Diagnostic techniques for cultural heritage: applications of synchrotron infrared spectroscopy to the study of a painting cross sections

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Sinbad IR beamline @ DaΦne

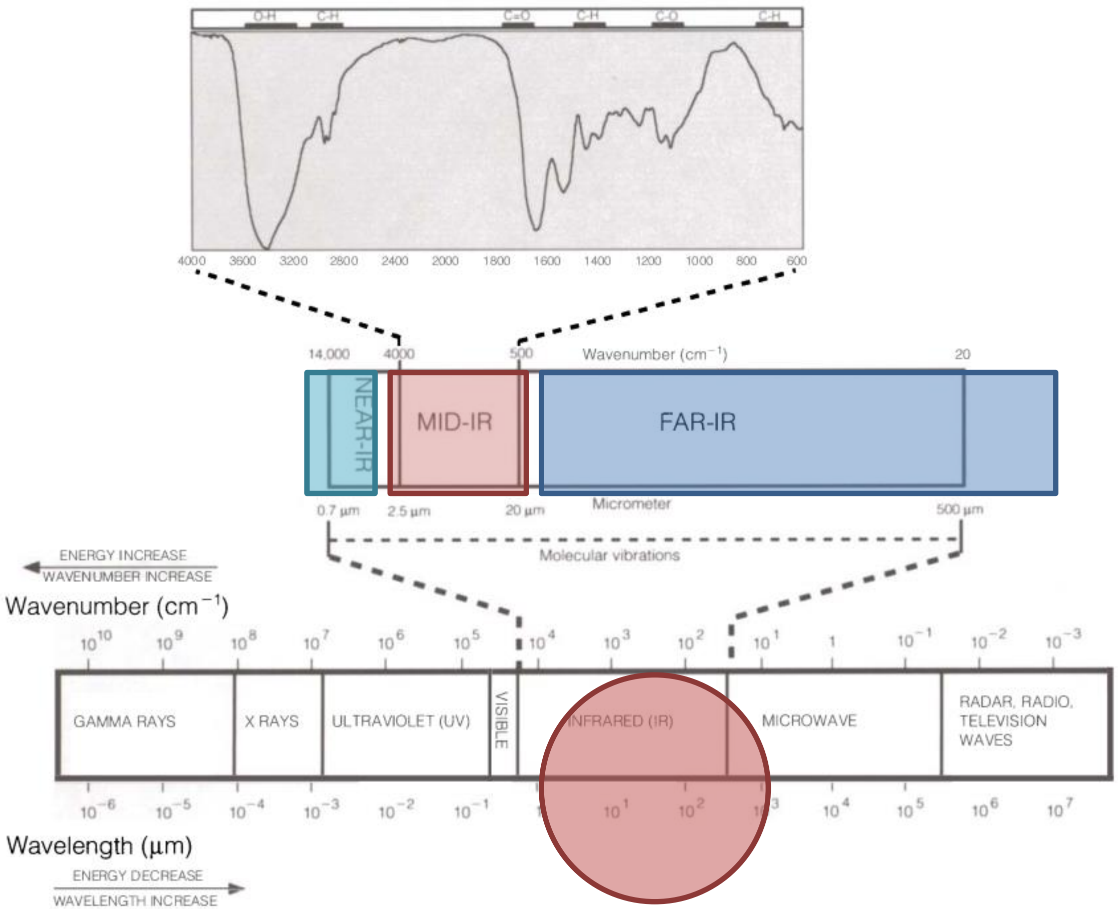
INFN-International Masterclass 2014

Layout

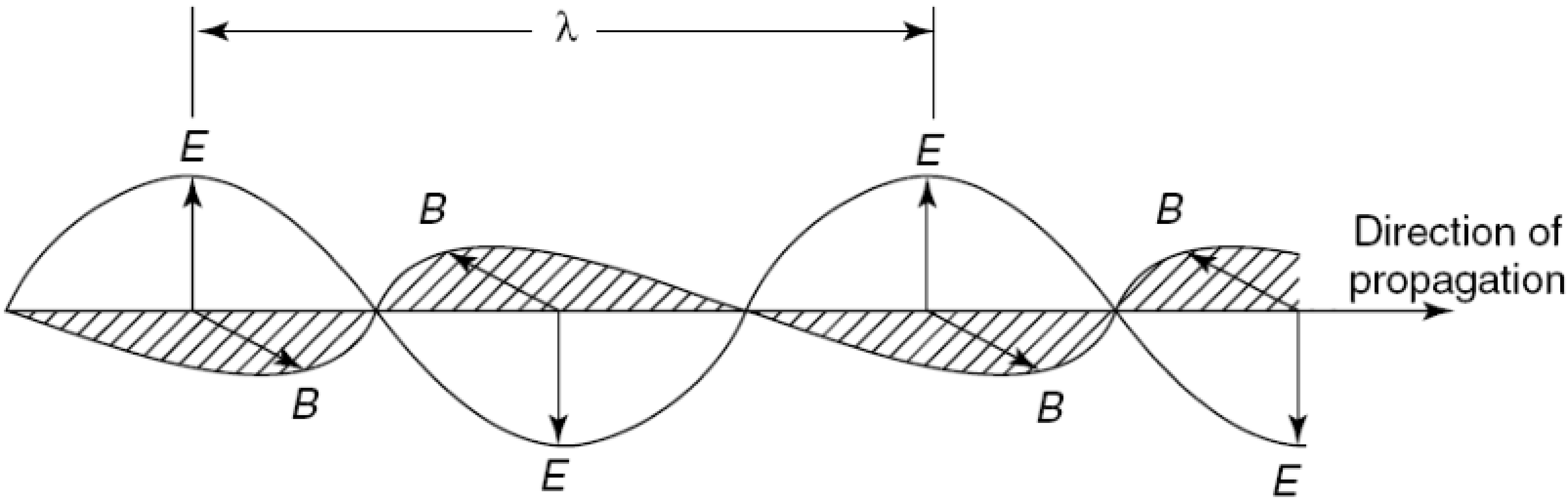
- FT-IR spectroscopy in cultural heritage
- Sampling techniques: transmission, reflection, Attenuated total reflection (ATR) and Diffuse reflection (DRIFT)
- Infrared imaging and microscopy:generating chemical images from a sample
- FT-IR Analysis of a painting cross section

