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Infrared Spectroscopy and Microscopy using Synchrotron Radiation (Basics) Infrared Spectroscopy and Microscopy using Synchrotron

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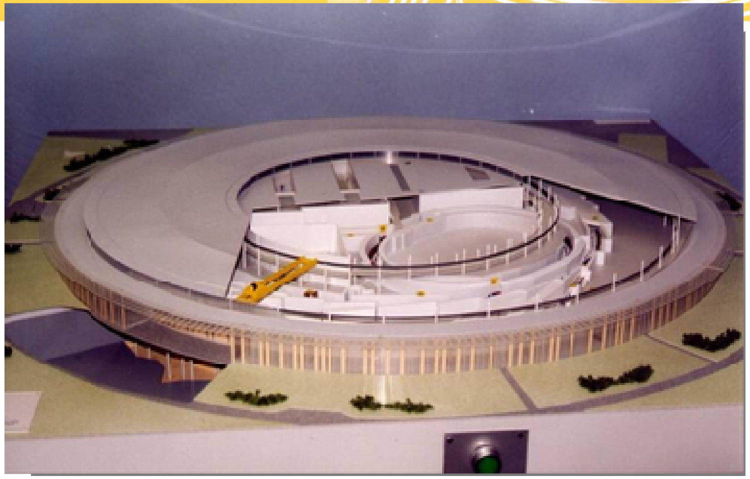

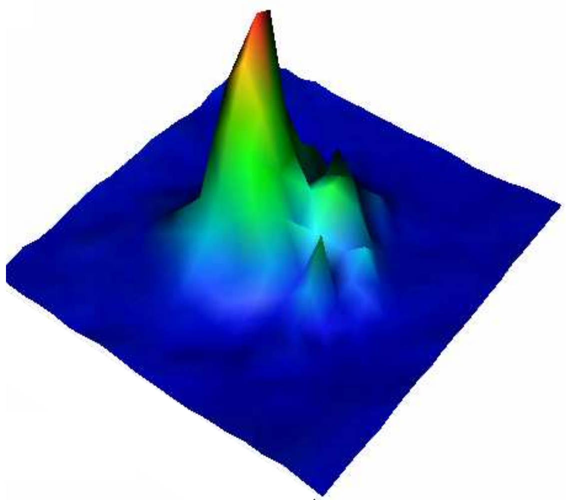

Infrared Spectroscopy and Microscopy using Synchrotron Radiation (Basics)

Paul Dumas

SOLEIL Synchrotron (France)

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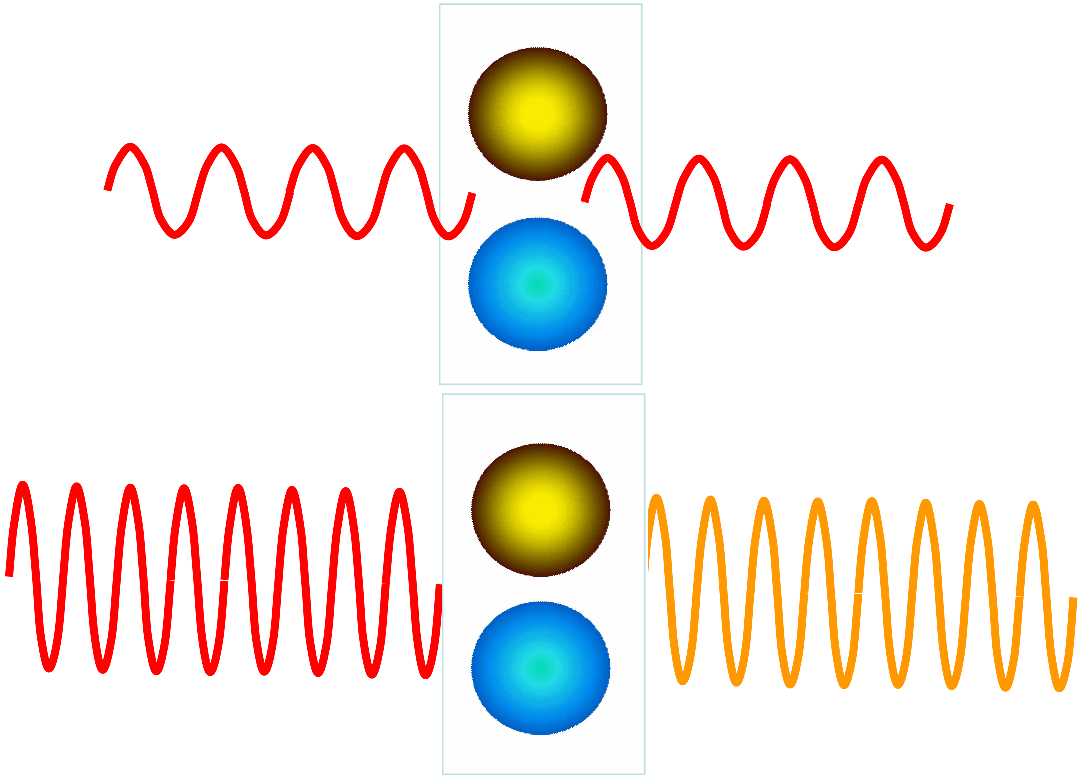
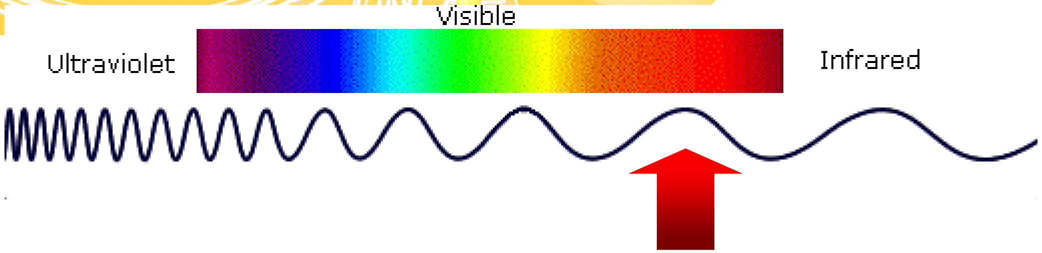
Vibrational motions

All matters, atoms, molecules and all kind of substances vibrate . Only at absolute zero temperature (-273.15 ℃ o r -459.67℉), that all stop vibrating.



The Infrared energy range



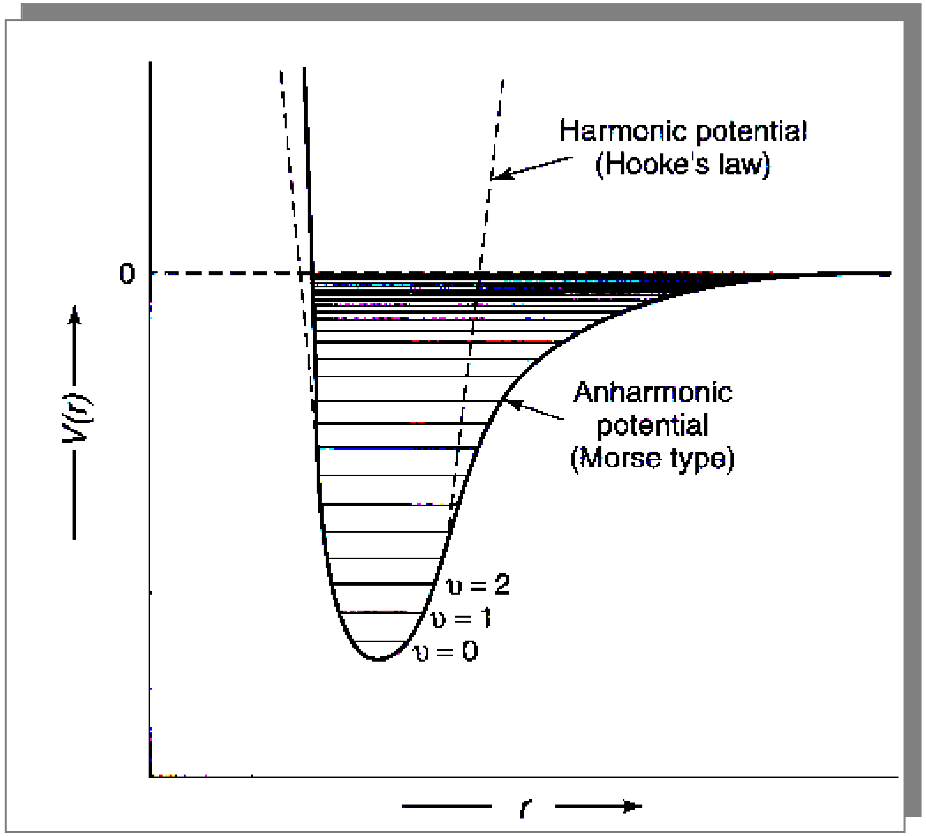
✓ **Energy range: 1 to ~500 µm**
(10000 to 20 cm-1 or 1.23 to 0.0025 eV)

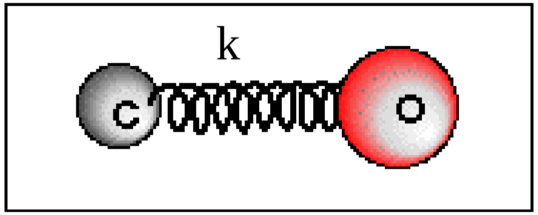
- ✓ ~1 to ~2.5 µm (10000-4000 cm^{-1}) **Near IR**
- ✓ ~2.5 à 20 µm (4000-500 cm^{-1}) **Mid- IR**
- ✓ ~20 à ~2500 µm (500-50 cm^{-1}) **Far IR**

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

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

Compound identification using vibrational motions





m_1 m_2

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

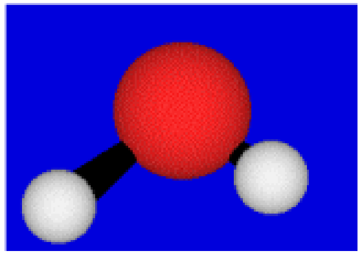
Frequency shift with:

