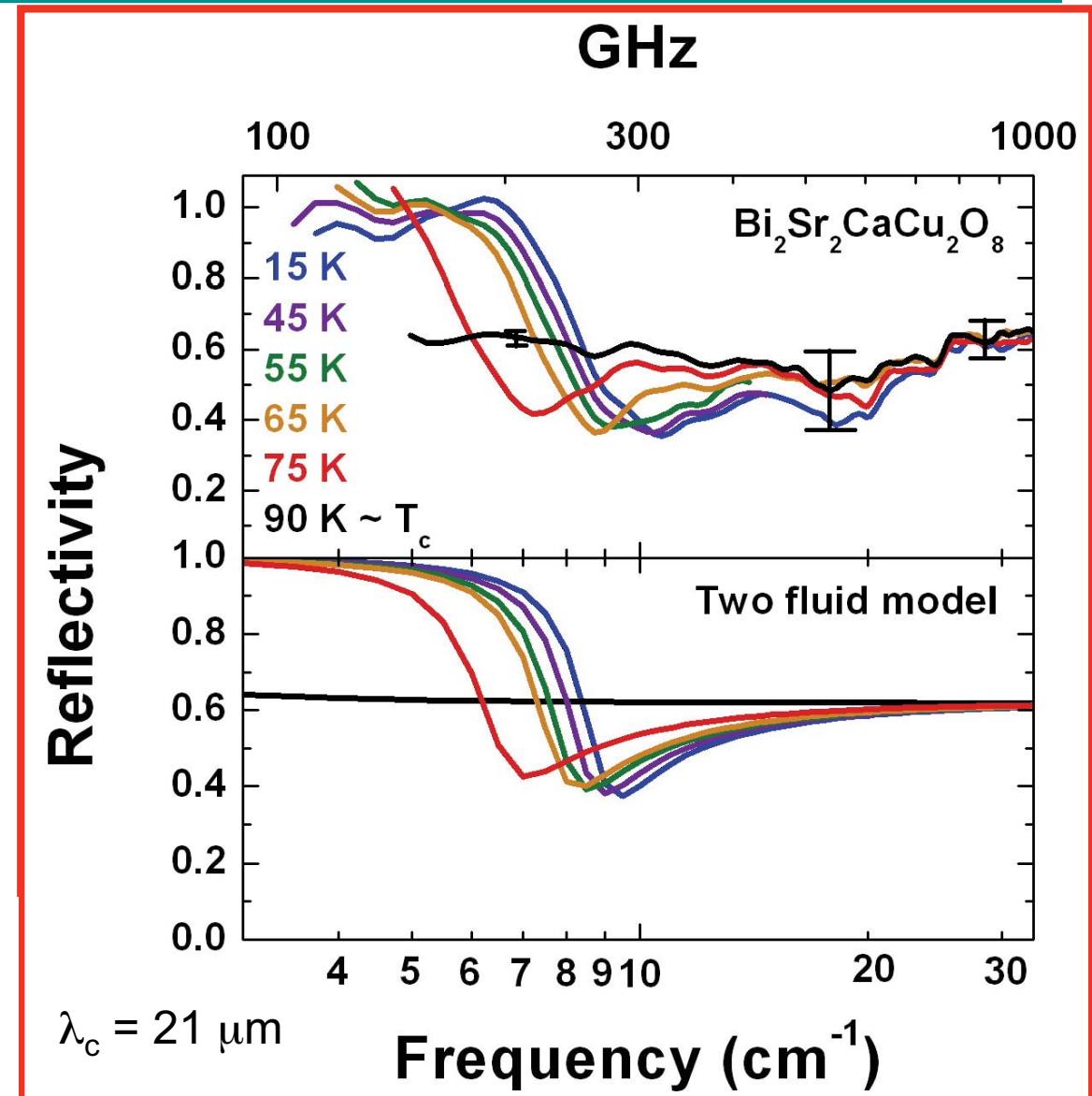
Anal Bioanal Chem (2003) 376 : 626–630



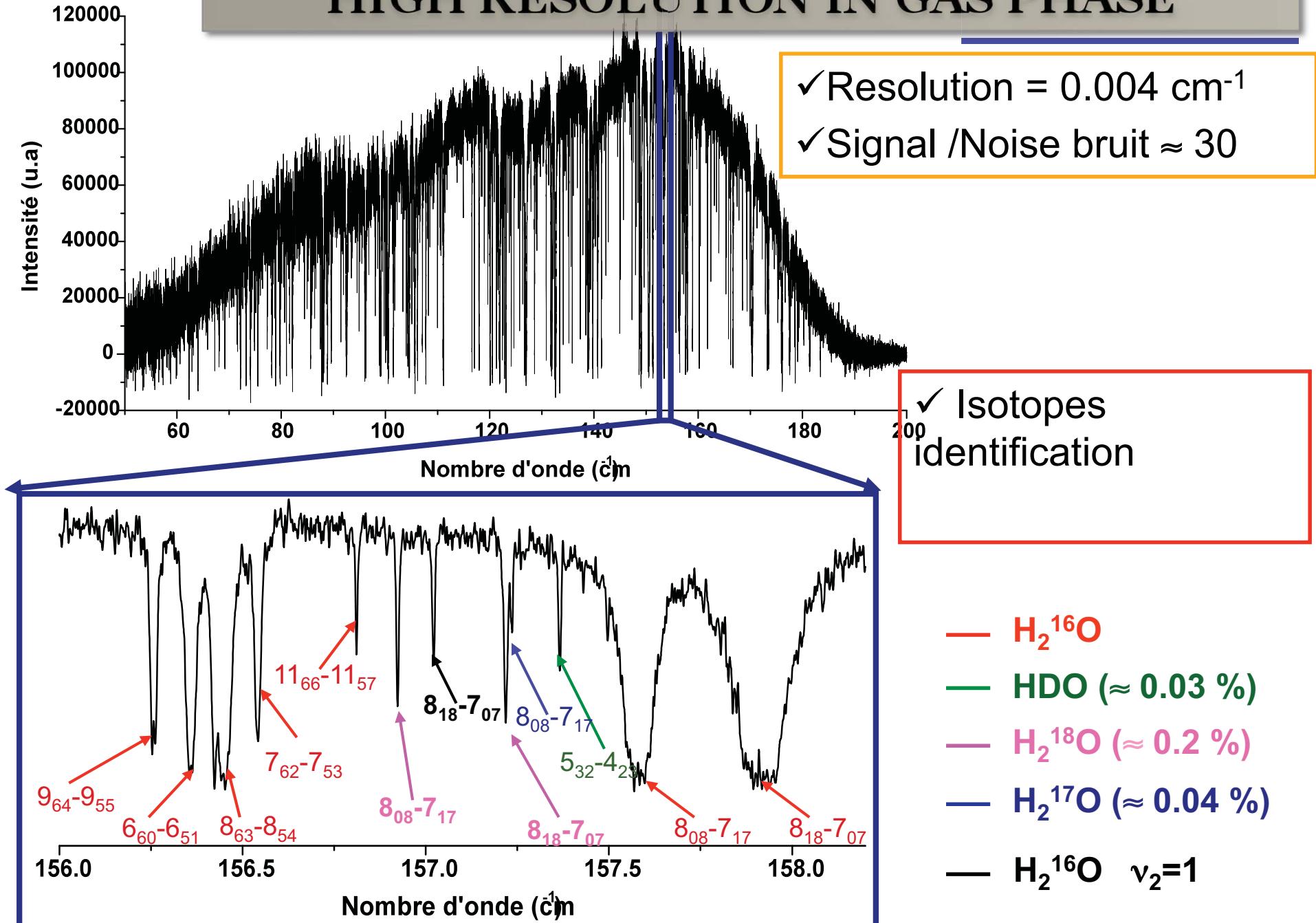
First CSR Science: JPR in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$



+ Indications for inhomogeneous superfluid
 Singley, Martin, Schade, et al.,
PRB **69**, 092512 (2004)