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR): physical principles

Electromagnetic spectrum and IR



The EM field



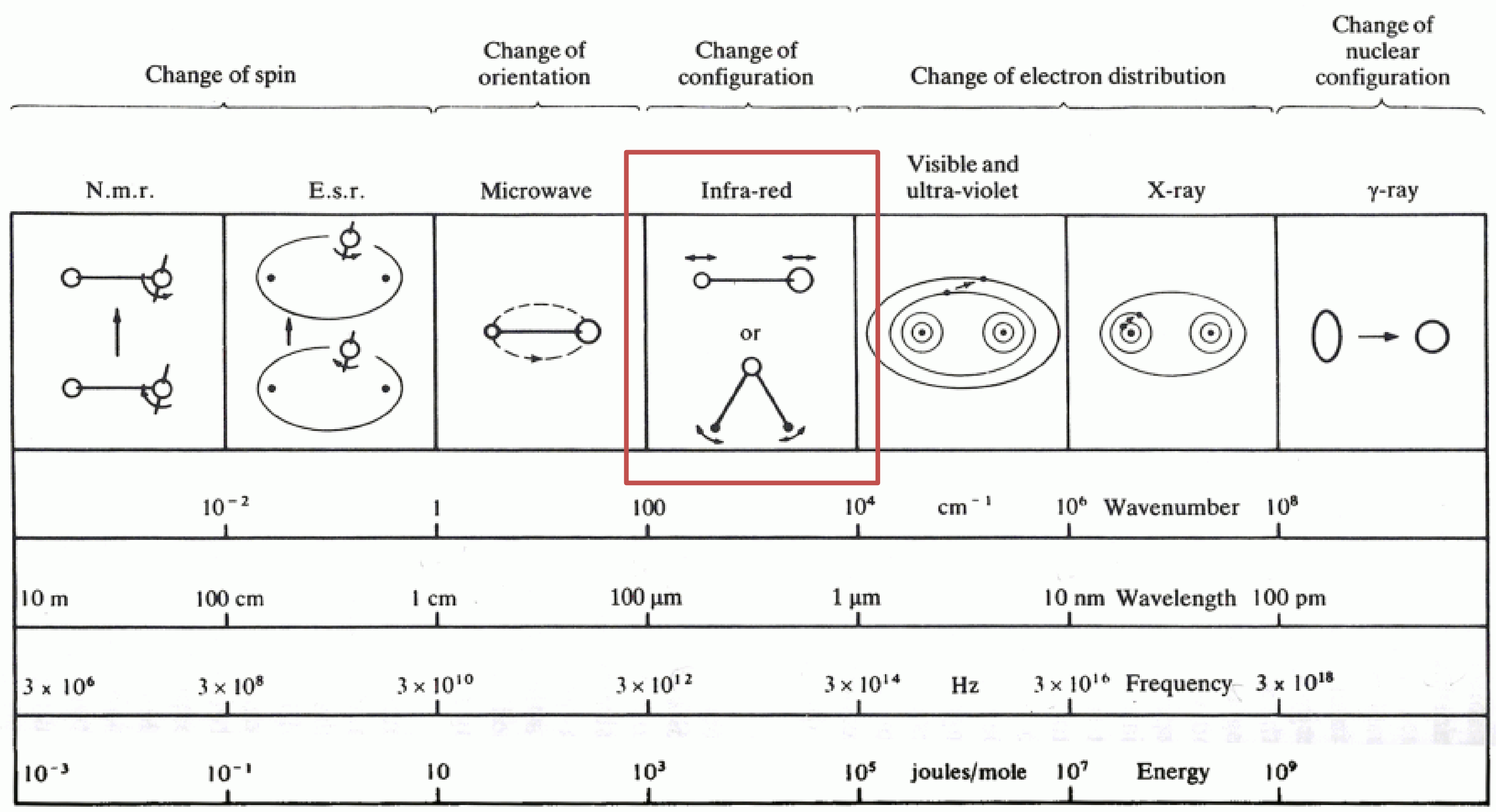
IR Units

- Visible and IR light are both EM radiation, differing only for the wavelegth. They both propagate in vacuum at the light speed *c*.

  - Wavelength λ (**μm**)
  - Frequency ν (**Hz**: $\nu=c/\lambda$)
  - Energy E (**eV**: $E=h\nu$)
  - Wavenumber $\tilde{\nu}$ (**cm^{-1}**)

$\tilde{\nu}$ (cm^{-1})= 1/λ (cm)