- nature of atoms

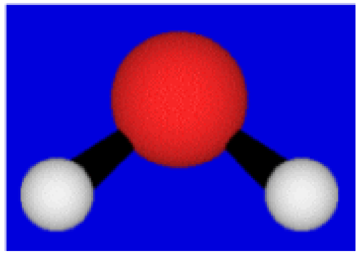
- environment change

IR frequency domain and vibrations

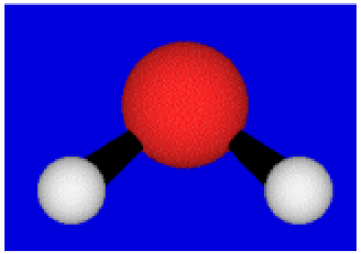
~3.3 μm



3756 cm-1

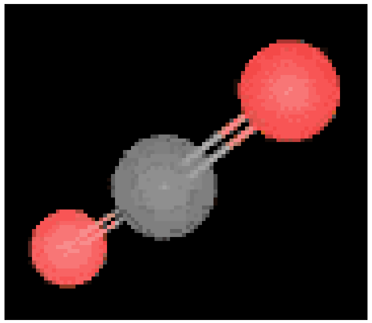


3652 cm-1

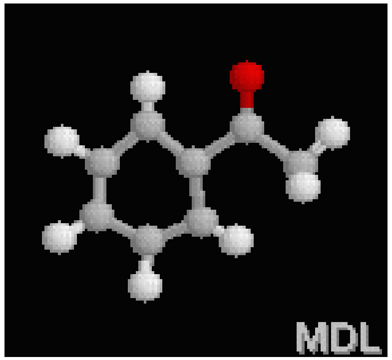


1595 cm-1

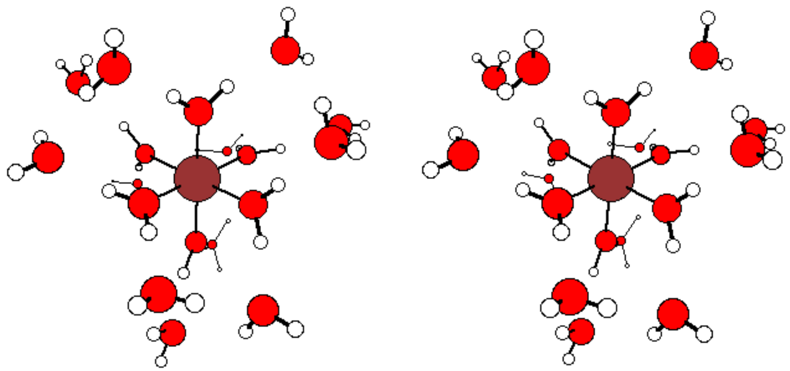
~6 μm



~10 μm



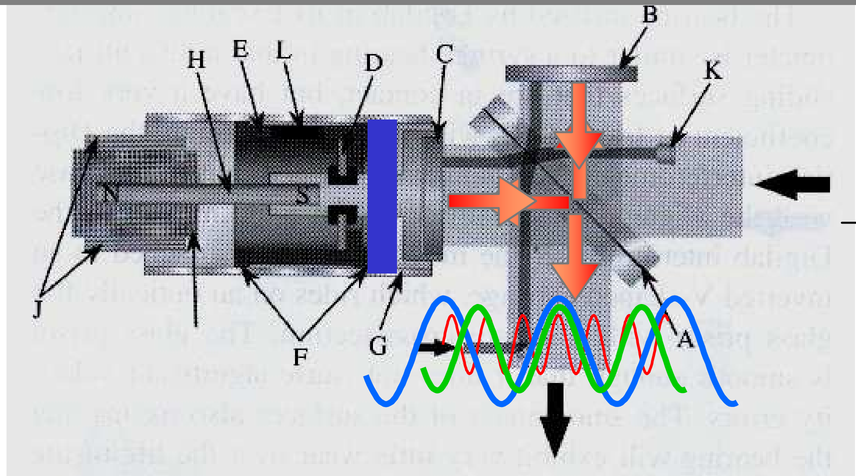
~30 μm

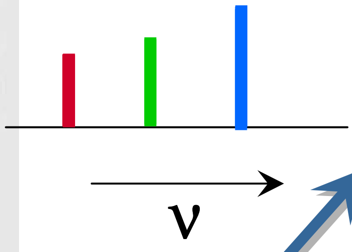


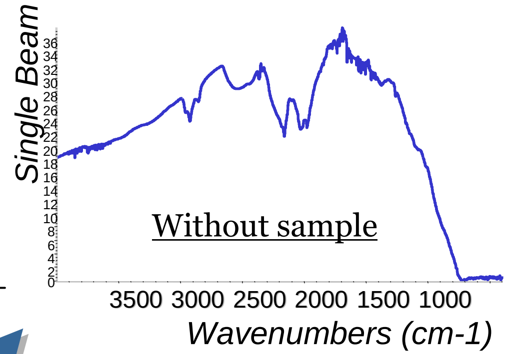
But also IR reflectivity and conductivity ….
(brodband change)

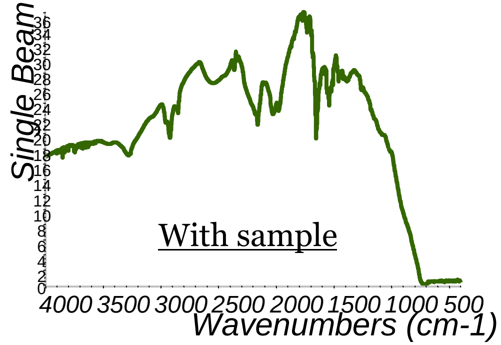
Fourier Transform Spectroscopy

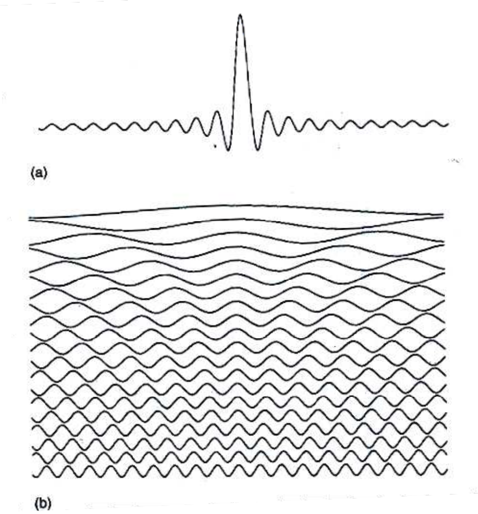
No monochromator, all wavelengths collected



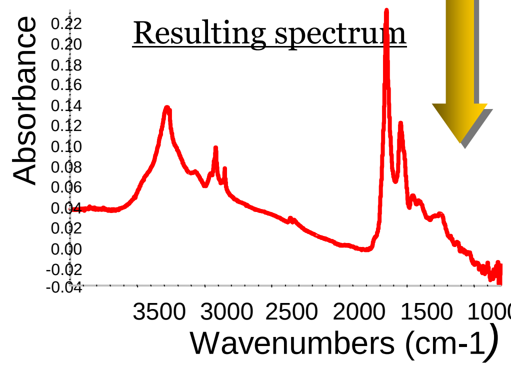








Fast Fourier Transform



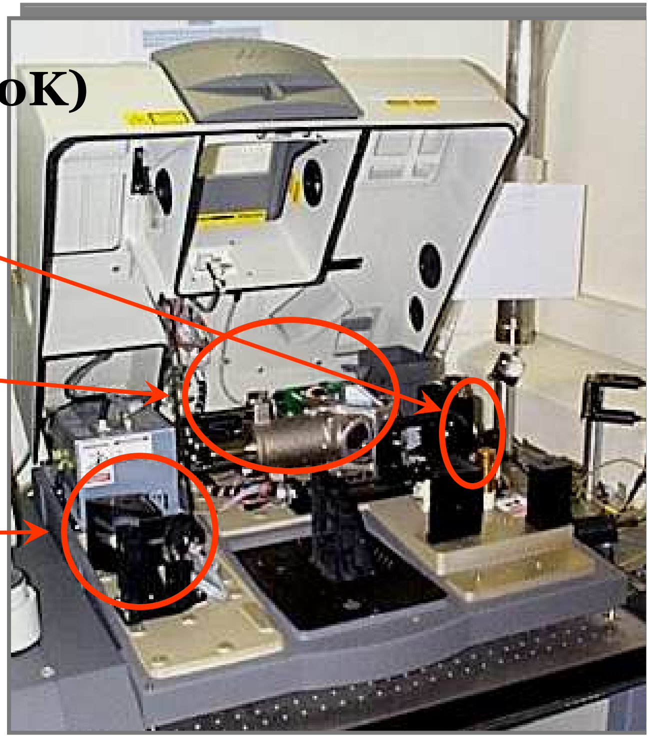
Infrared spectroscopy today…

- ✓ **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



Main features

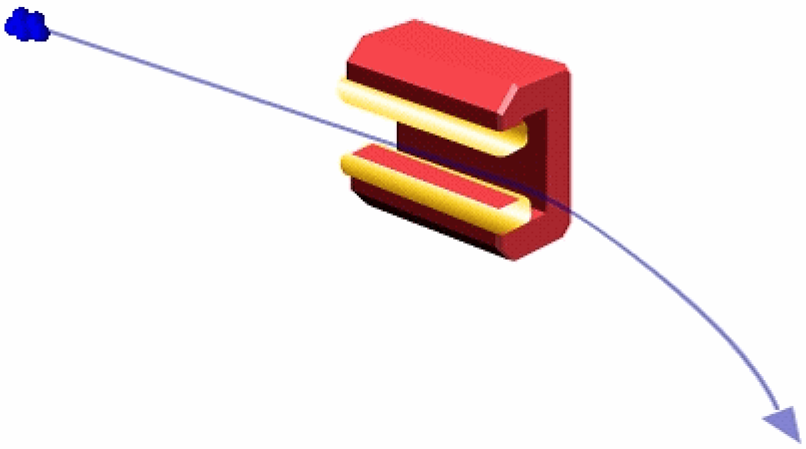
- Each functional group has an ensemble of motions (vibrational) specific of the molecular group (fingerprint)

- 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.