HIGH RESOLUTION IN GAS PHASE



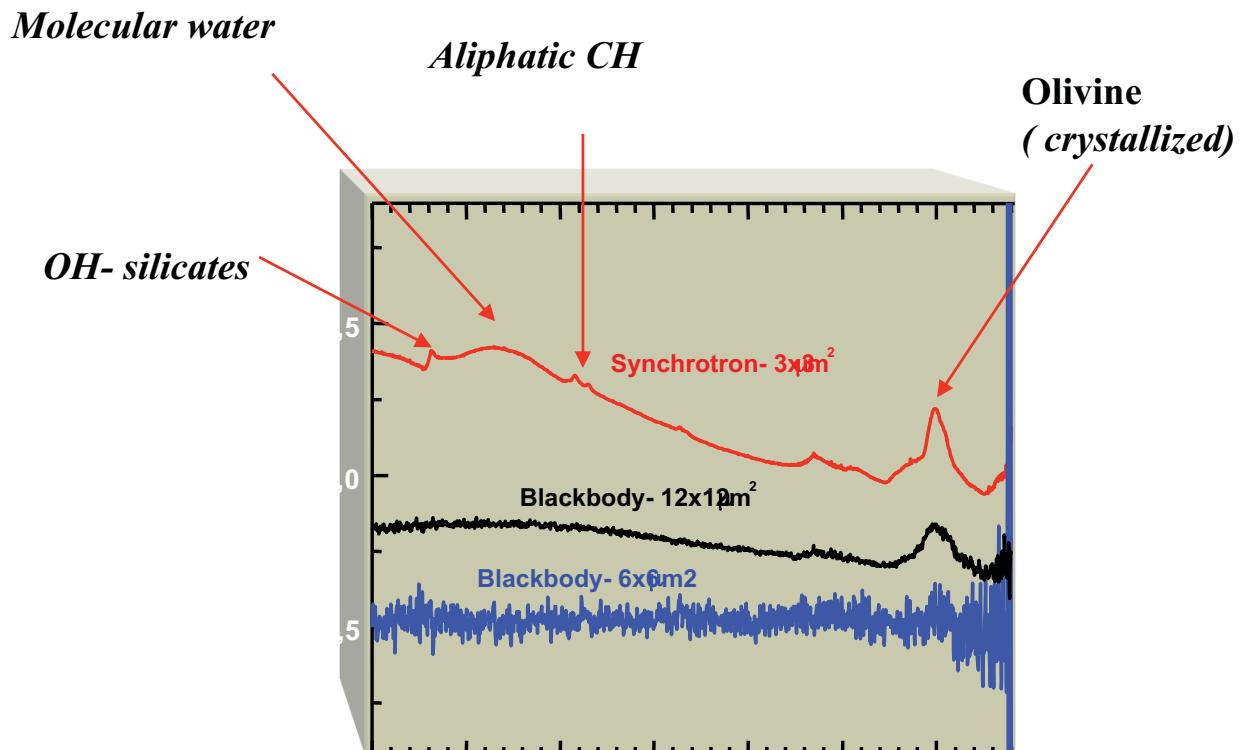
APPLICATIONS IN THE MID-INFRARED DOMAIN

1- Space Science

IDENTIFYING SMALL INTERSTELLAR PARTICLE



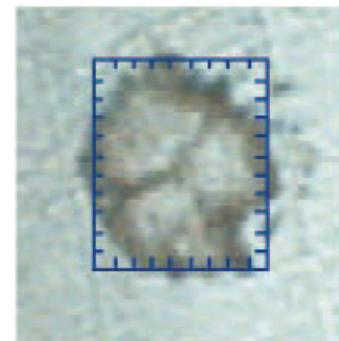
“Orgueil” particules



Ph. Raynal, L. D'Hendecourt, J. Borg, J.P. Bibring , G.P. Williams and P. Dumas

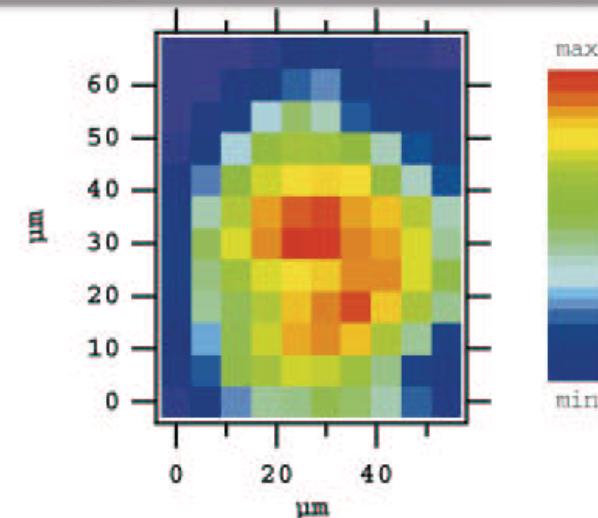
IDENTIFYING SMALL INTERSTELLAR PARTICLE

Aperture= 3x3 μm

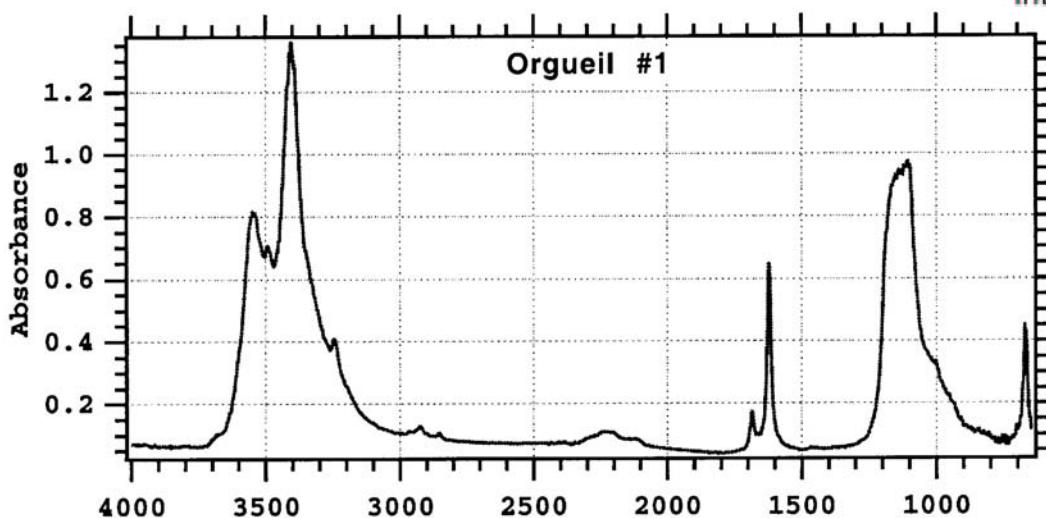


\longleftrightarrow
40 μm

- optical snapshot



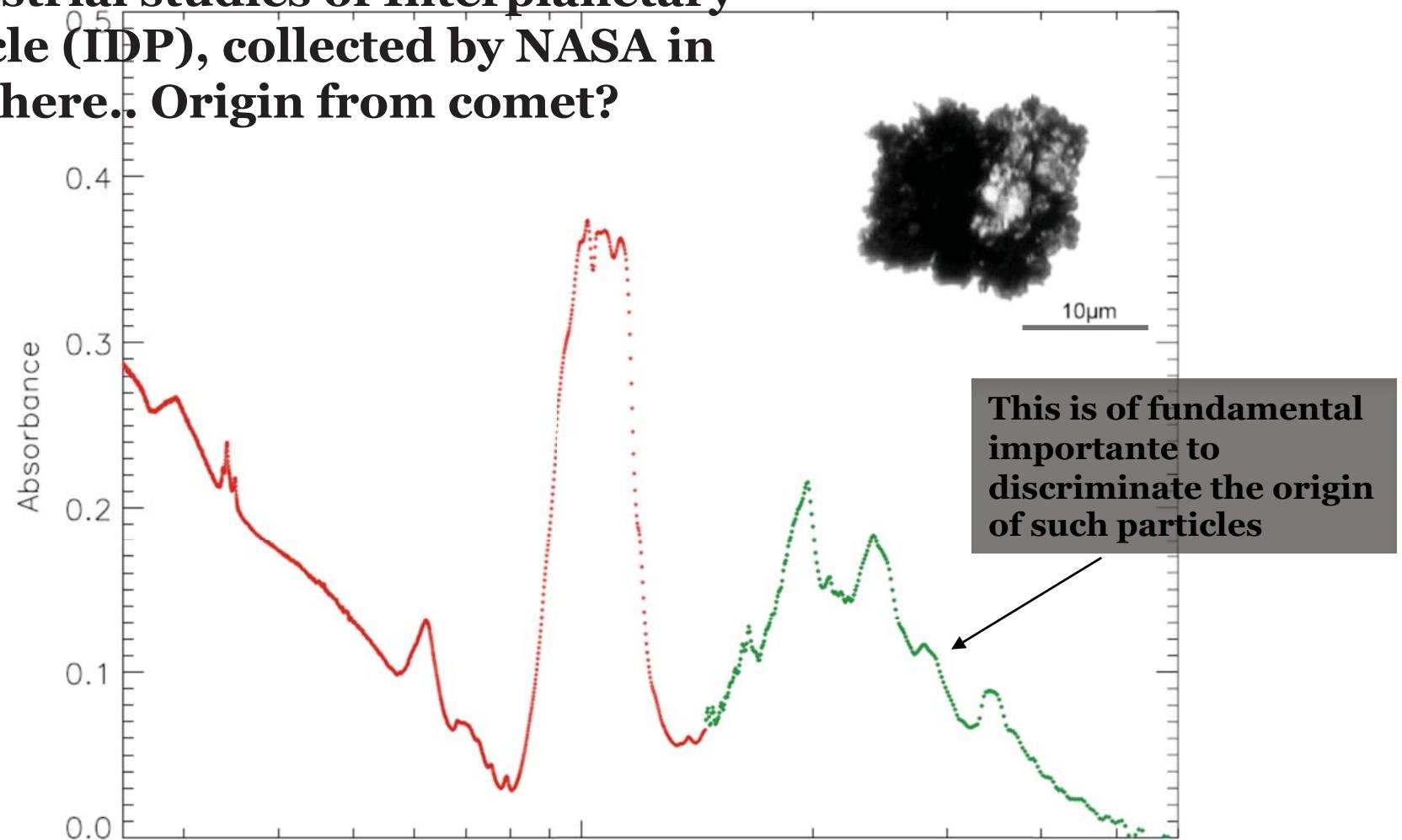
- mapping of the stronger H_2O bands;
integrated Absorbance, [3800; 3000] cm^{-1} range



Chemical image of water distribution inside a 40 μm particle

IDENTIFYING SMALL
INTERSTELLAR PARTICLE

Extra terrestrial studies of Interplanetary
Dust Particle (IDP), collected by NASA in
the stratosphere.. Origin from comet?