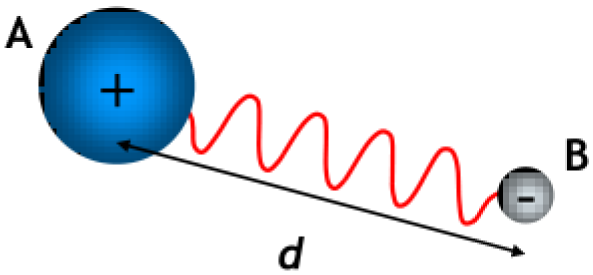
What happens when «light» interacts with matter



$E_{total} = E_{translational} + E_{rotational} + E_{vibrational}$

Every molecule interacts with the IR EM field?

- Ther is an interaction if there is a <u>variation of the electric dipole moment</u>:



$$\mu = |\delta e| \cdot d$$

IR active modes

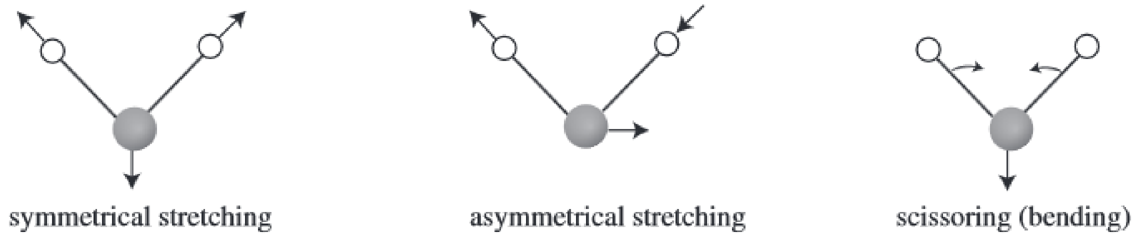


Figure : Stretching and bending vibrational modes for H_2O

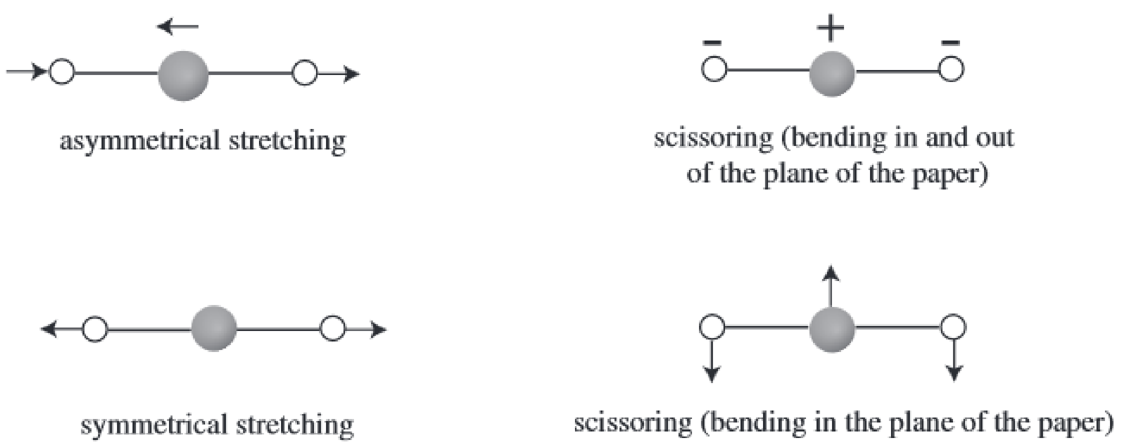
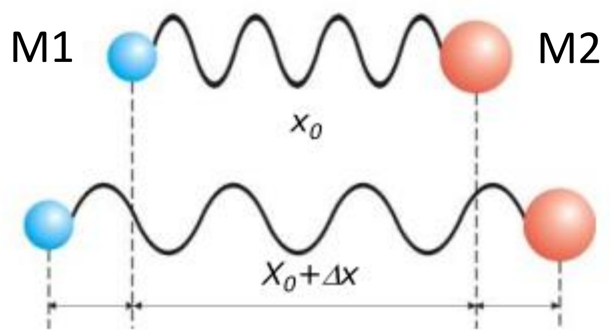