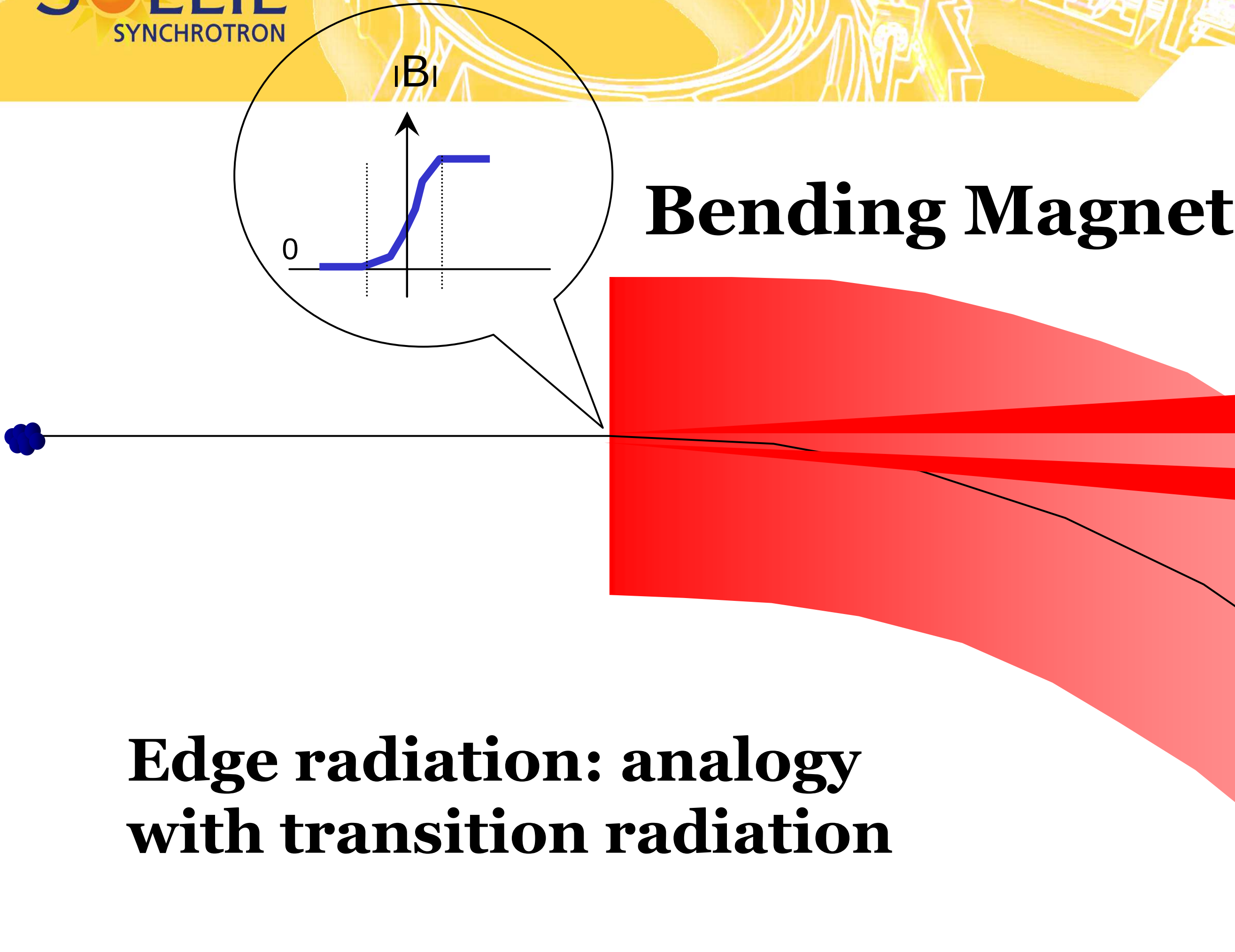
- The technology is rather simple, and the data are obtained quite quickly (few seconds).

Synchrotron Infrared Emission: Properties and Characteristics



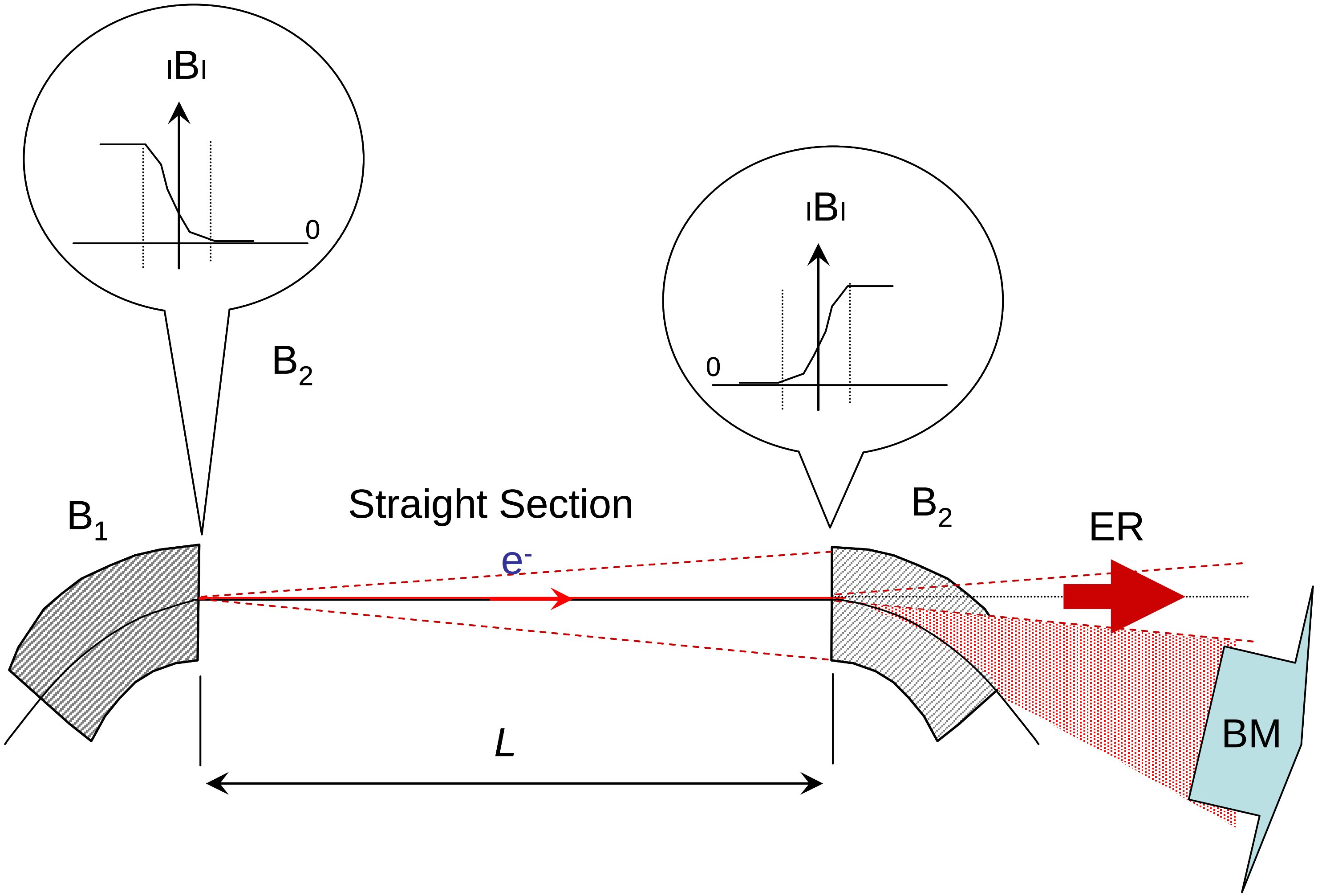
Where are the main important source of IR emission?

Bending Magnet



Edge radiation: analogy with transition radiation

Interferences due to the edge emission of the upstream dipole



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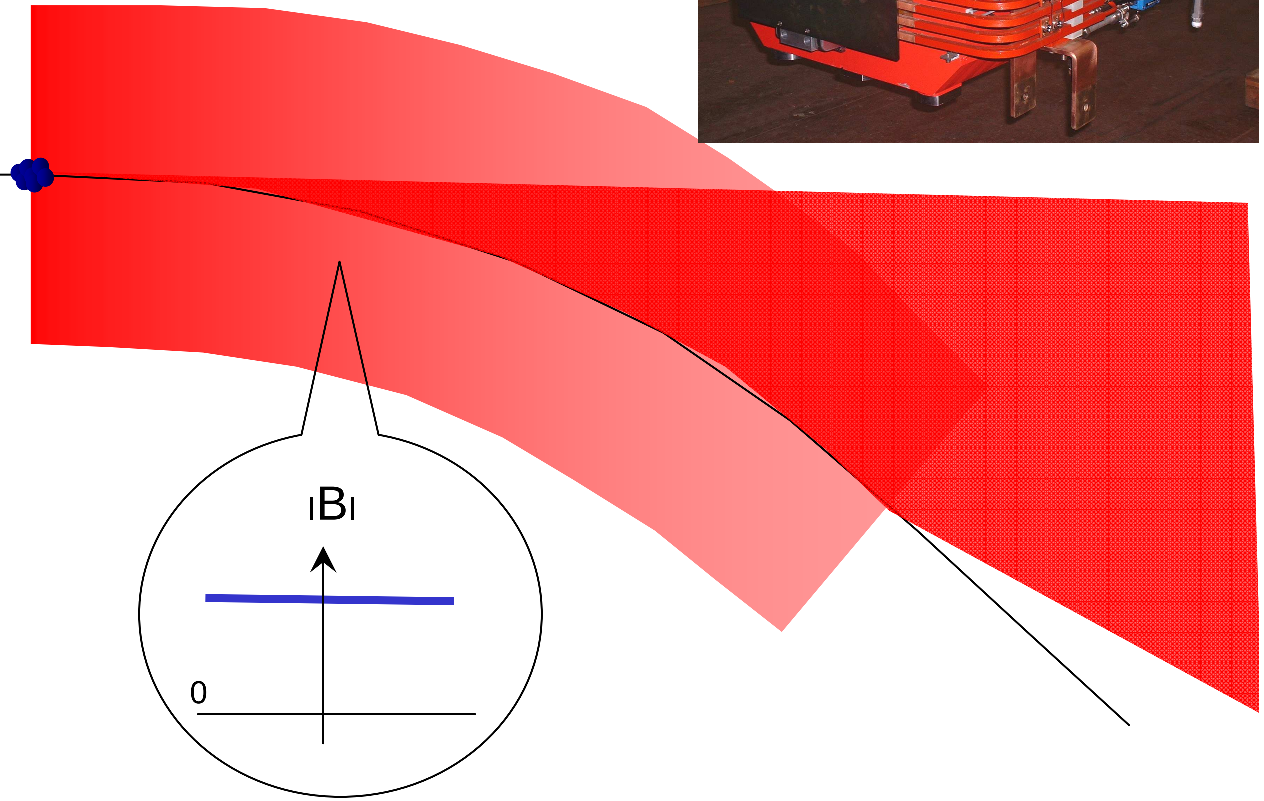
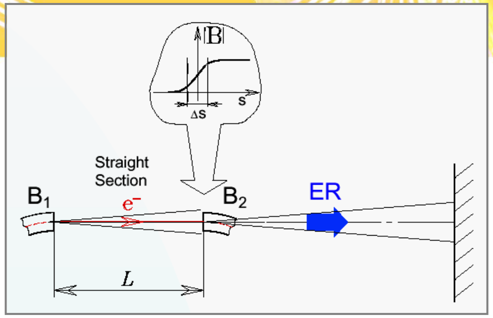
Bending Magnet