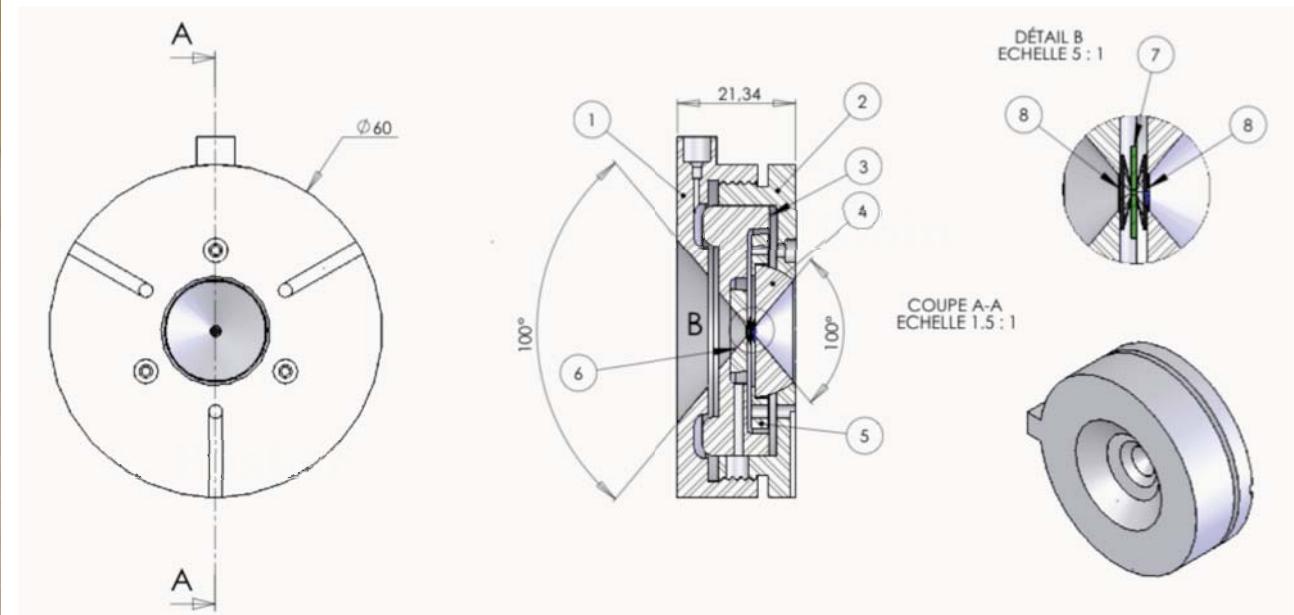


Extension to the far-IR microscopy important for a thorough identification

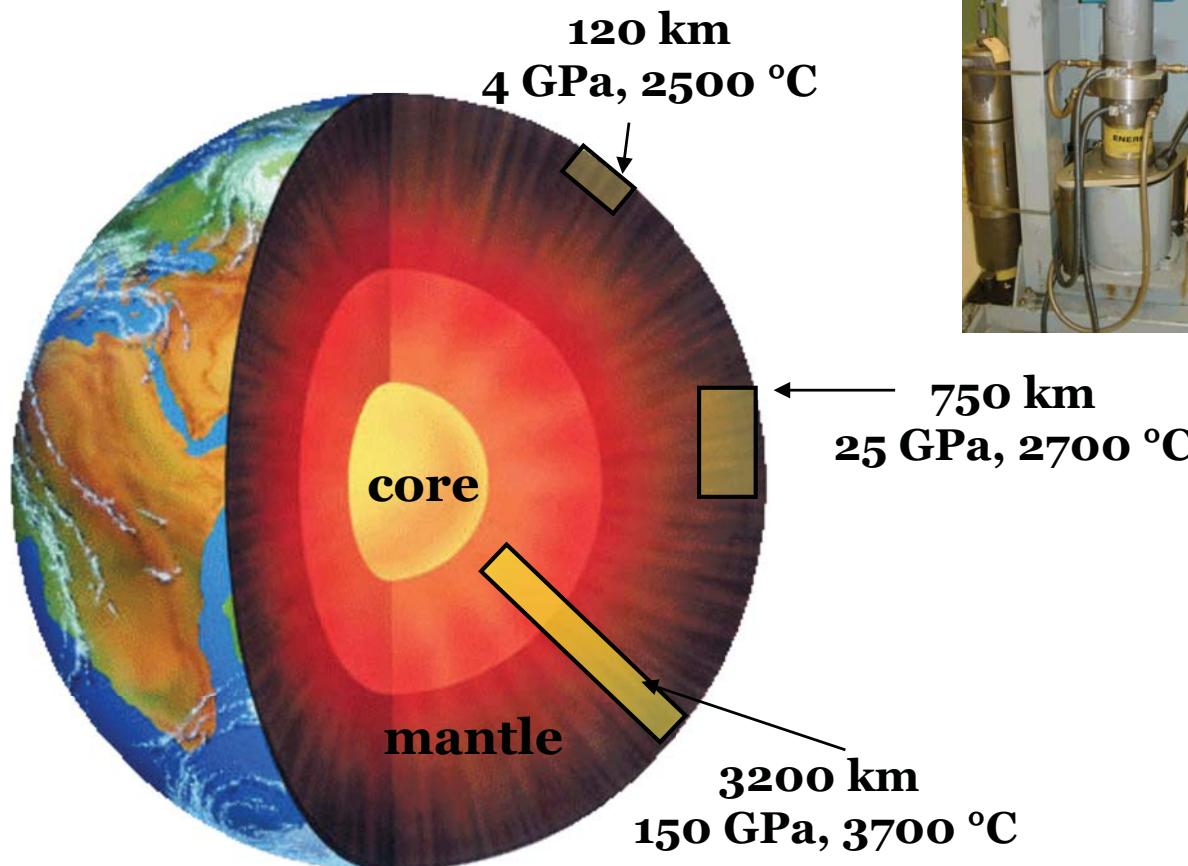
APPLICATIONS IN THE MID-INFRARED DOMAIN

2- High Pressure studies

Requires a Diamond (Moissanite) anvil cell



EARTH SCIENCES STUDIES AT FOREFRONT OF SUCH STUDIES



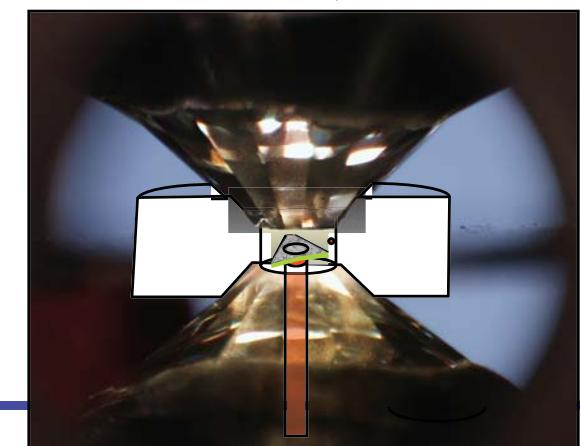
0.1 cm



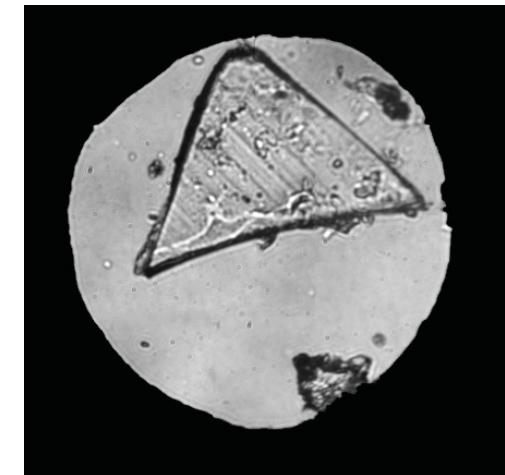
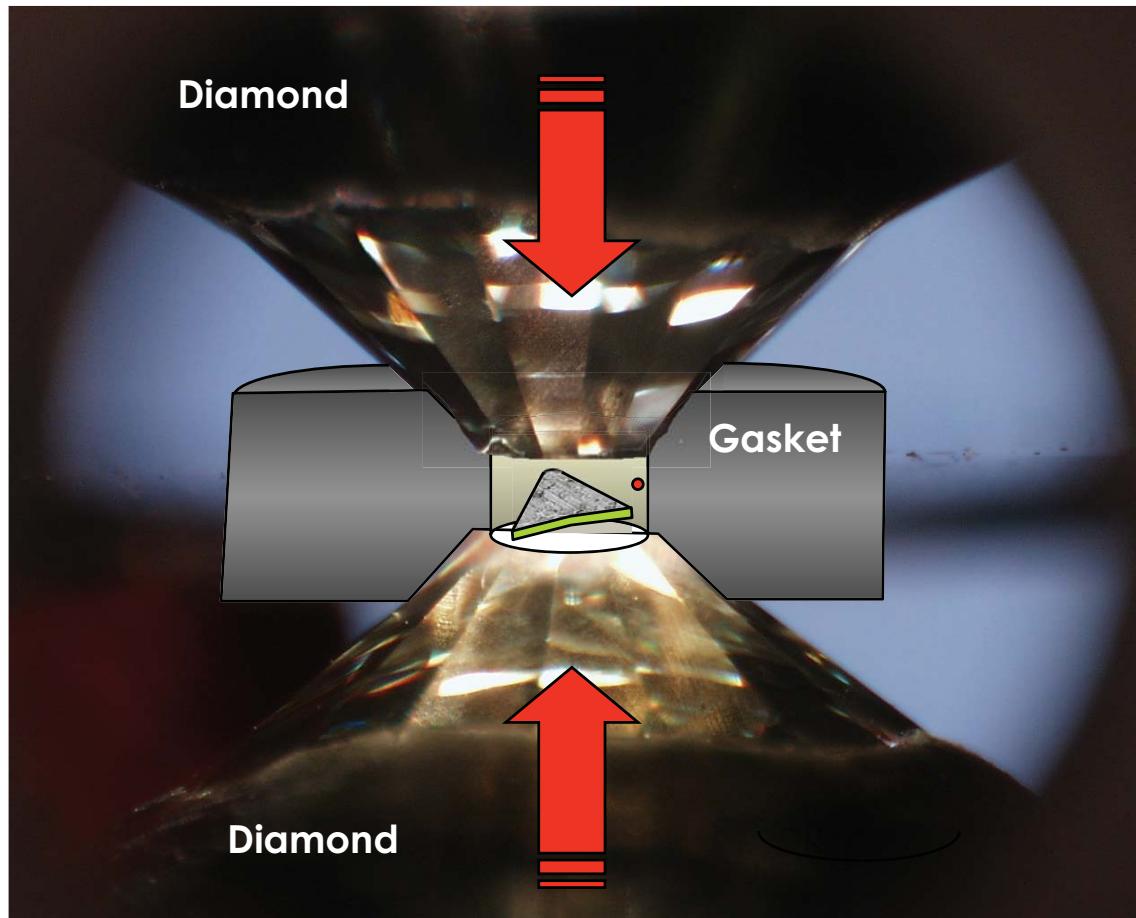
100 μm



10 μm

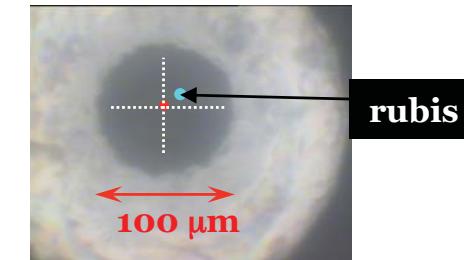
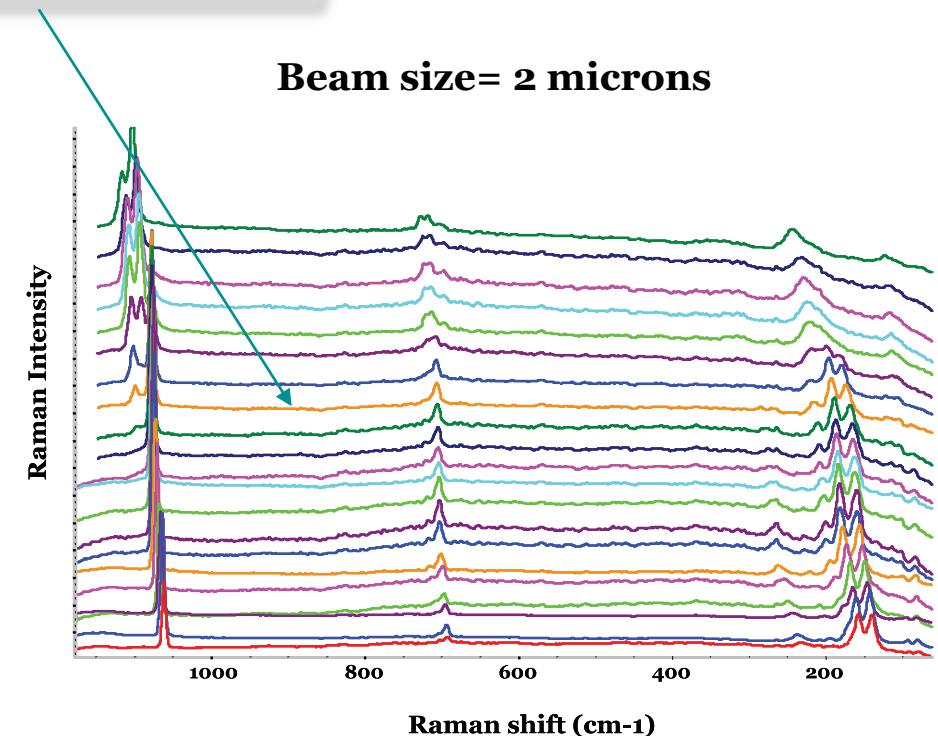
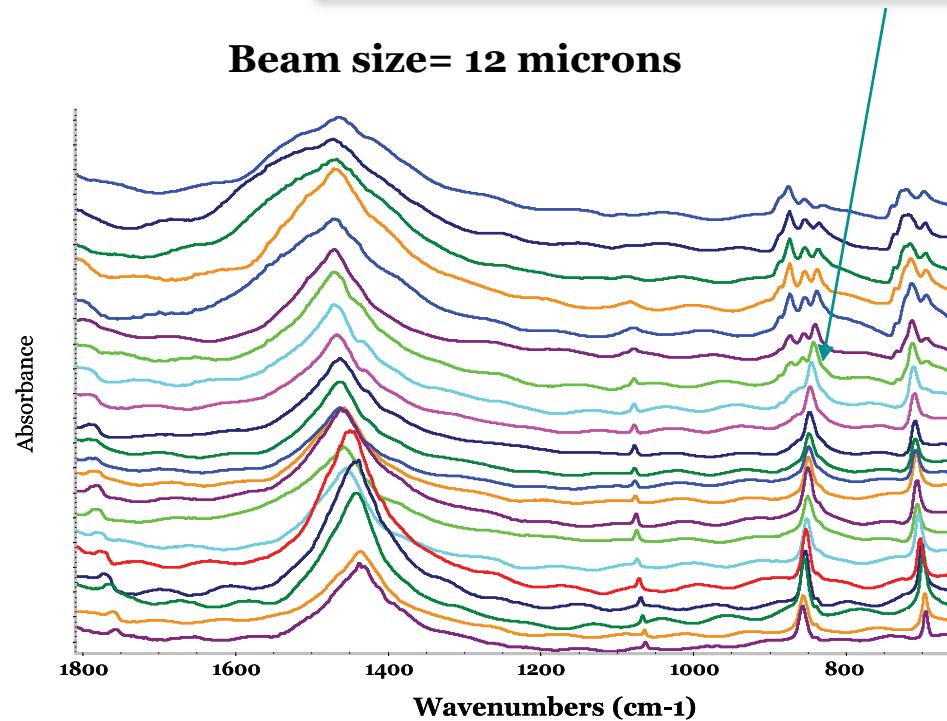