Figure : Stretching and bending vibrational modes for CO_2

- O_2, H_2, Cl_2, N_2 are not IR active!



$$\nu = \sqrt{\frac{k}{m}}\ \text{vibration frequency}$$

$$m = \frac{M1 \cdot M2}{M1+M2}\ \text{(reduced mass)}$$

Increasing *k* (bond strength) the frequency increases
Decreasing *m*, the frequency increases.

C-C, C-O, C-N → 800-1300 cm^{-1}
C=C, C=O, C=N → 1700 – 1900 cm^{-1}
C≡C, C ≡O, C ≡N → 2000-2300 cm^{-1}

C-H, N-H, O-H → 2700-3800 cm^{-1}

Modi normali di vibrazione

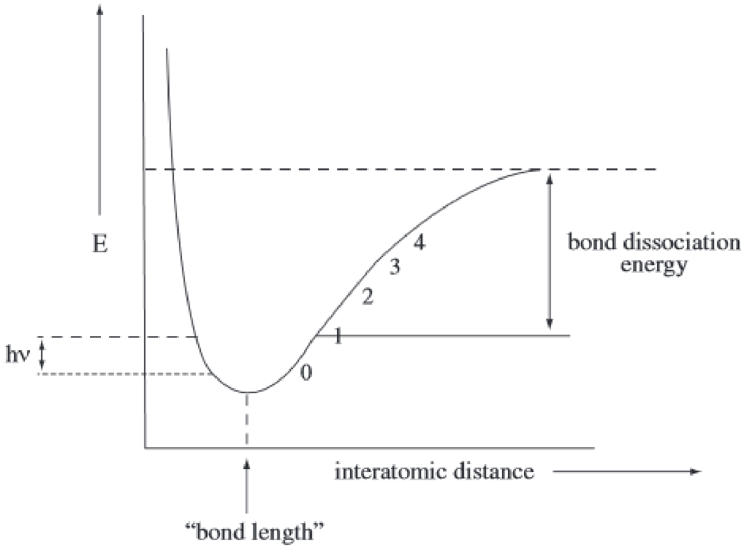


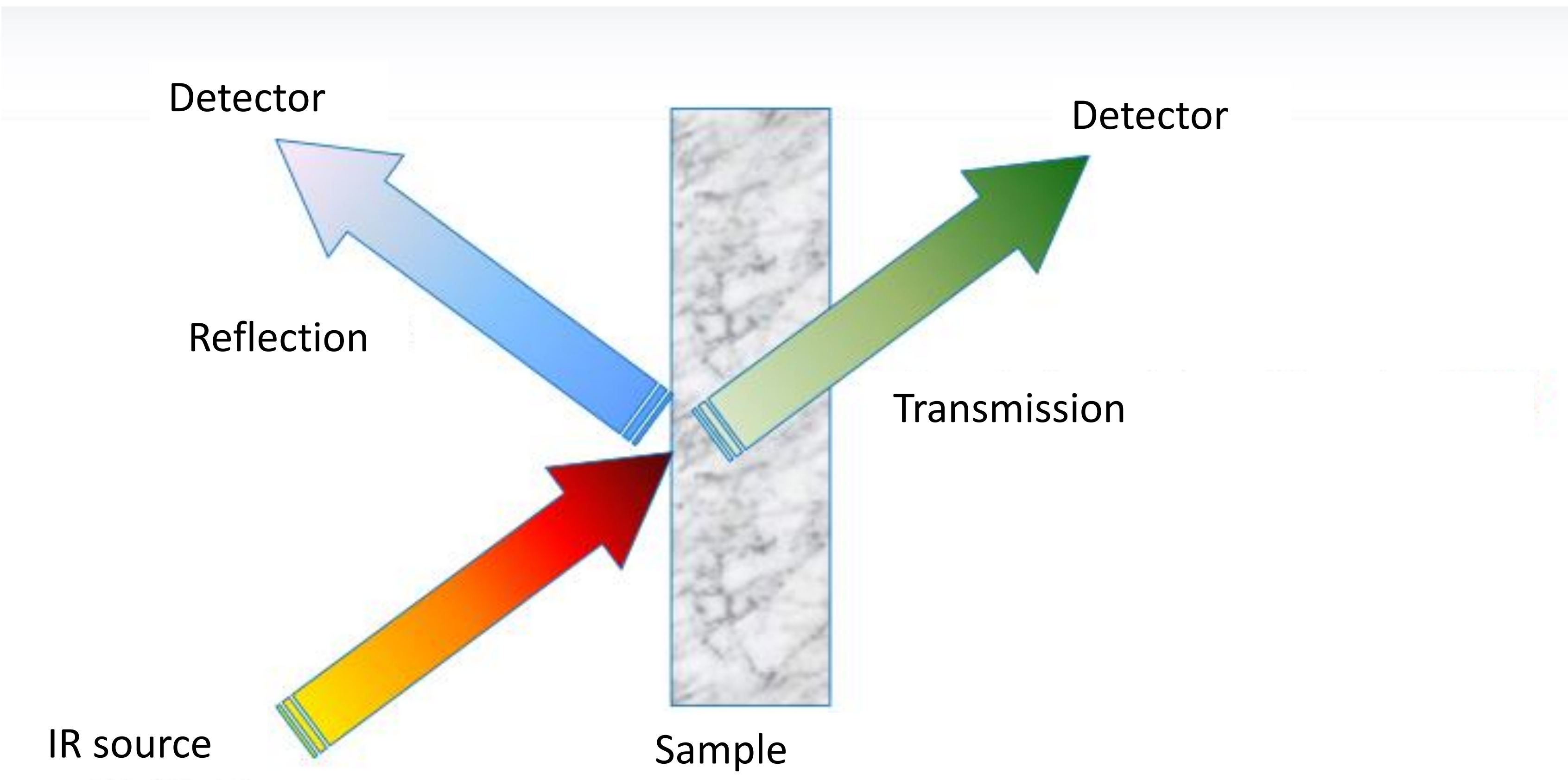
Figure 15.8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