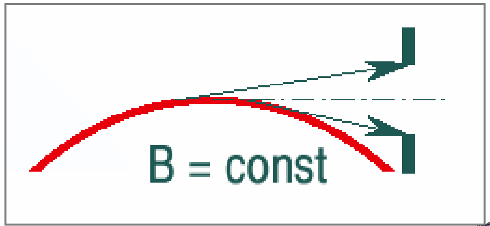
Constant Field Emission

Synchrotron radiation and infrared emission

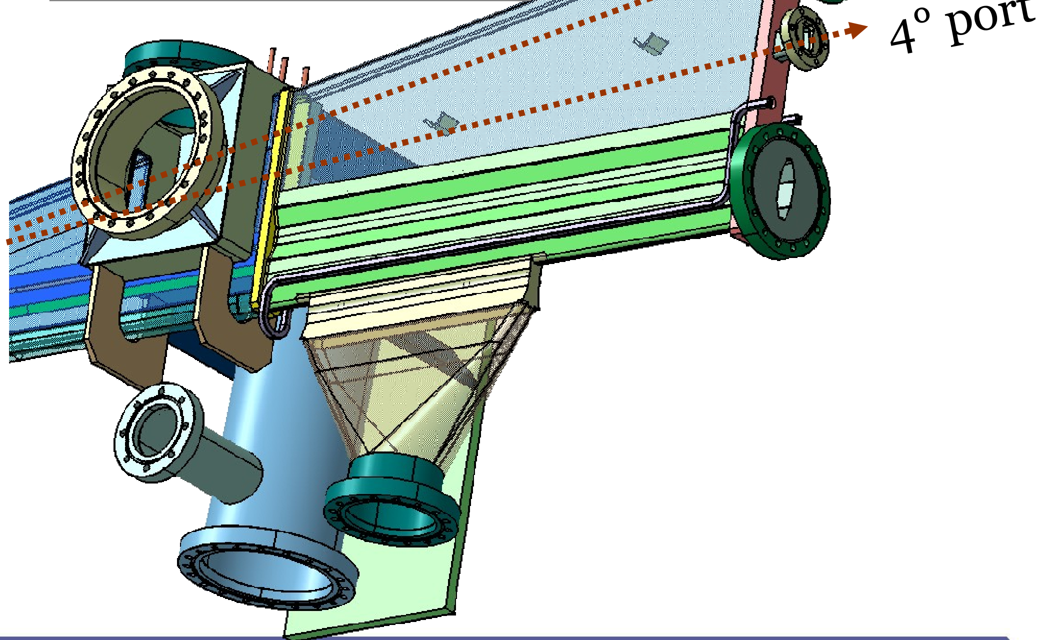
Edge emission:

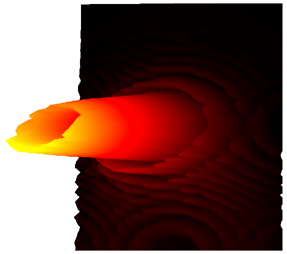


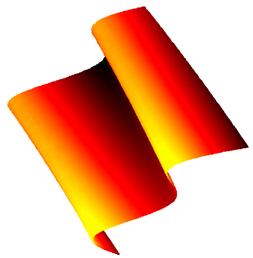
Bending magnet emission:



Exemple for 10µm wavelength

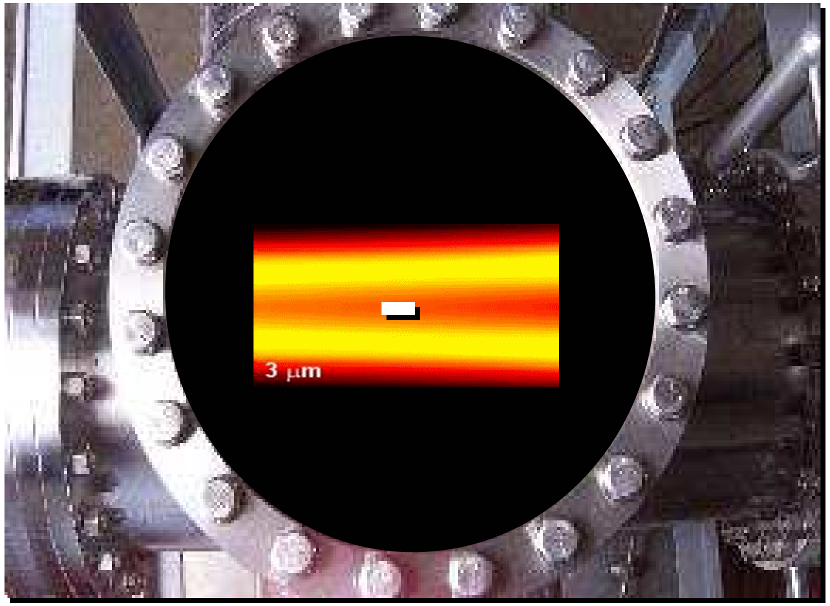




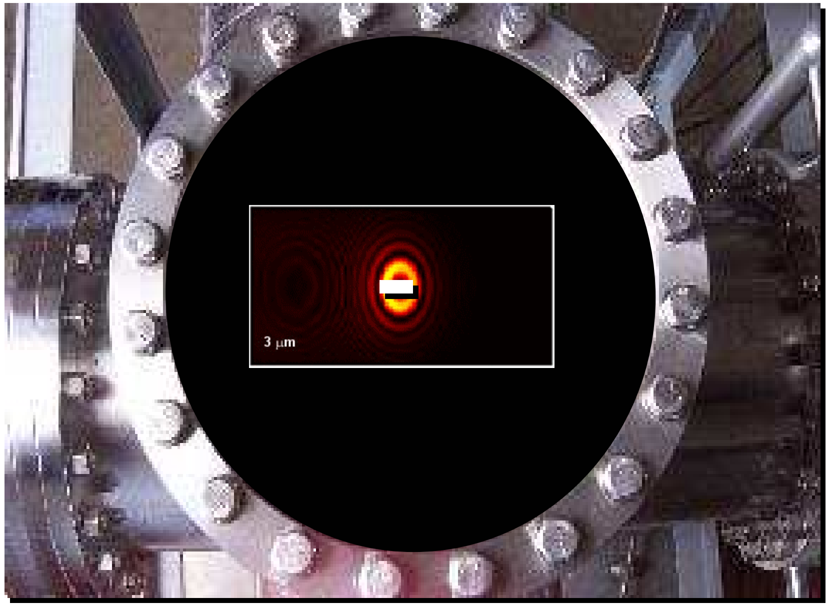


History of synchrotron IR ?

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



Bending magnet radiation



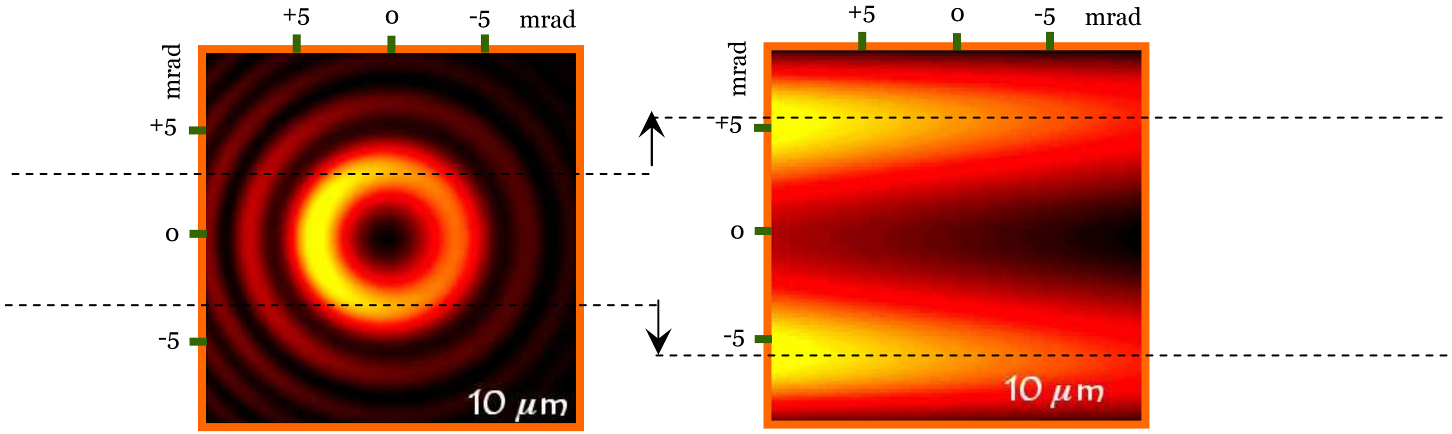
Edge radiation

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

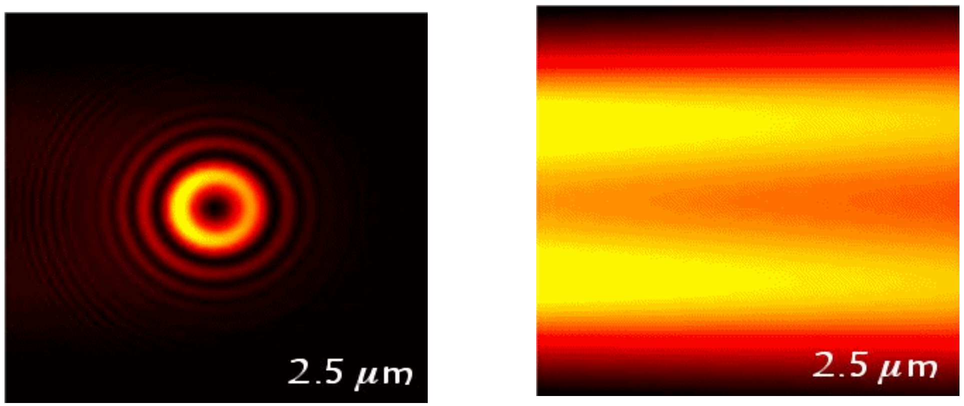
Edge radiation versus bending magnet

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



Emission angles for infrared radiation

For bending magnet radiation, the 'natural opening angle' (the total angle required to leave 90% of the light emitted outside the chamber) is given by a simple formula :