DAC (Diamond Anvil Cell) IN DETAILS



L. Puskar, M.J. Tobin, I. Yousef et al.

Phase transition over 8.1 GPa

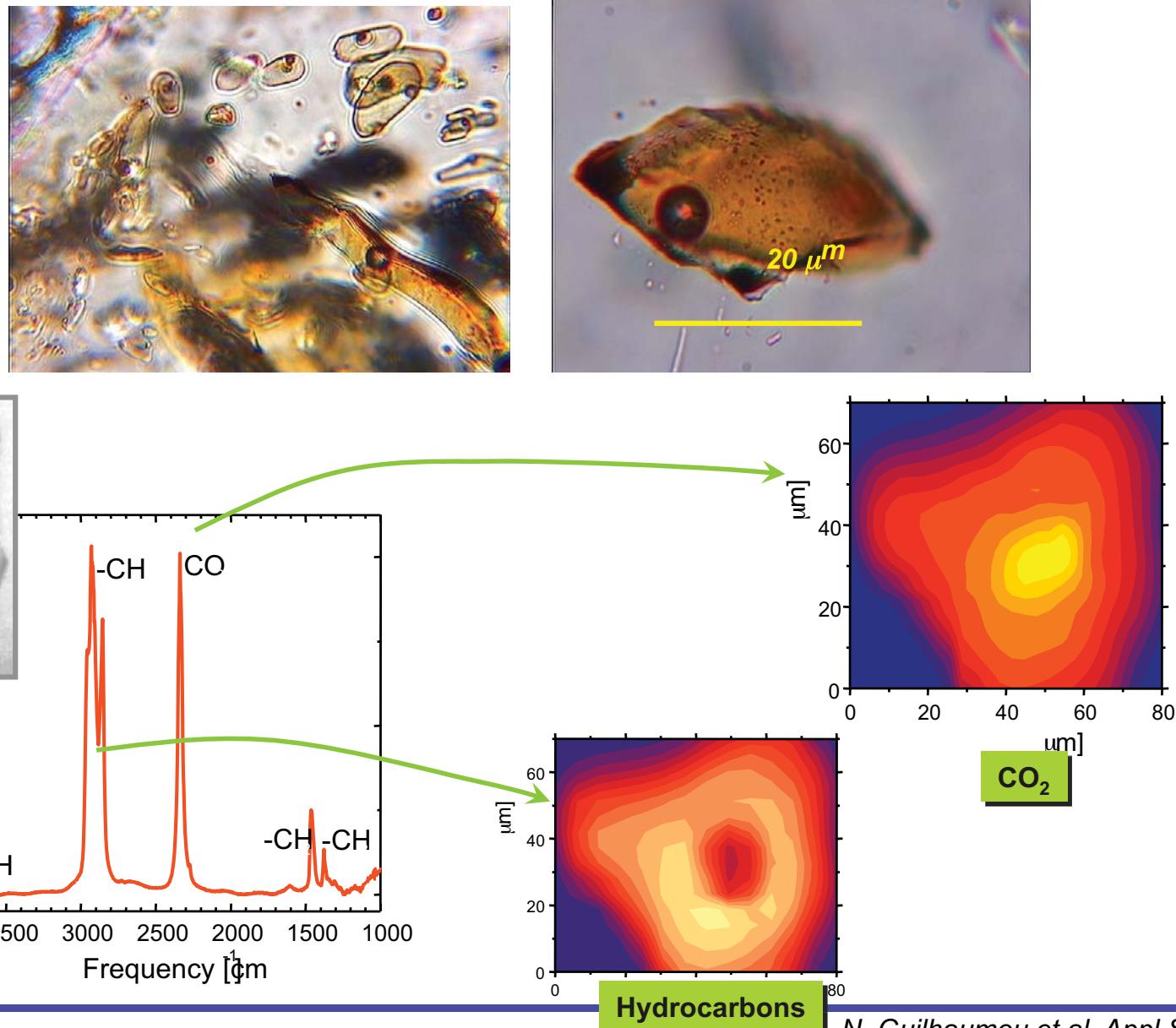


When possible, combination Raman and Synchrotron-IR very potential

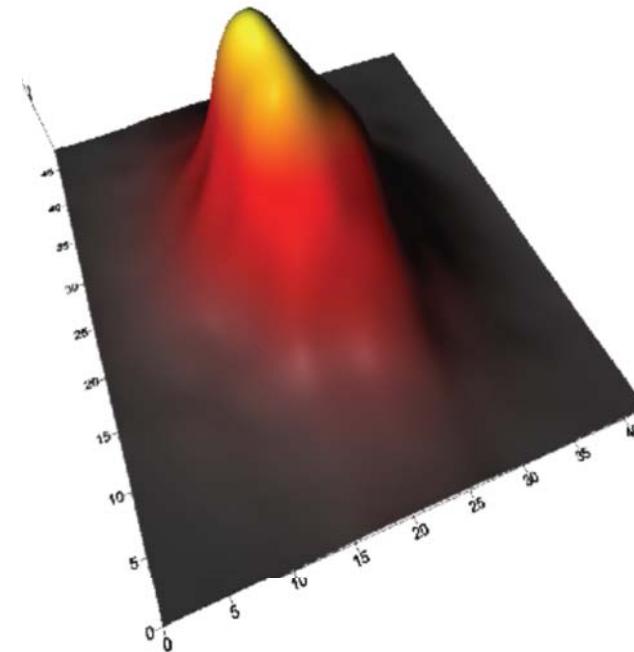
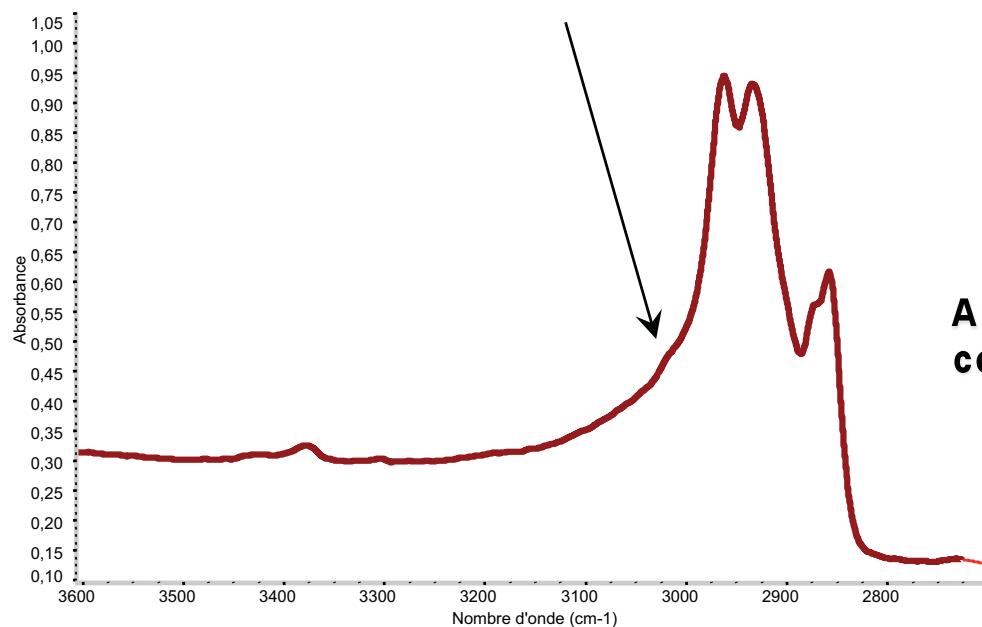
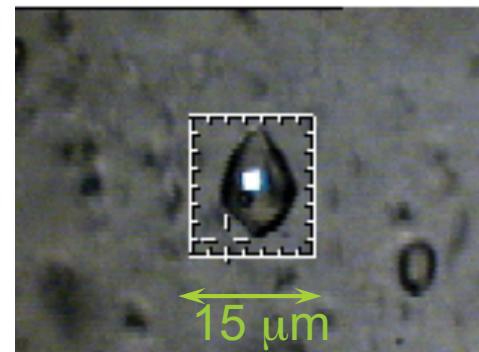
APPLICATIONS IN THE MID-INFRARED DOMAIN