$$E = \left(n + \frac{1}{2}\right) h\nu$$

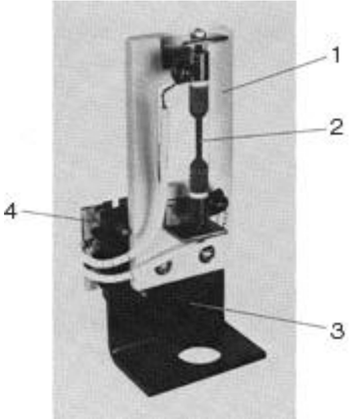
(quantized energy levels)

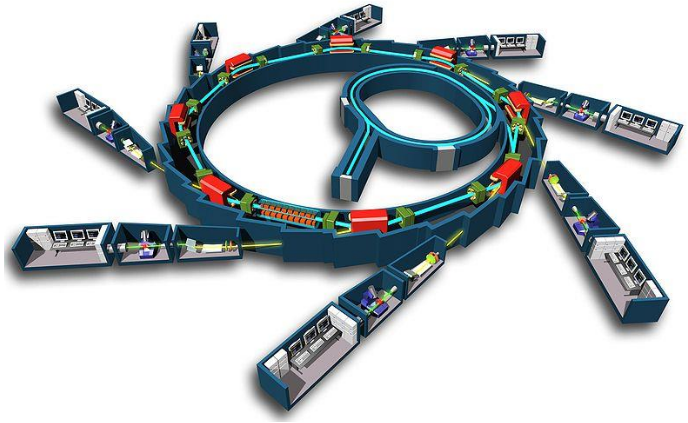
- 3N-6 (non linear molecule)
- 3N -5 (linear molecule)

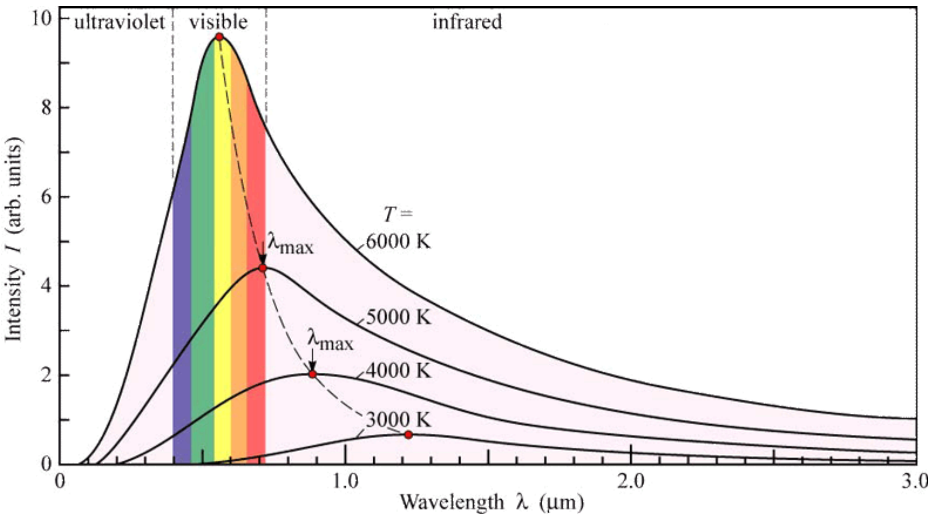
Fourier Transform Infrared Spectroscopy (FT-IR)