$$\theta_{natural}(radians) = \left(\frac{3\lambda}{4\pi\rho}\right)^{1/3}$$

For edge radiation one can estimate the angular size of the first interference ring of the intensity distribution, at a distance *z*: .

$$r_{\perp 1}/z \approx 2\left[2\lambda(z+L)/(zL)\right]^{1/2}$$

How do they compare in intensity?

(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*

How do they compare in intensity?

(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 ≈ 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

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

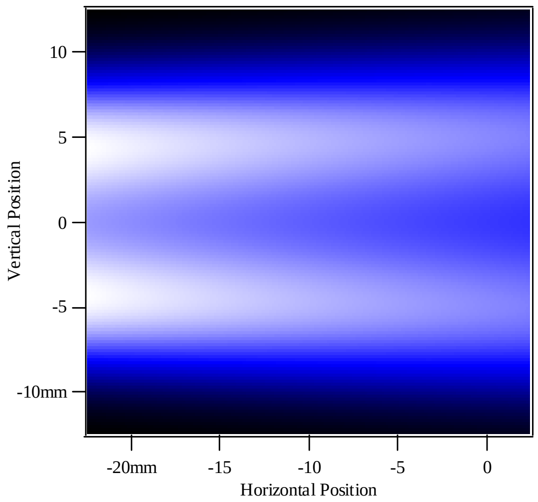
Multichannel Detection with a Synchrotron Light Source *G.L. Carr, O. Chubar and P. Dumas*

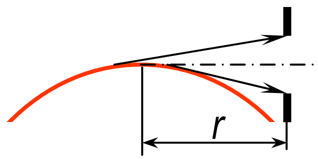
SOLEIL SYNCHROTRON

Australian Light Source

Infrared Synchrotron Radiation from Bending Magnet

Intensity Distribution in transverse plane close to the source



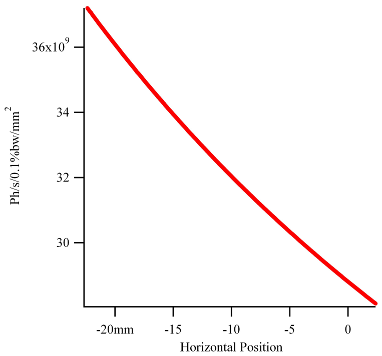


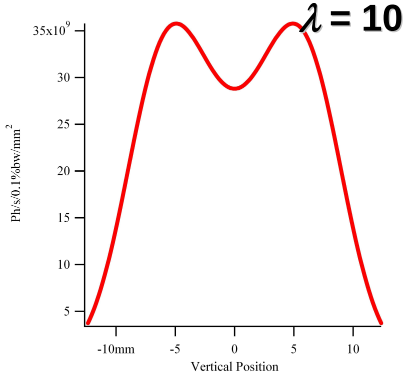
Natural Opening Angle:

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

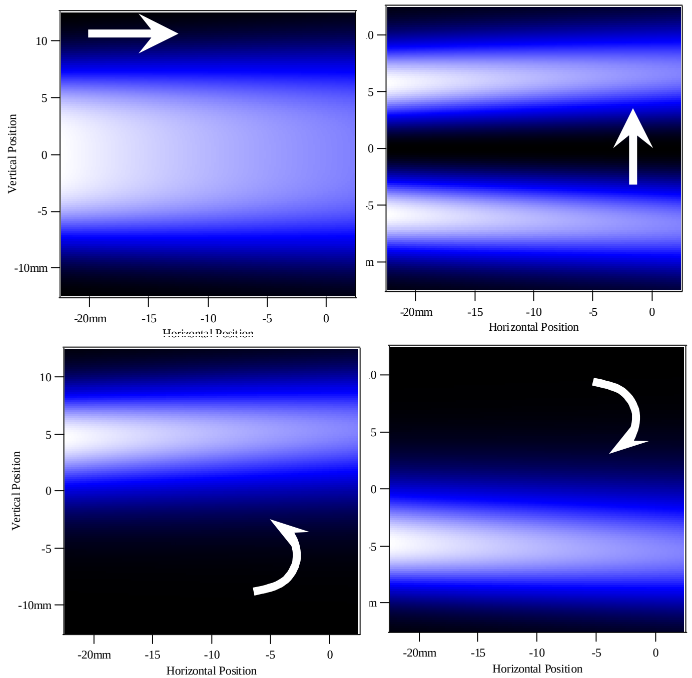
$$(\lambda >> \lambda_c)$$

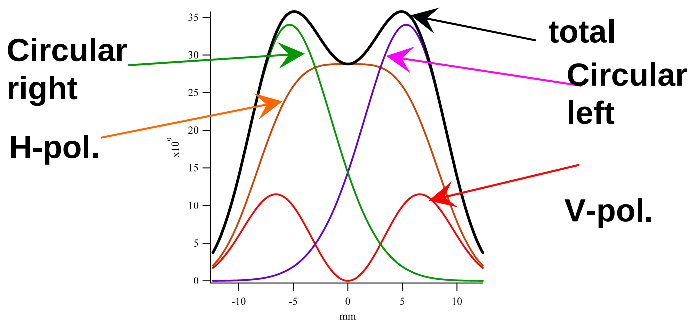
E **= 3.0 GeV;** ***B*** **= 1.30 T**
ρ=7.69 m
I **= 200 mA**
λ = 10 µm,r= 1.23 m





Intensity Distributions at Various Polarizations

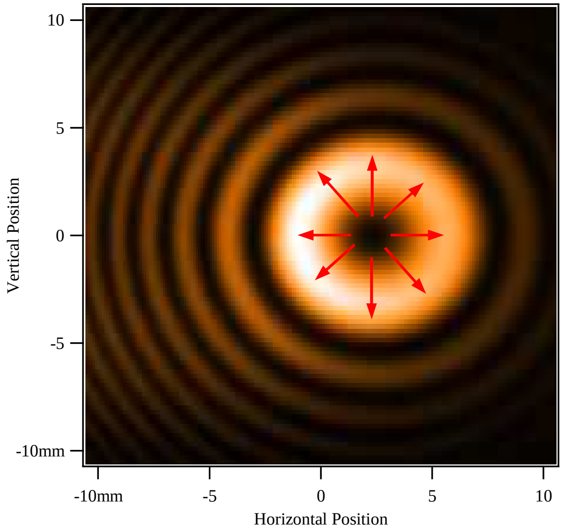


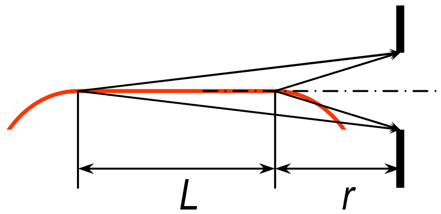


Infrared Synchrotron Radiation from Edge of bending magnet

SOLEIL SYNCHROTRON

"Pure ER" is polarized "Radially"

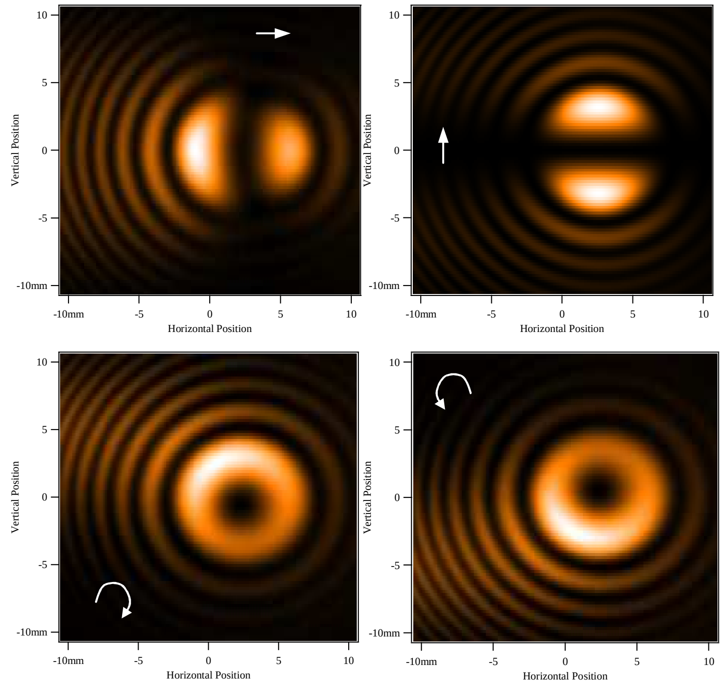




E = 3.0 GeV
B_{max} = 1.30 T
I = 200 mA

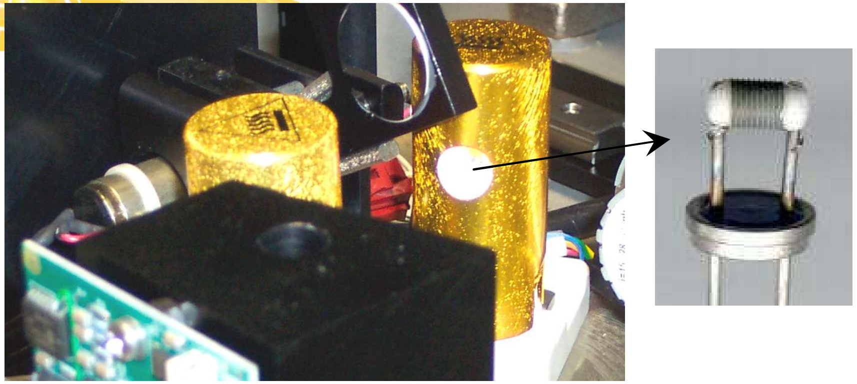
L = 5 m
r = 1.23 m
λ = 10 µm

Intensity Distributions at Various Polarizations



Is the synchrotron IR beam very intense?