3- Earth Science

INCLUSIONS IN ROCKS



Inclusion in calcite Benzenic C=H

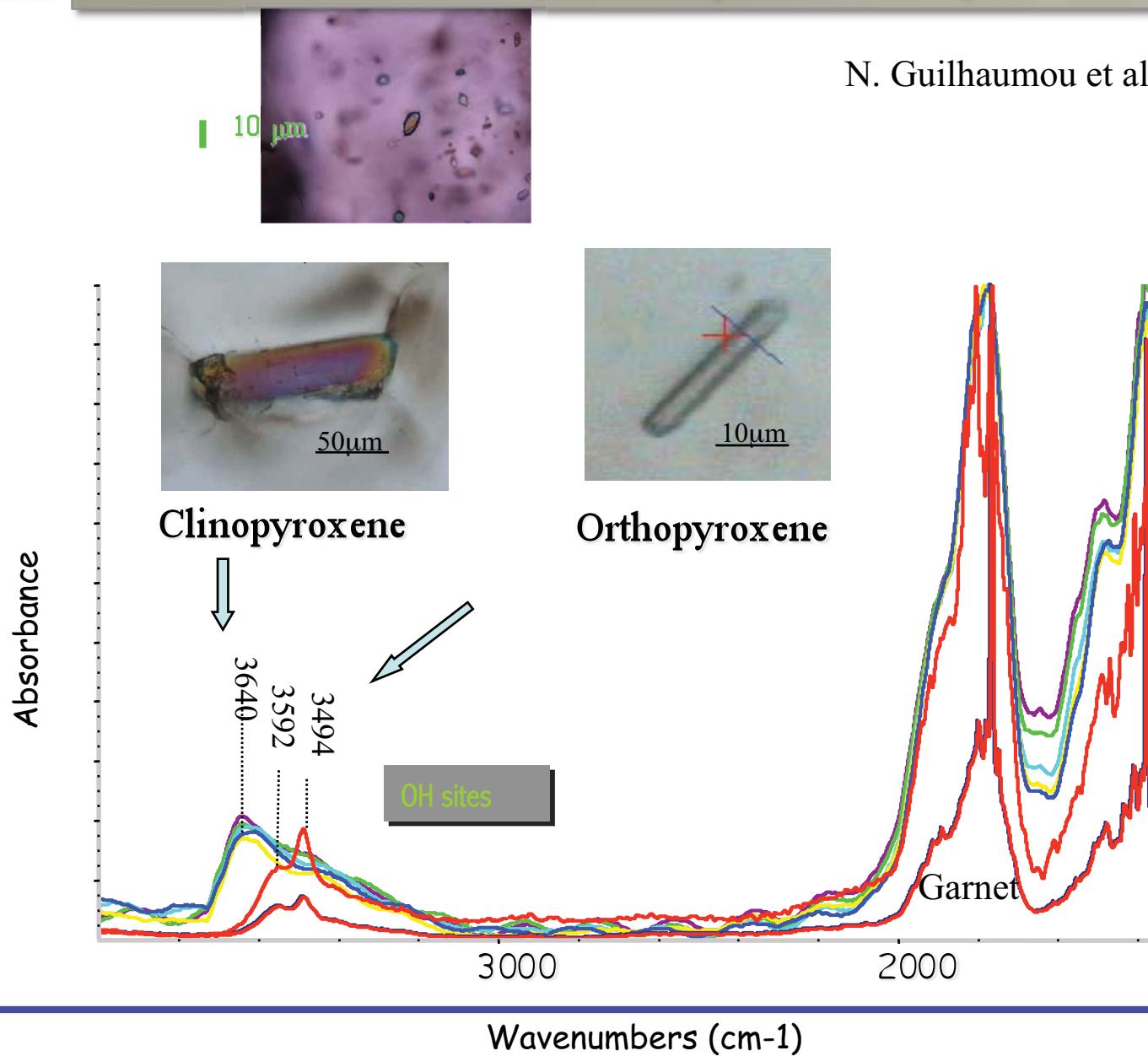


Analysis realized with aperture,
confocal, of $3 \times 3 \mu\text{m}^2$

N. Guilhaumou , P. Dumas et al.

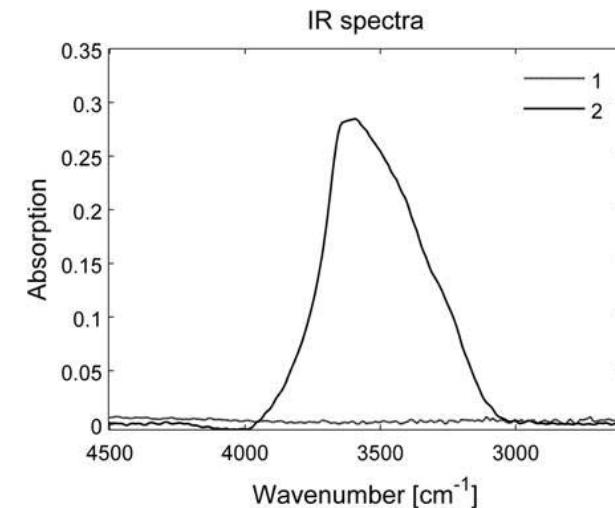
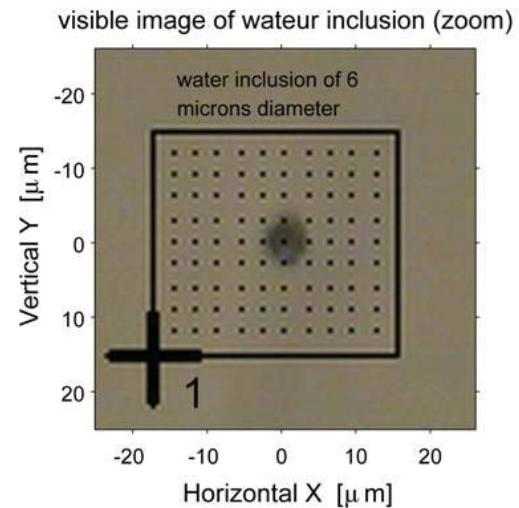
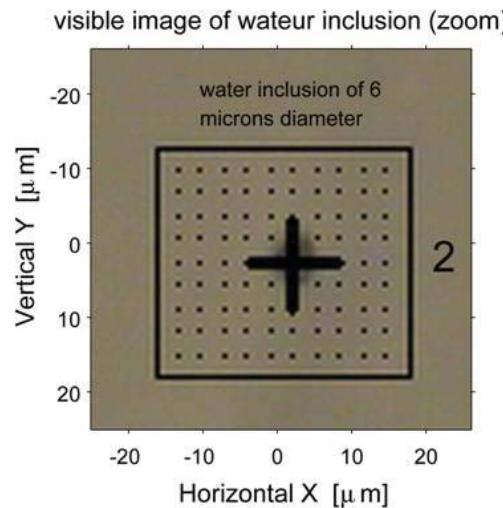
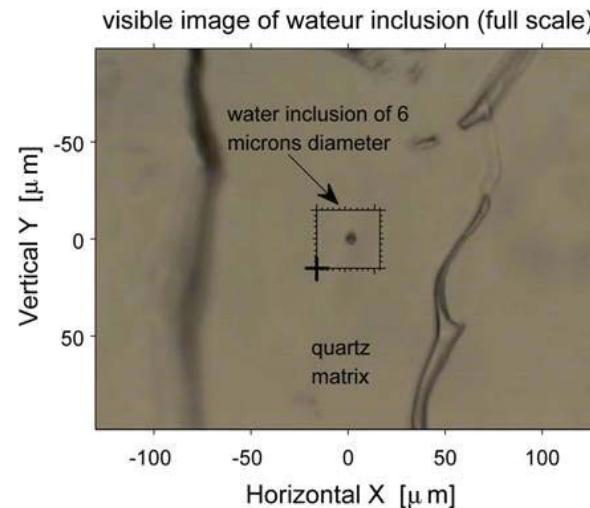
WATER IN DEEP SEATED MINERALS (200-400 KMS)

N. Guilhaumou et al.

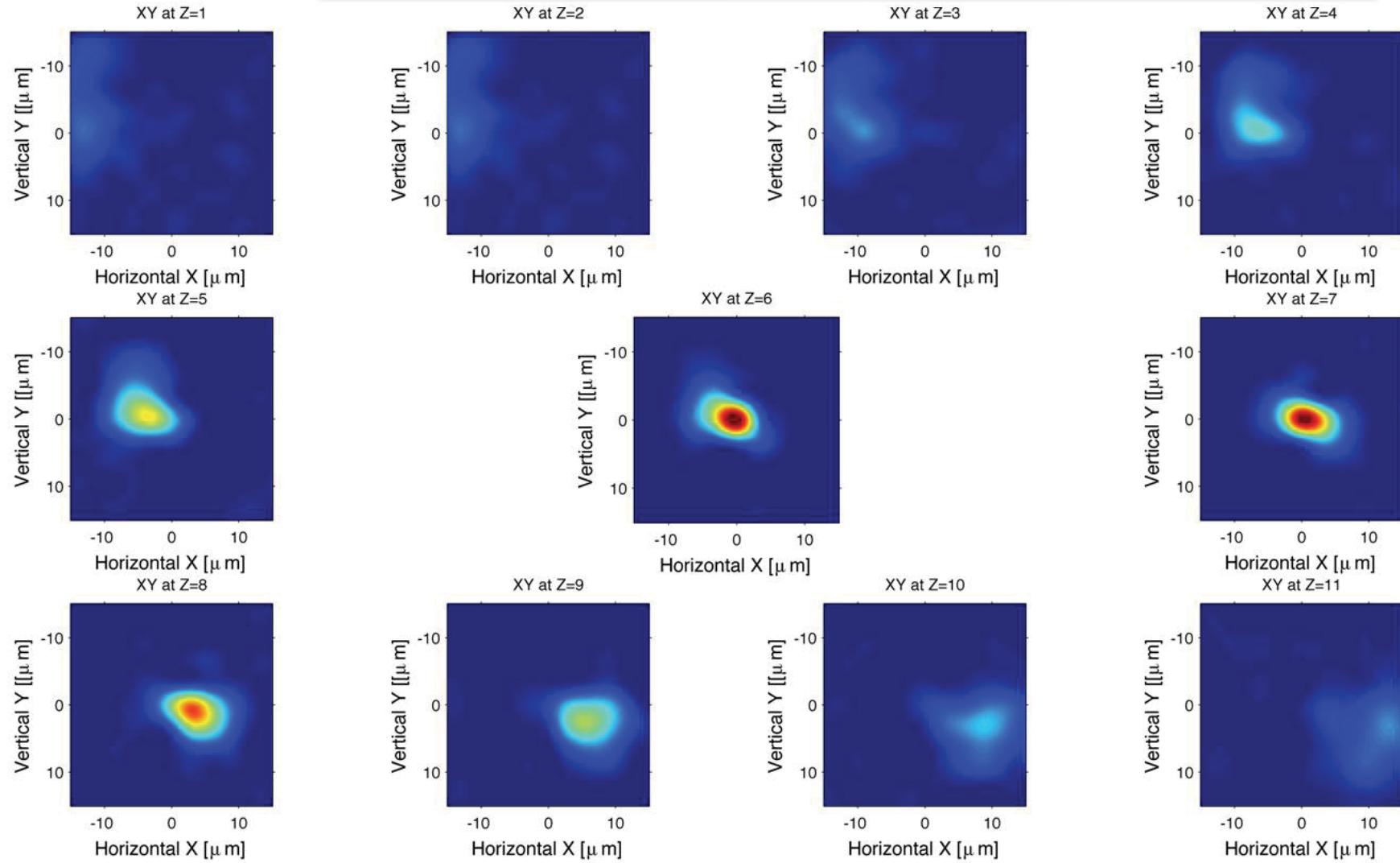


EXPLOITING THE CONFOCAL PROPERTIES FOR INCLUSIONS

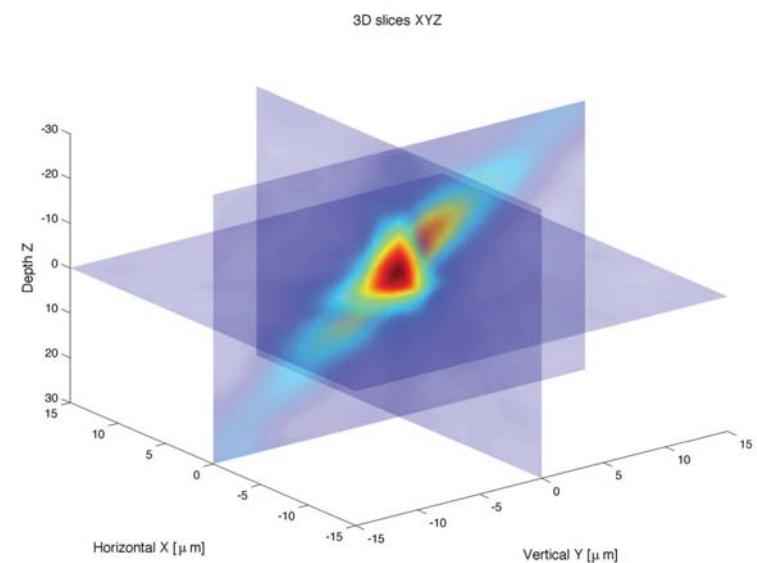
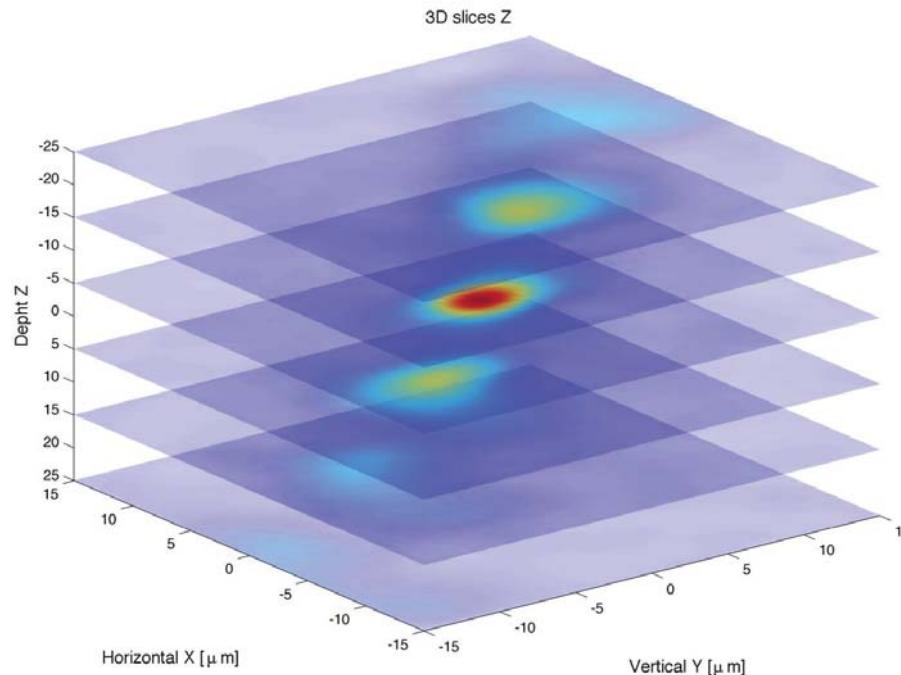
**L. Mercury, F.
Jamme and P.
Dumas
In preparation**