Detector
Detector
Reflection
Transmission
IR source
Sample

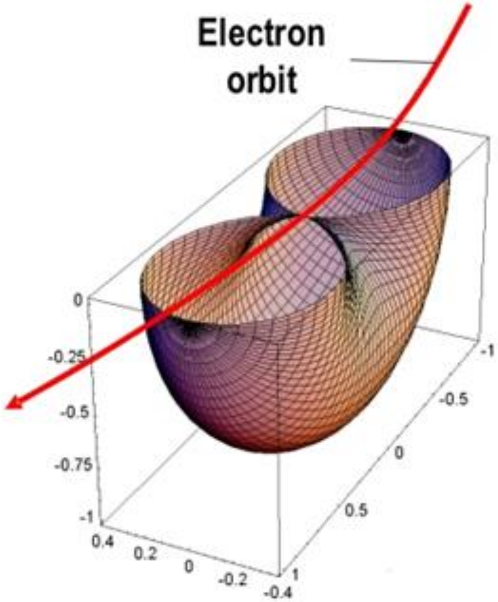
IR sources


1
2
3
4

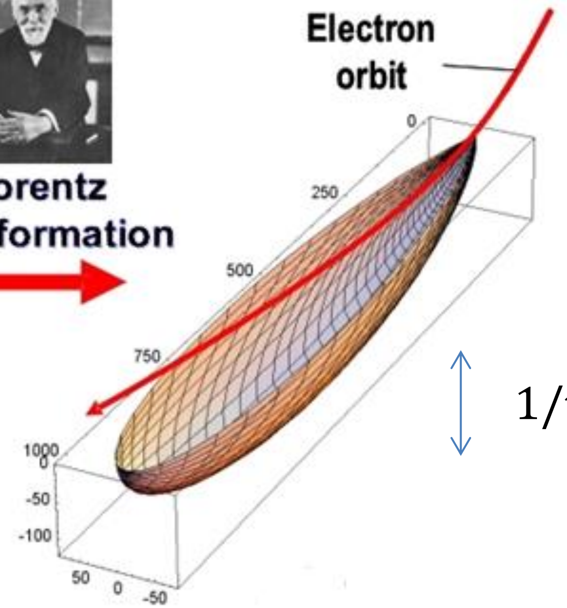



ultraviolet
visible
infrared
T =
6000 K
5000 K
4000 K
3000 K
λmax
λmax
Intensity I (arb. units)
Wavelength λ (μm)
0
2
4
6
8
10
0
1.0
2.0
3.0

Synchrotron radiation



Lorentz transformation



$1/\gamma$

Every moving electric charge emits EM radiation.

$$\beta = v/c$$

$$\gamma = \frac{1}{\sqrt{1-\beta^2}}$$

Per β=0.99 1/γ= 10 mrad

Classic ($v << c$)

Relativistic ($v \approx c$)