Blackbody radiation



S_{src} The spectral flux emitted by isotropic black-body source into a solid angle $\Omega = 2\pi \sin\theta_r$ (where 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

c =Speed of light

λ =Radiation wavelength

k_B =Boltzmann constant

S_{src} =Source area

S_{src}

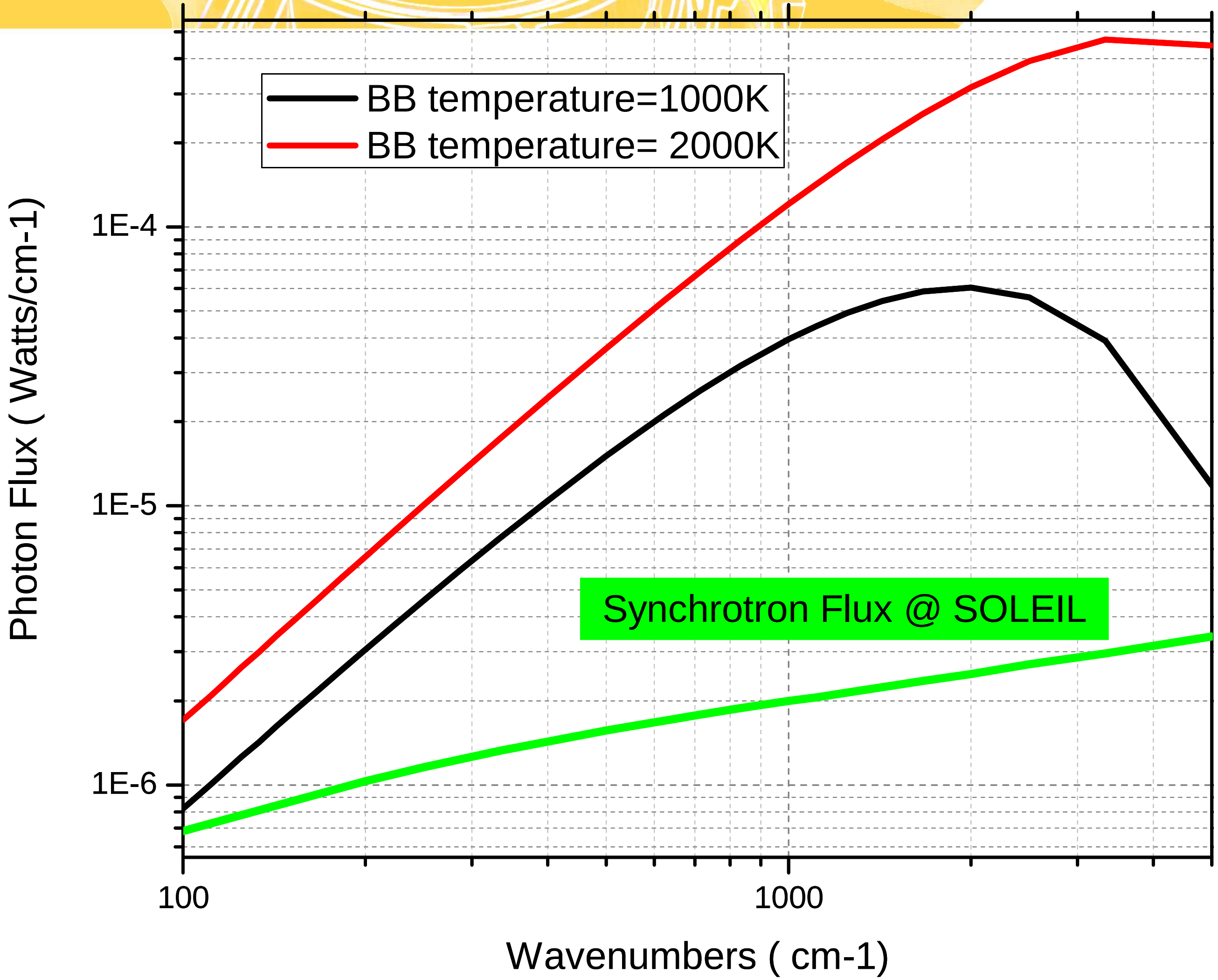
Blackbody radiation

Convertir photons/sec/0.1%bw in Watts/cm-1

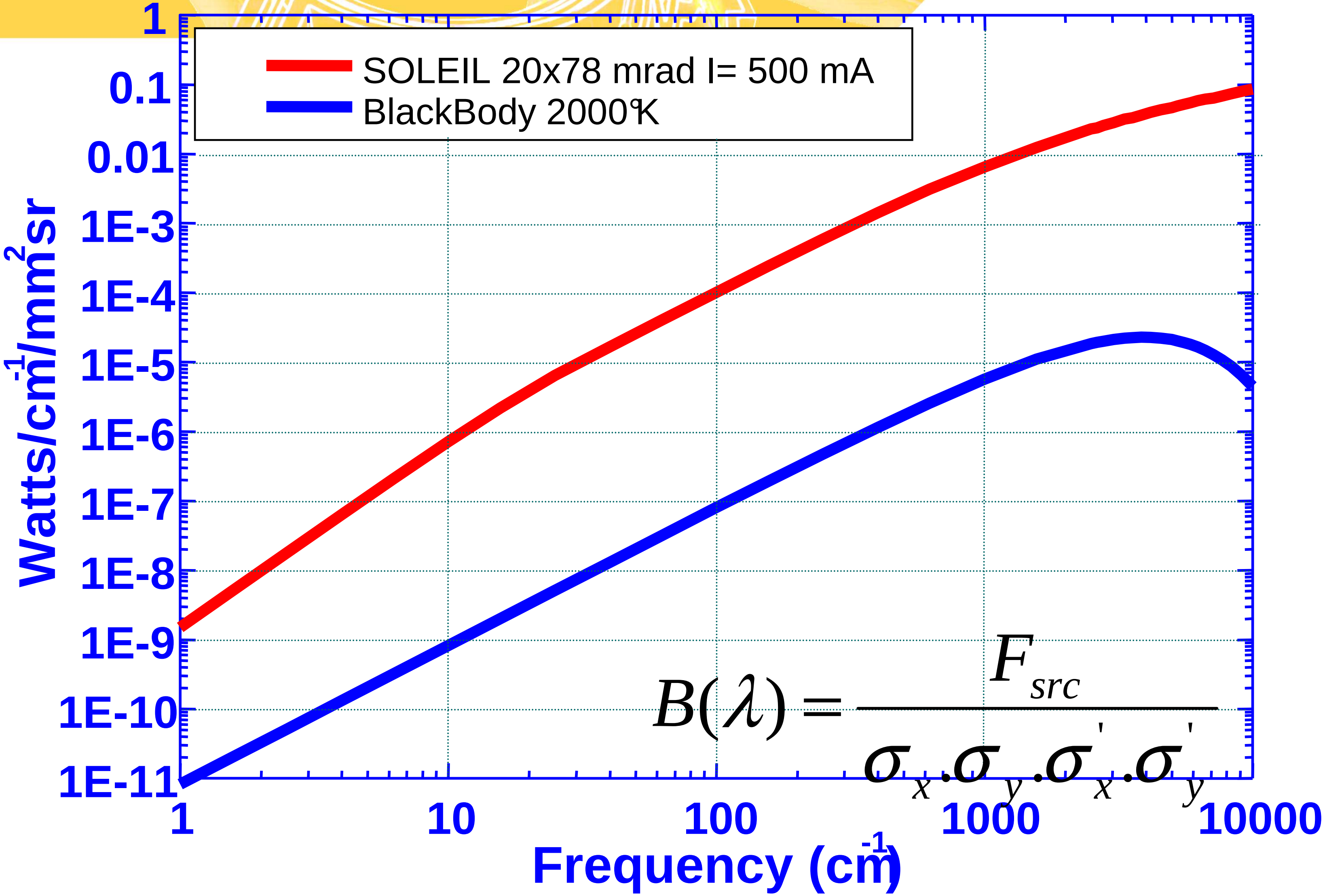
$$\left(\frac{dW}{d(1/\lambda)}\right)_{BB}\left[\frac{W}{cm^{-1}}\right] \approx 3.74\cdot 10^{-2}\,\frac{S_{src}[mm^2]\sin\theta_r}{\lambda^3[\mu m]}\left[\exp\left(\frac{1.44\cdot 10^4}{\lambda[\mu m]T[K]}\right)-1\right]^{-1}$$

Consider all emitted photons from the blackbody , over al solid angle

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

Brightness in the infrared region(1)

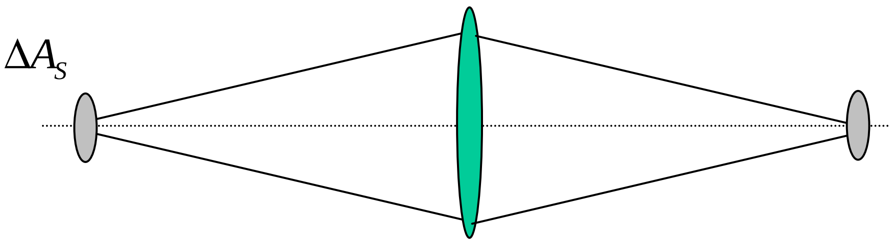
Synchrotron Center	Energy (GeV)	Maximum operating current (mA)	Horizontal electron source size (µm)	Vertical electron source size (µm)
*ESRF(France)**	6.0	200	~44	~9
*Spring-8(Japan)**	8.0	100	~83	~19.5
Elettra(Italie)	2.0	300	~239	~13.5
MaxII(Sweden)	1.5	200	~350	~14.5
SOLEIL (France)	2.75	500	~180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