2D CHEMICAL IMAGES AT VARIOUS Z POSITION (1 Micron Step)



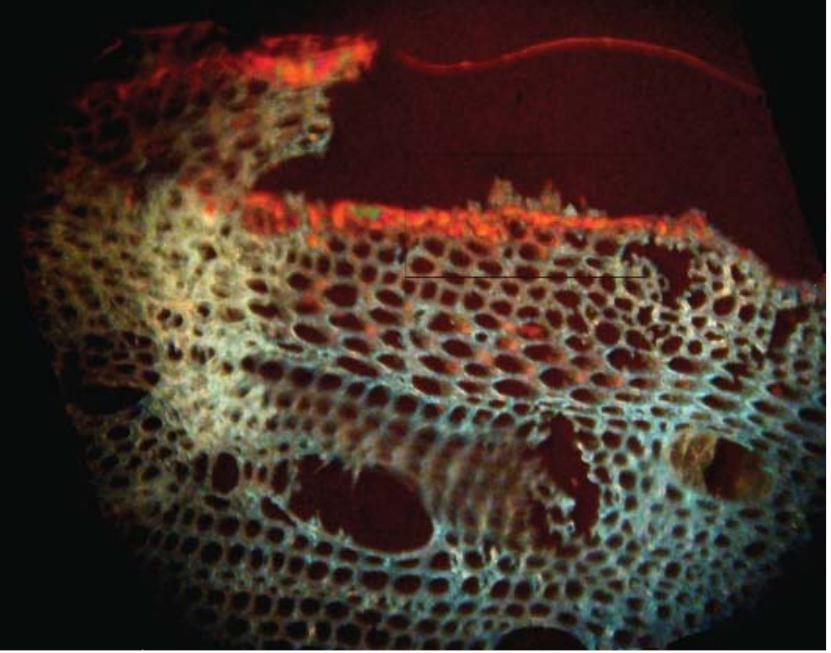
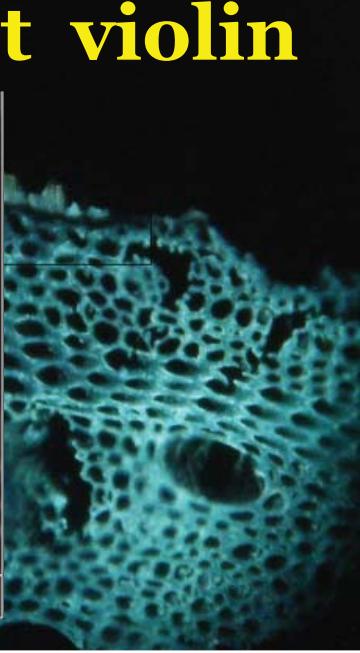
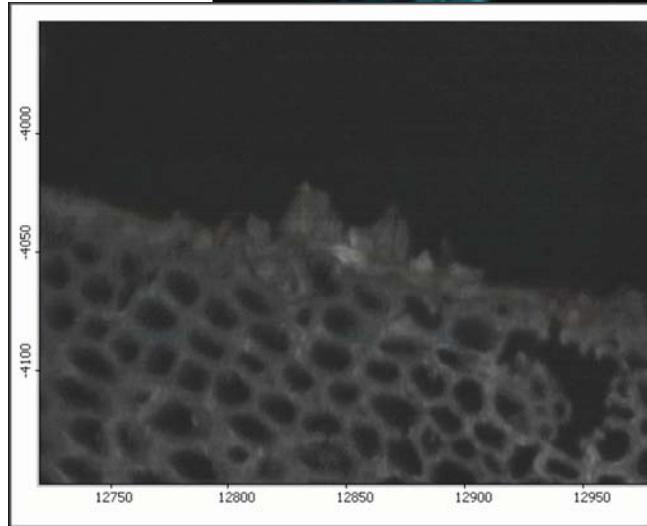
3D CHEMICAL IMAGE OF WATER



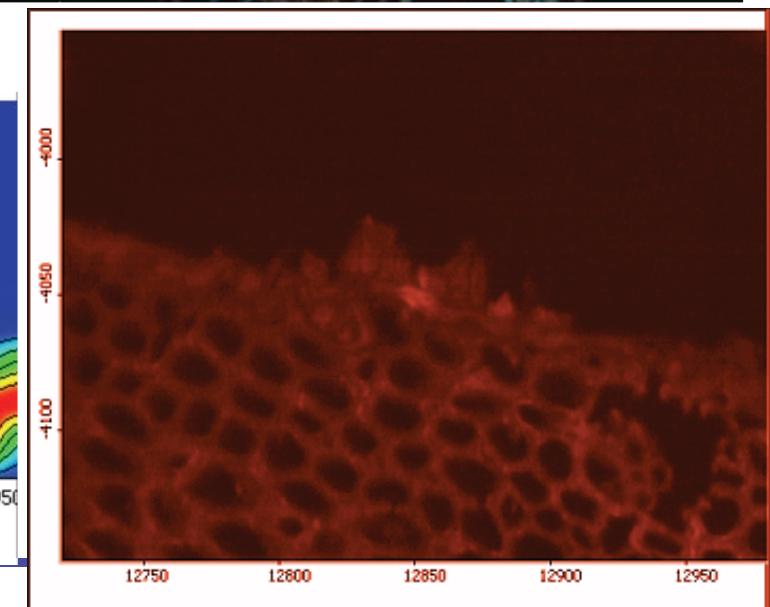
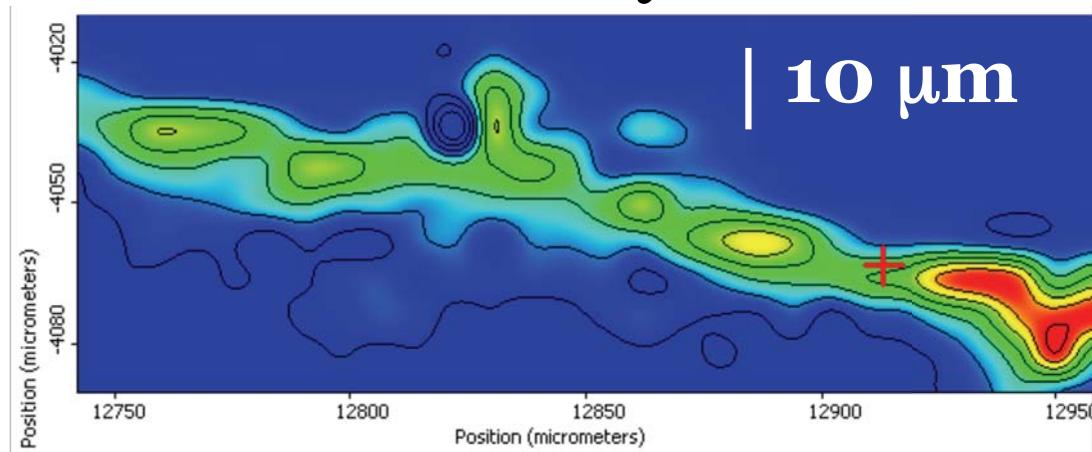
APPLICATIONS IN THE MID-INFRARED DOMAIN

4- Archeaology, Cultural Heritage

Ancient violin



Protein layer



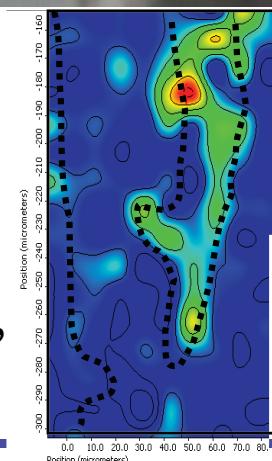


Portrait of Nicolaes van Bambeeck
Rembrandt (Leiden, 1606 - Amsterdam,
1669)