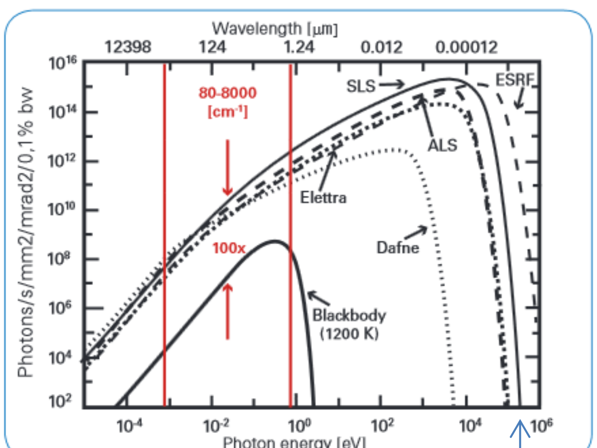
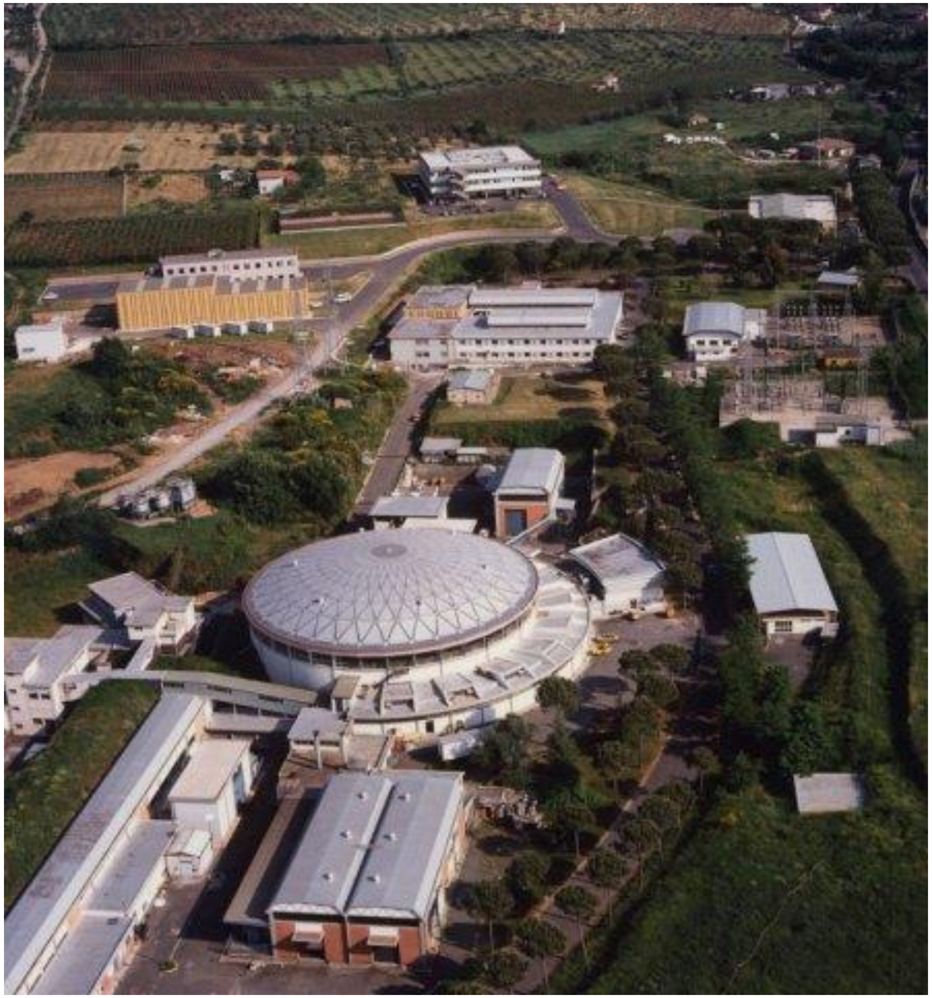
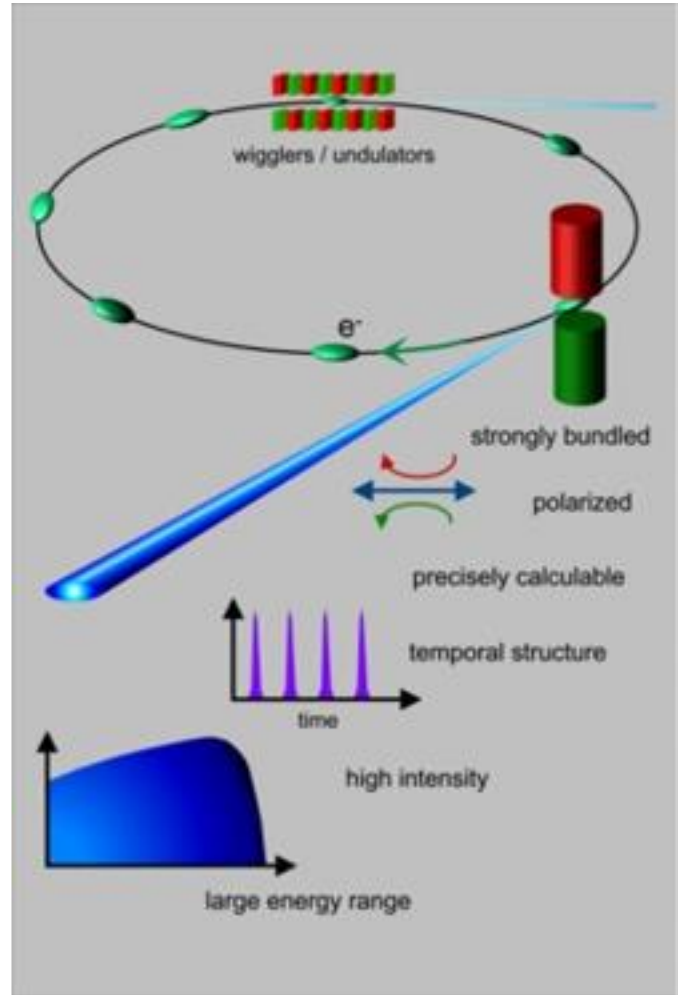