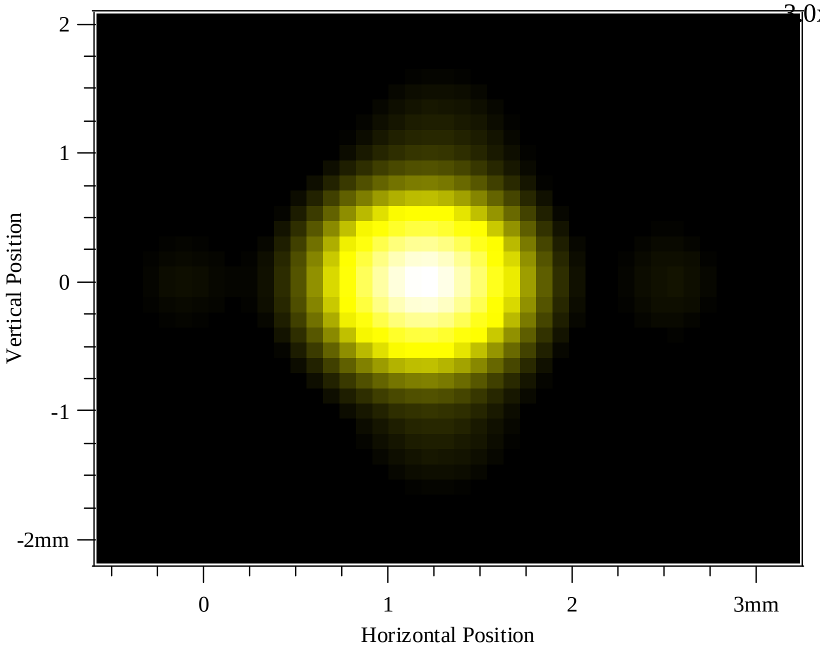
To obtain a rough estimation of the diffraction-limited SR source size : $\sim \left(\lambda^2 \rho\right)^{1/3}$

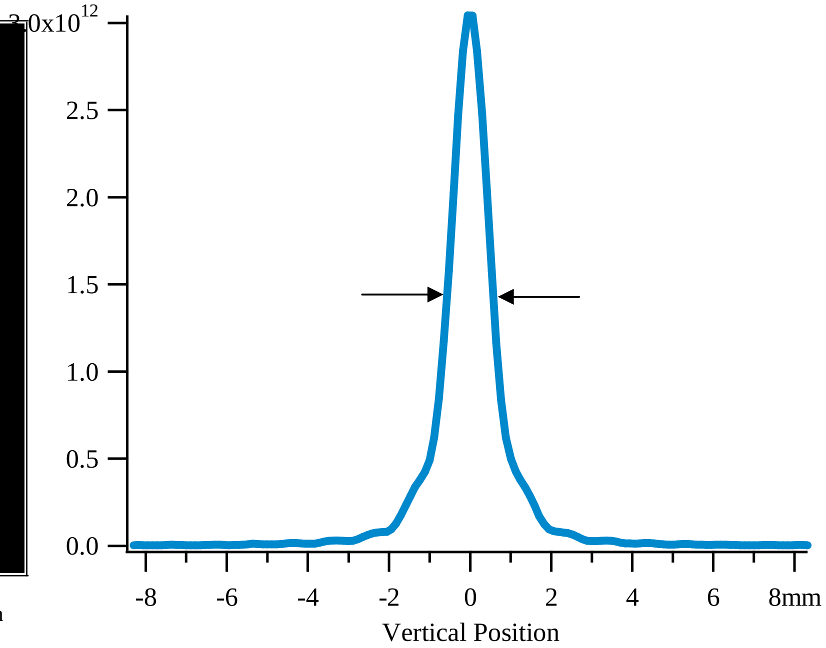
Numerical methods of Fourier optics can be used :back-propagation of the wavefront (at a specific wavenumber) to the source position, or by simulating of the radiation focusing at optical magnification equal to 1



Brightness in the infrared region(3)

Apparent source size @ Australian synchrotron
λ=10 μm



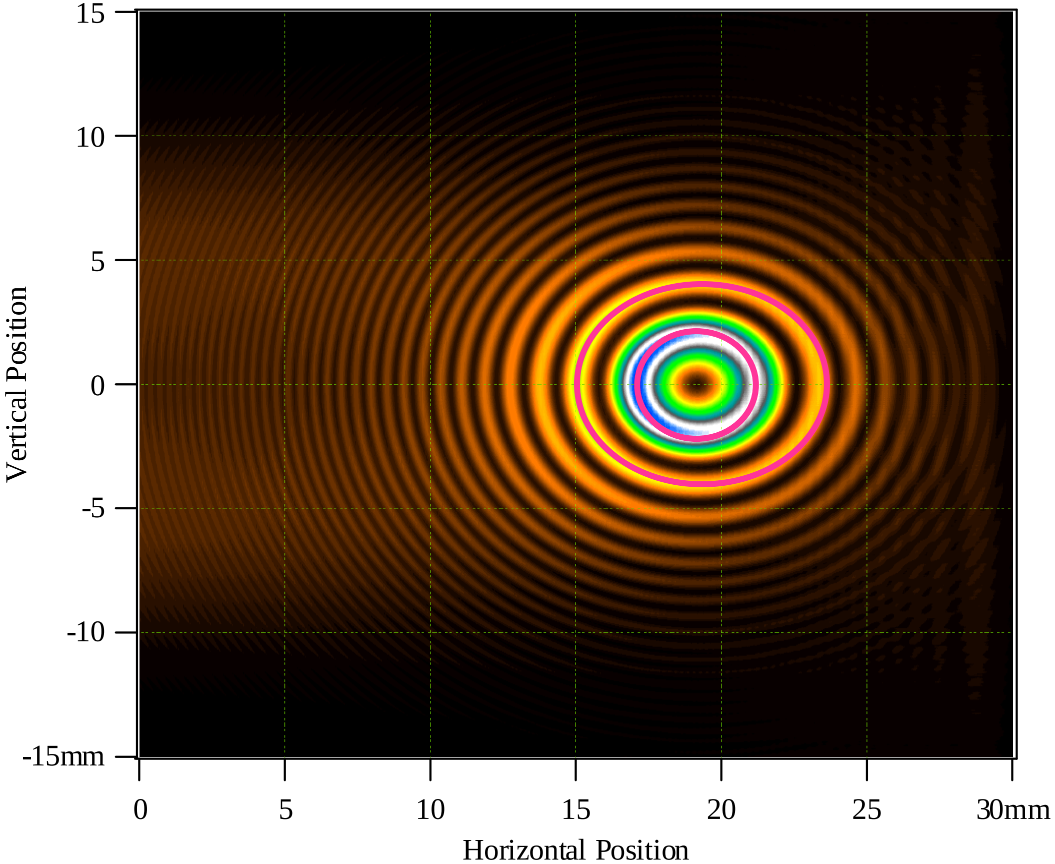


$\sim \left(\lambda^2 \rho\right)^{1/3}$ → **0.9 mm**

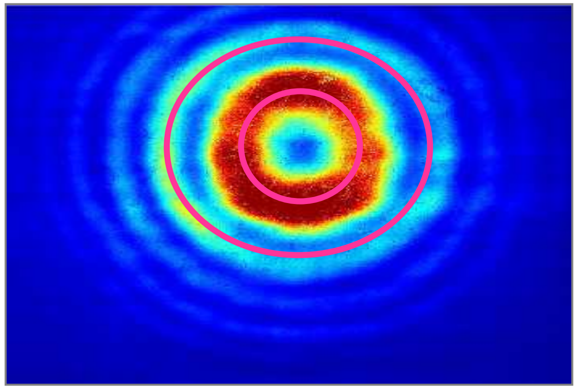
Are we confident with the simulations?

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

Measured at the ESRF beamline

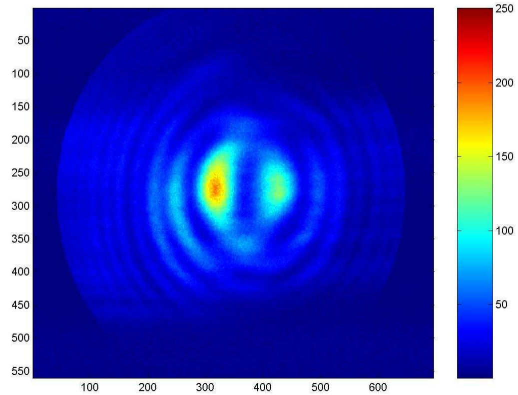


Recorded with a CCD camera
at 6.2 meters from source
λ= 0.52 microns

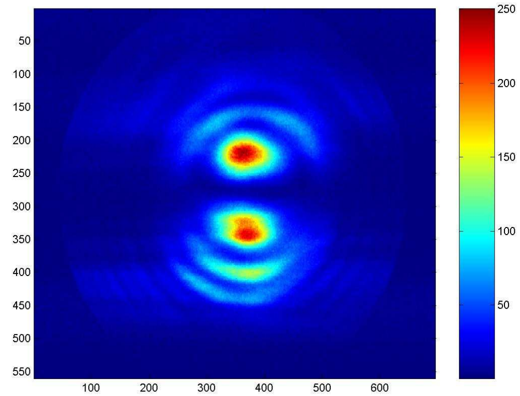


Edge radiation observed at IR beamline ESRF

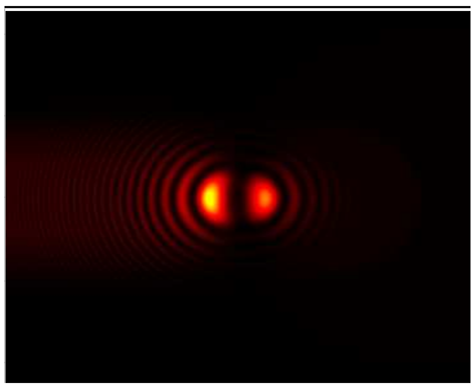
Measurements done with a CCD camera, 10m from source, filter=700nm