**Synchrotron IR with $12 \times 12 \mu\text{m}^2$,
reflection mode**

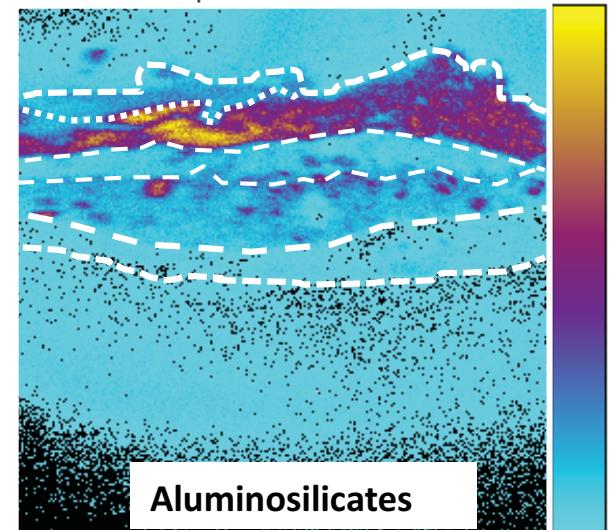
REMBRANDT FRAGMENT PAINTING

Fluorescence illumination

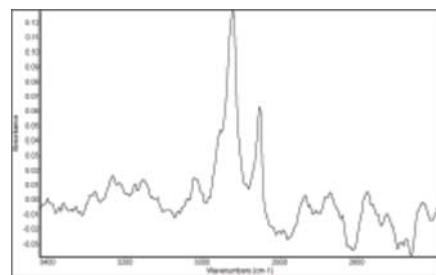


Field of view: $500.0 \times 500.0 \mu\text{m}^2$ emp.mif

— 100 μm



Alumino-silicates
mc:130 tc:7.530e+5



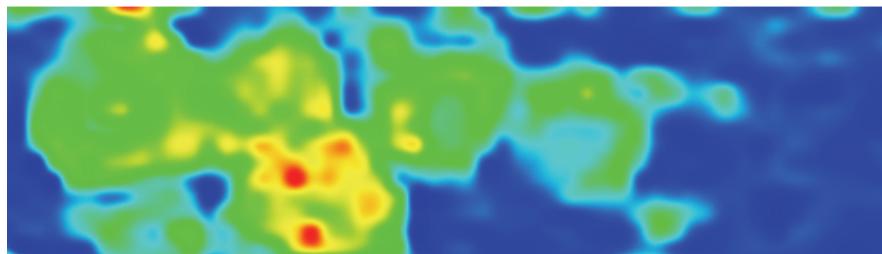
ToF SIMS

APPLICATIONS IN THE MID-INFRARED DOMAIN

5- Biology, Biomedical

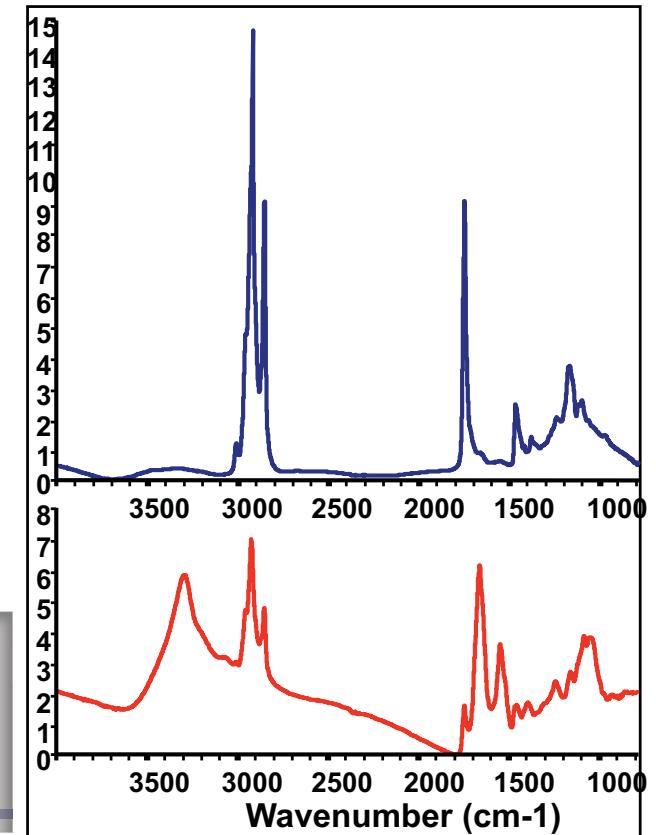
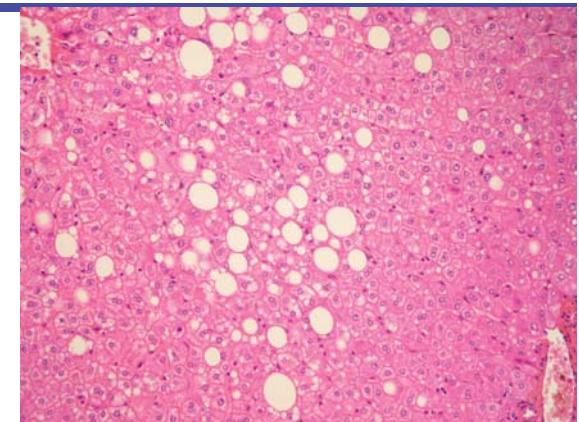
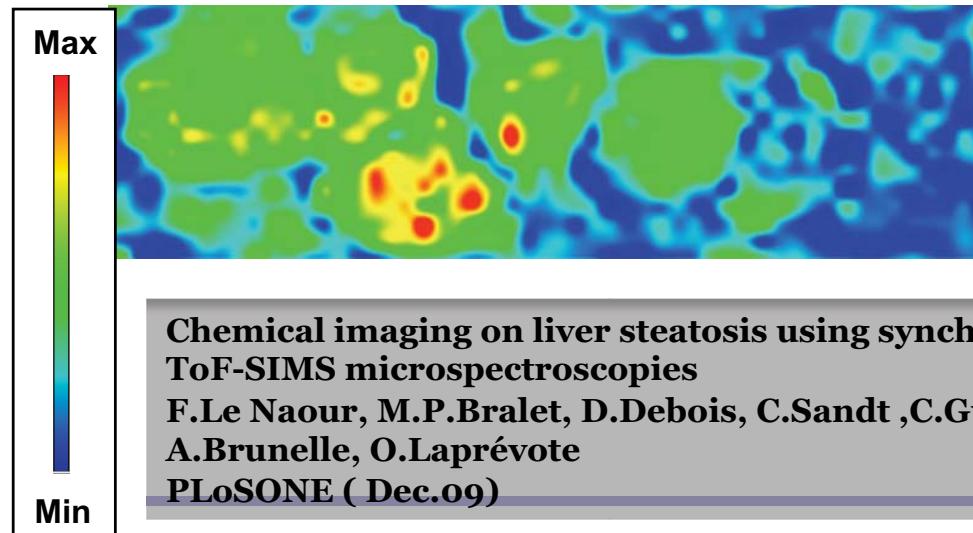
STEATOSIS ON LIVER

25 μm



**Unsaturated
lipids**

**Saturated
lipids**

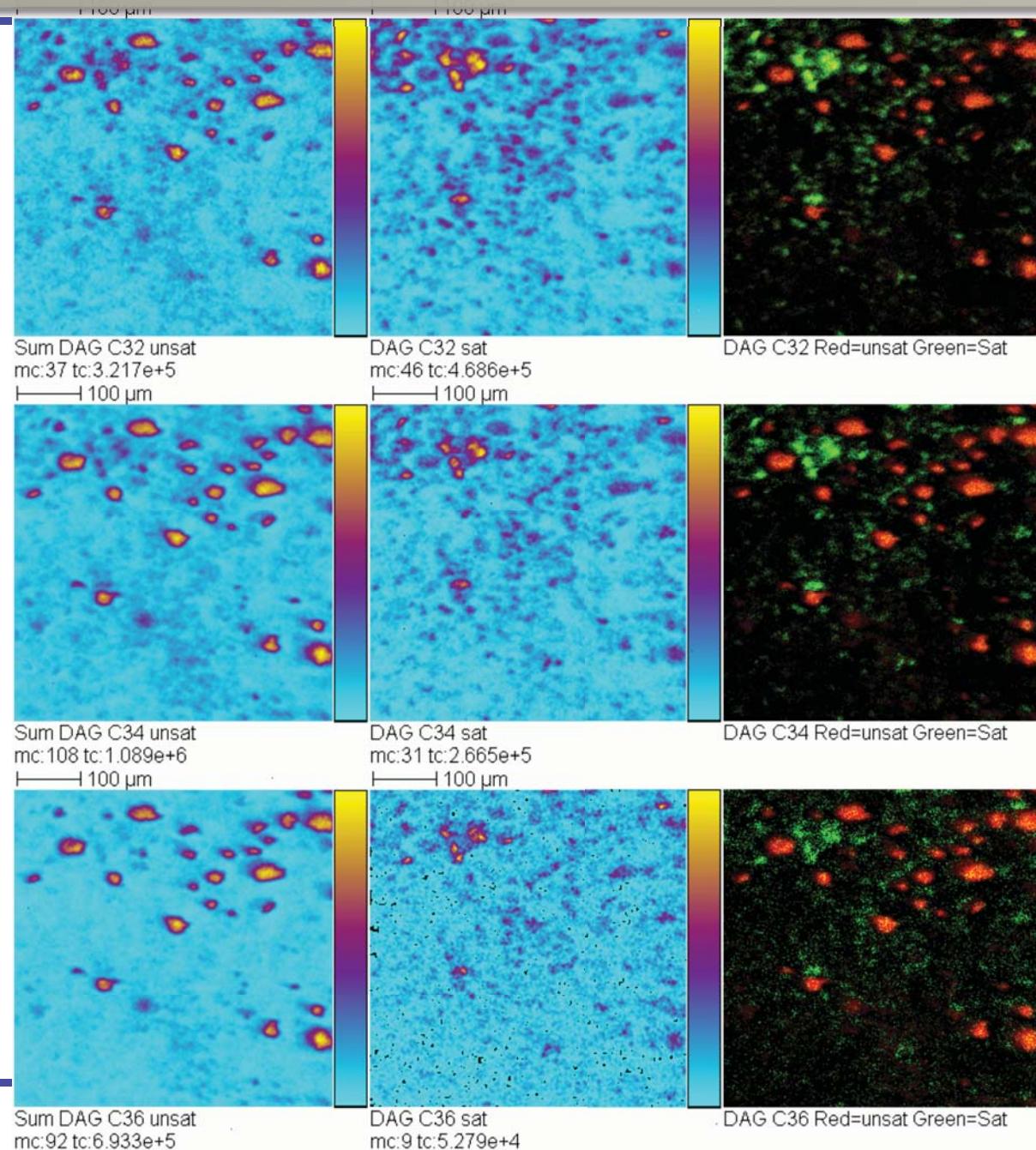


P. Dumas

STEATOSIS ON LIVER: COMBINING ToF SIMS

ToF-SIMS IV (Ion-Tof GmbH,
Münster, Germany)
reflectron-type TOF mass
spectrometer Primary ion
source: bismuth liquid metal
ion gun.

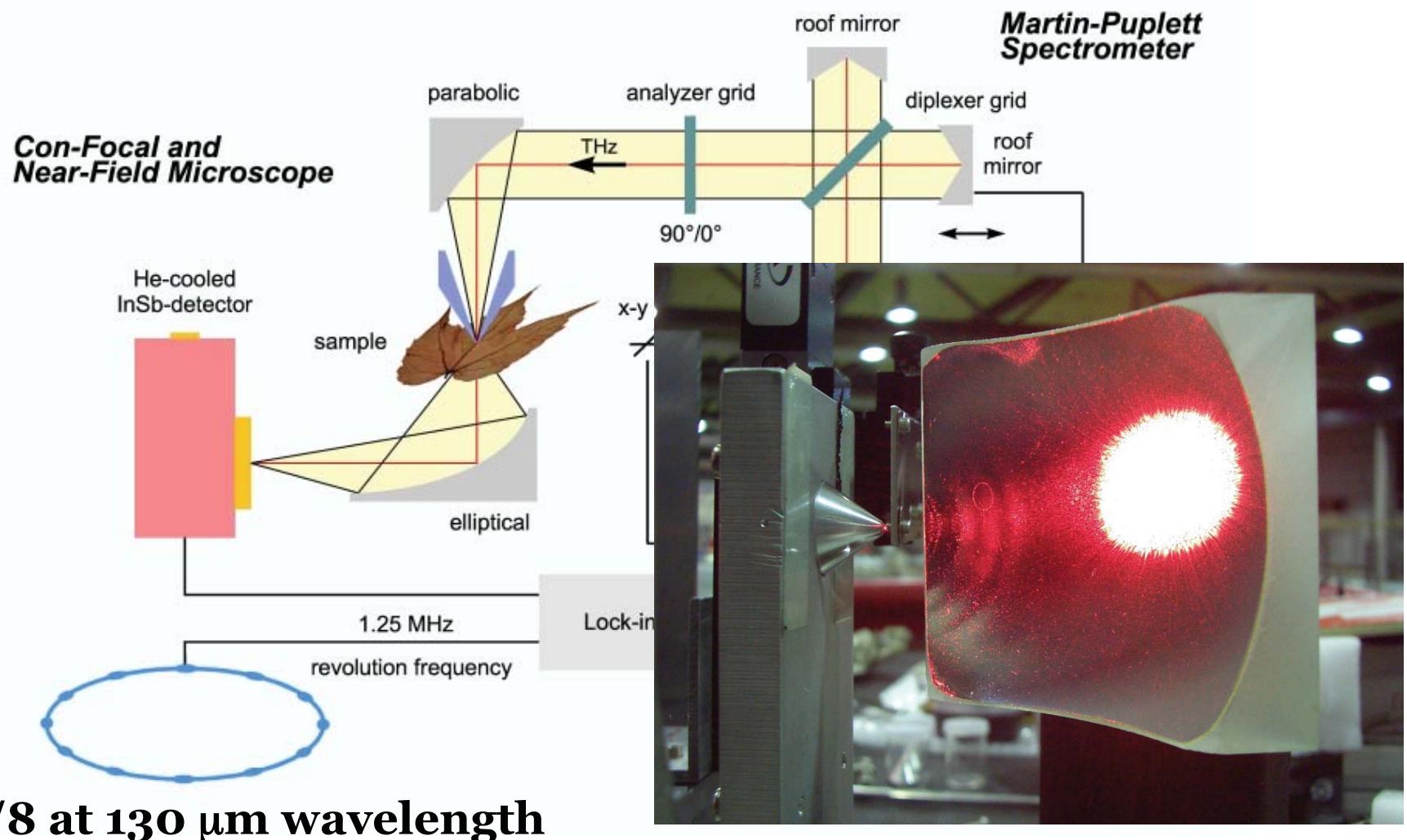
DAG= diacylglycerol



APPLICATIONS IN THE FAR-INFRARED DOMAIN

5- Near Field Microscopy

Courtesy of Ulrich Schade (Bessy-Germany)

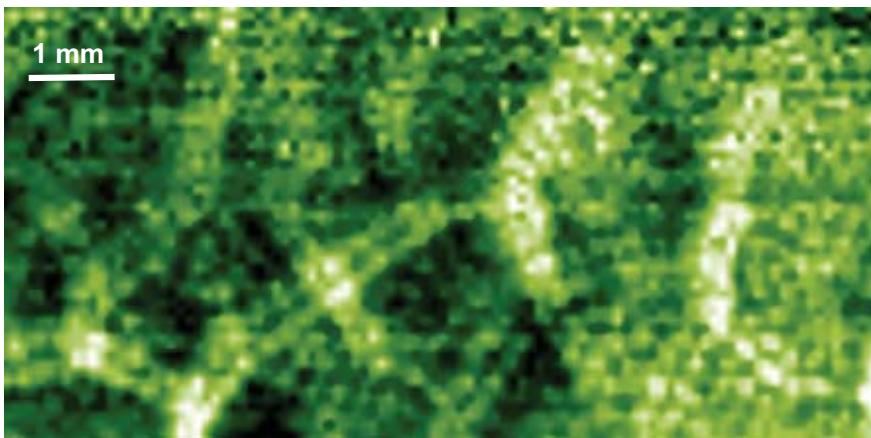


VIS- image



- **VIS and THz near-field image of a laurel leaf**
- **spatial resolution: $\sim 20 \mu\text{m}$**
- **spectral weight @ 1 mm wavelength (0.3 THz)**
- **veins and granular structure resolved**

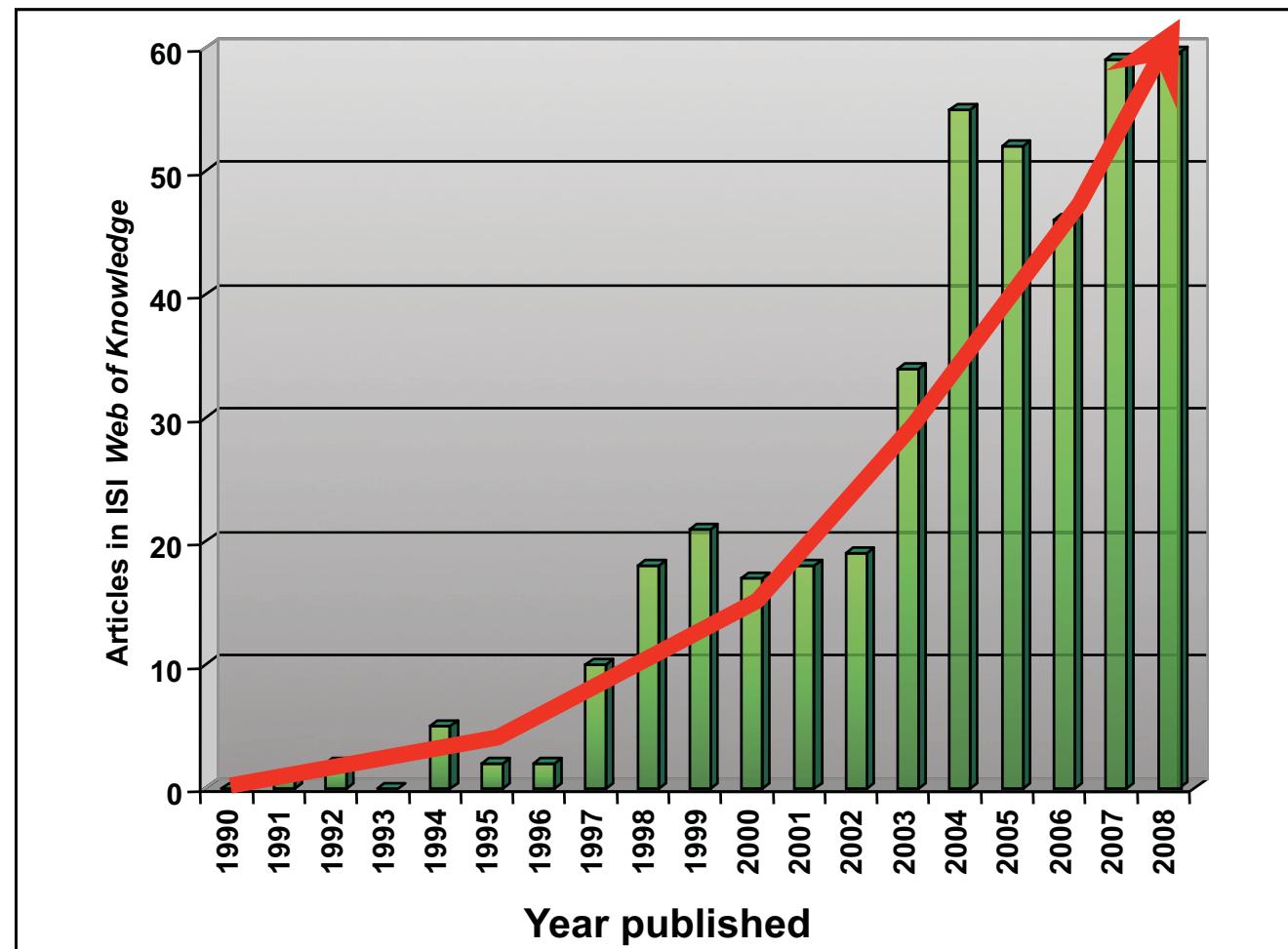
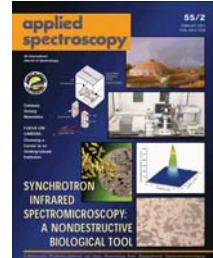
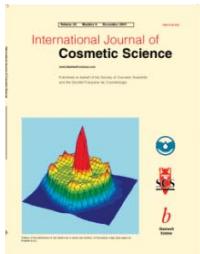
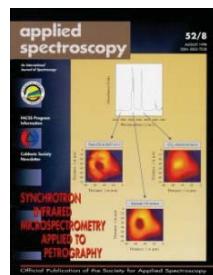
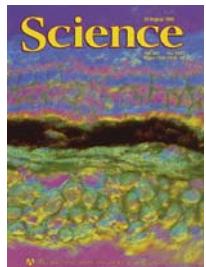
Near-field image



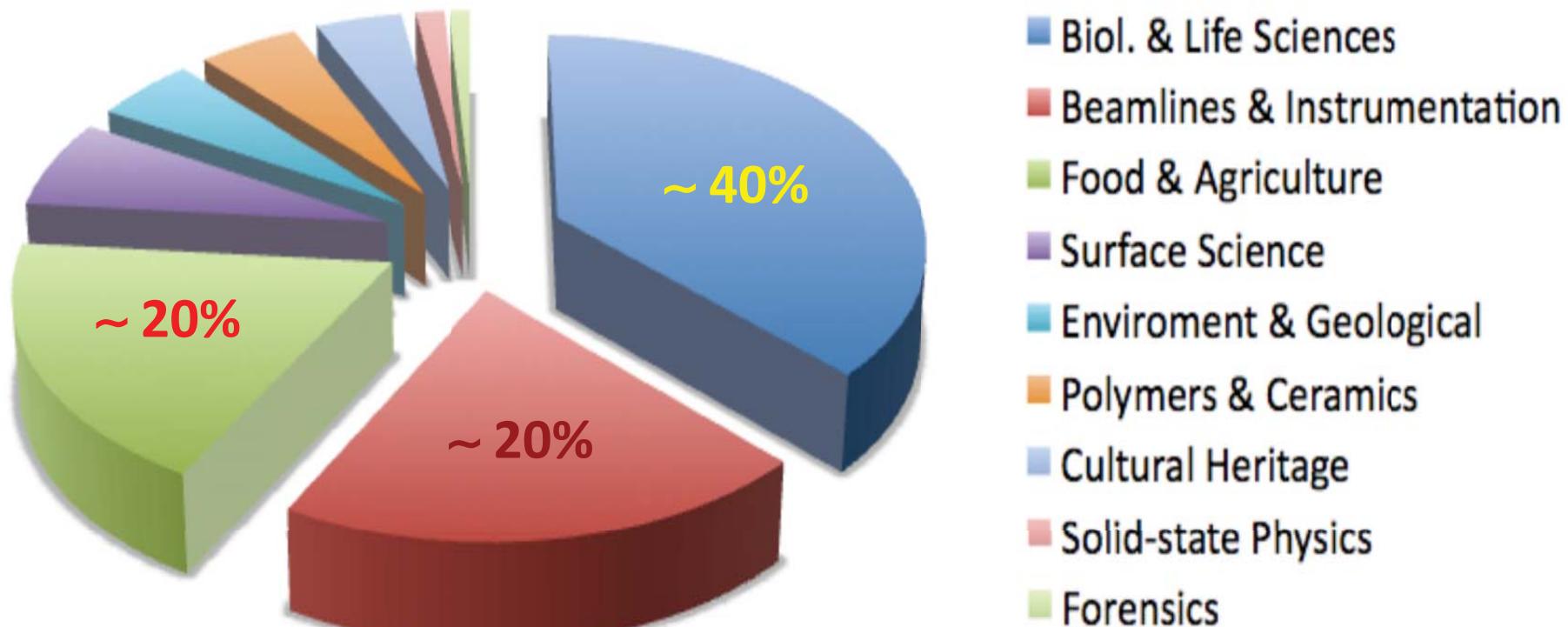
U. Schade et al., *APL* **84**
1422 (2004).

SYNCHROTRON INFRARED ACTIVITY WORDWIDE

Foreseen: 2 articles/week in 2010



From G. Santoro, G. Ellis (Madrid)



Last 270 ISI publications

From G. Santoro, G. Ellis (Madrid)

WORDWIDE STATUS



Operational

In construction

In design

- ✓ **Synchrotron radiation is a bright source of infrared photons**
- ✓ **Synchrotron infrared spectroscopy opened up new scientific challenges:**
 - Solid state physics
 - Surface science
 - Biology
- ✓ **Synchrotron infrared microscopy and imaging is increasingly popular not only in academic but also in application domains , as imaging will play major role with new methodologies**
- ✓ **Future is bright, including the filled gap of THz radiation**
- ✓ **Dynamics will be a future key issue (time domain investigation) and synchrotron source, will be among the « key players »**