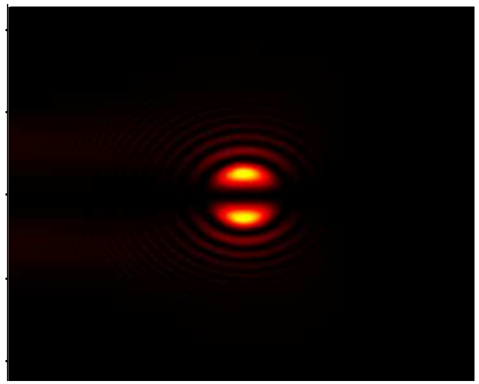


H-polarized

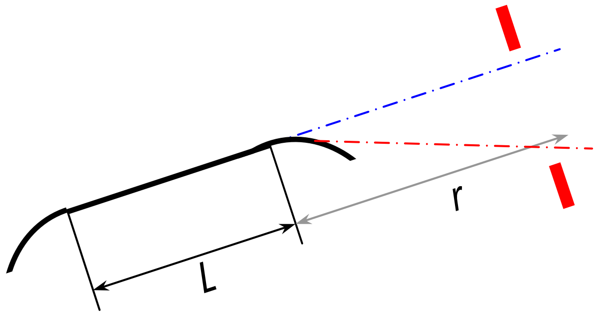


V-polarized



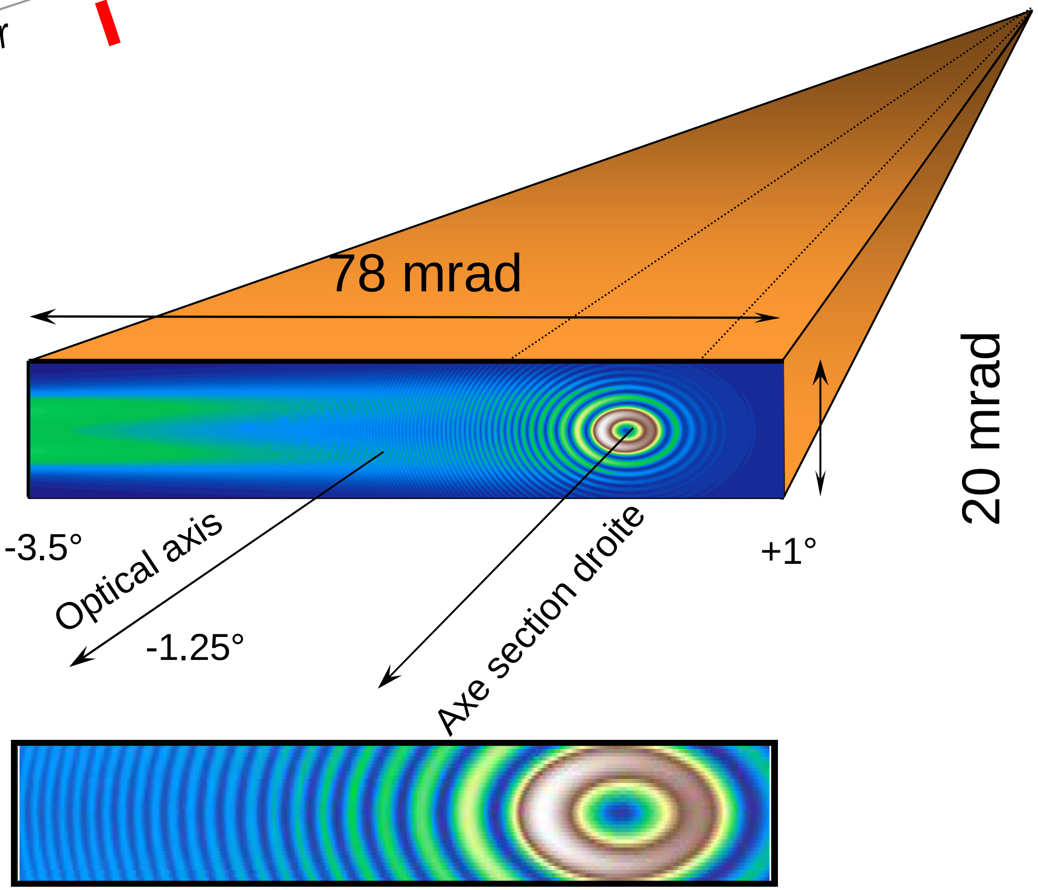


Collecting the two sources



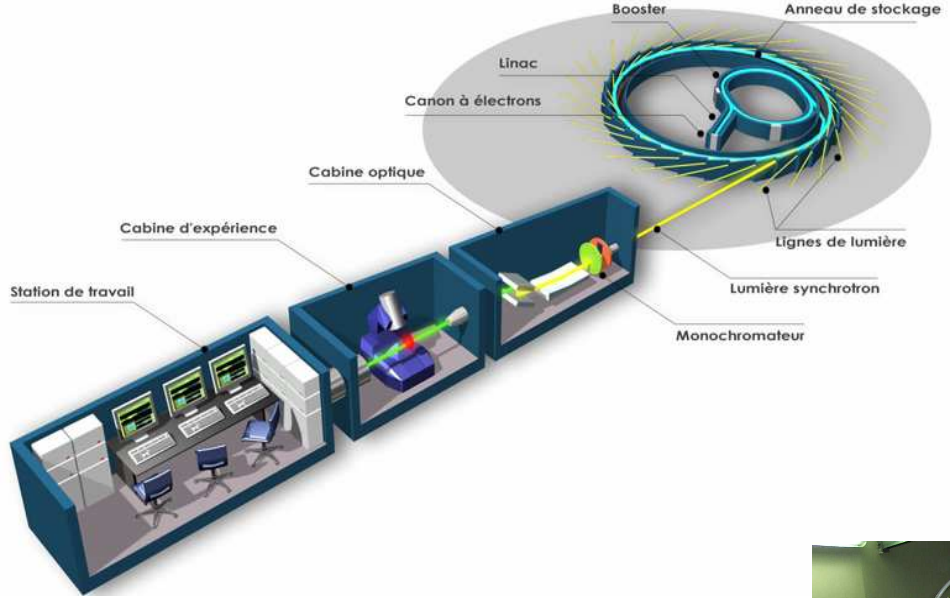
SOLEIL's case

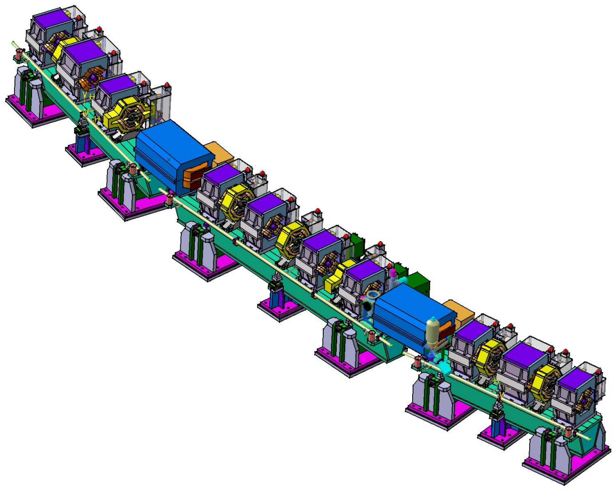
Emission @ 10 µm

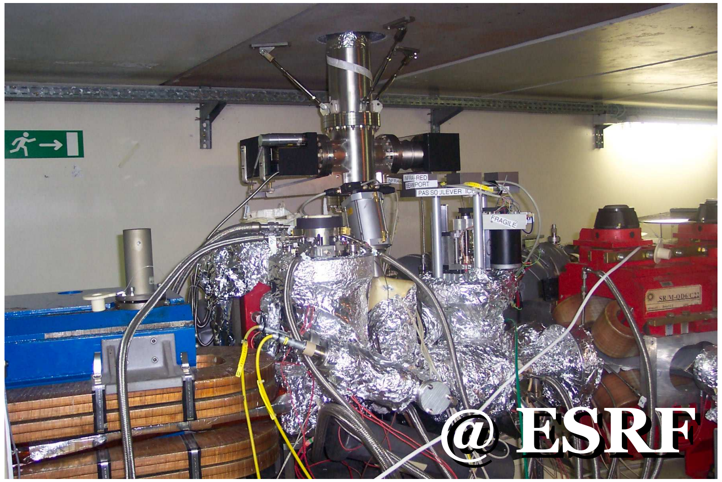


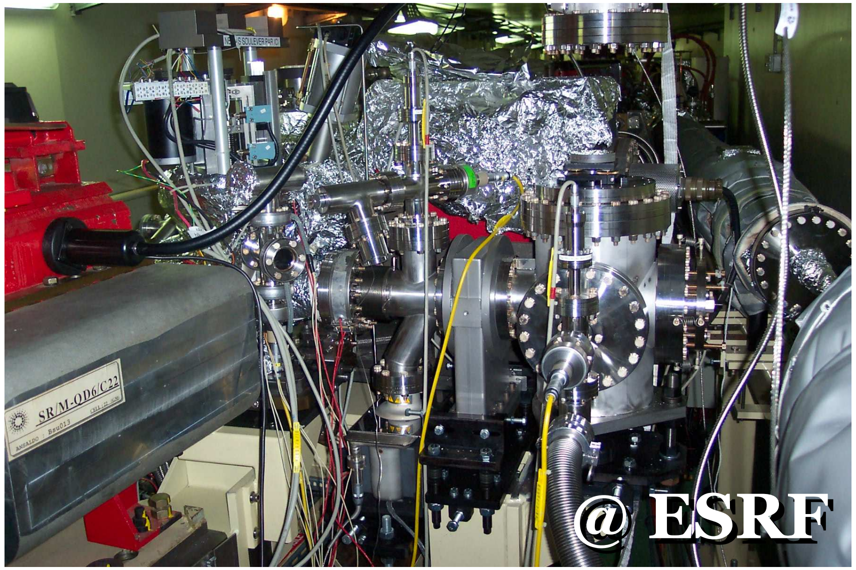
Emission @ 100 µm

Synchrotron radiation in the infrared









Extraction optics

Allows to collect 20 mrad vertical and 78 mrad horizontal

IR