Fig. 1: Advantages of the e-Synchrotron radiation source

Critical energy

$$brilliance = \frac{photons}{second \cdot mrad^2 \cdot mm^2 \cdot 0.1\% BW}$$





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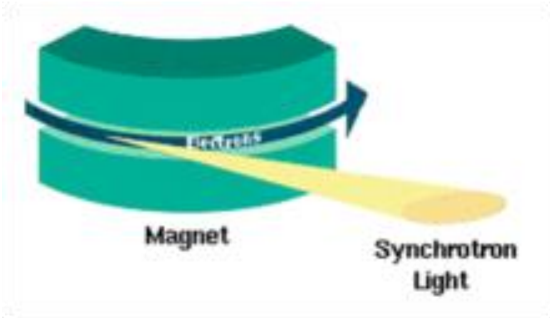
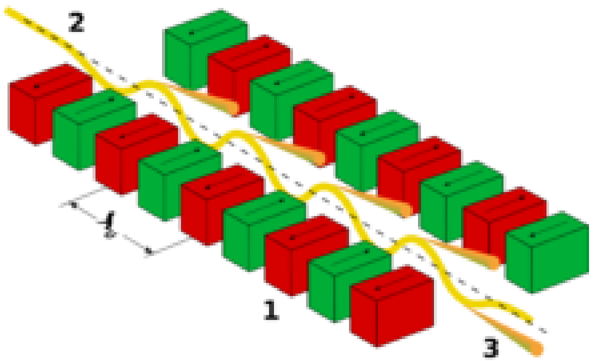
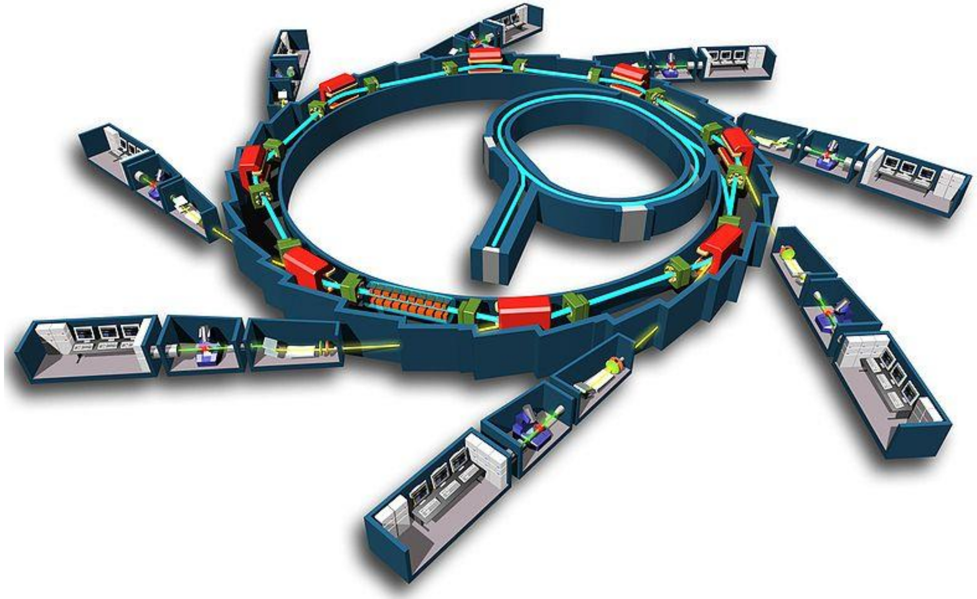
The beamlines





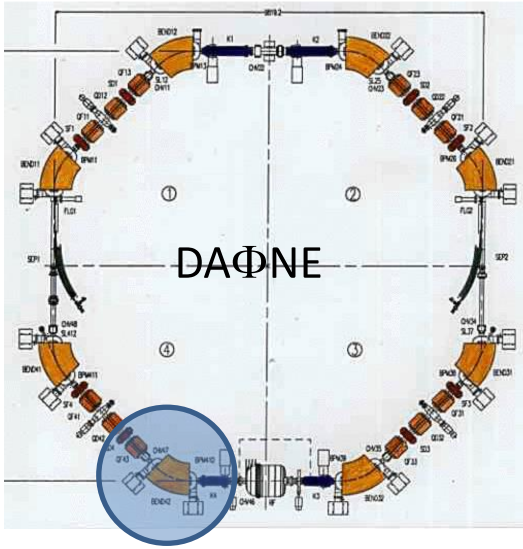


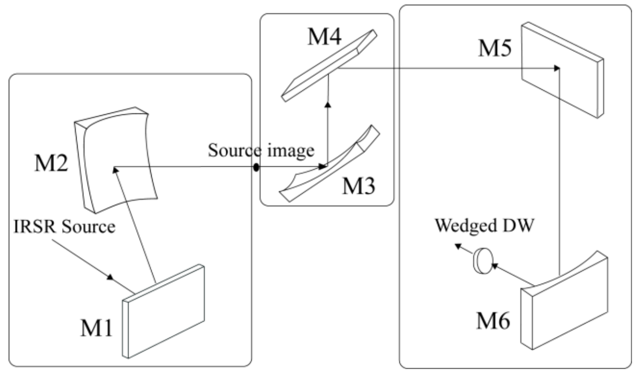
The IR SINBAD beamline

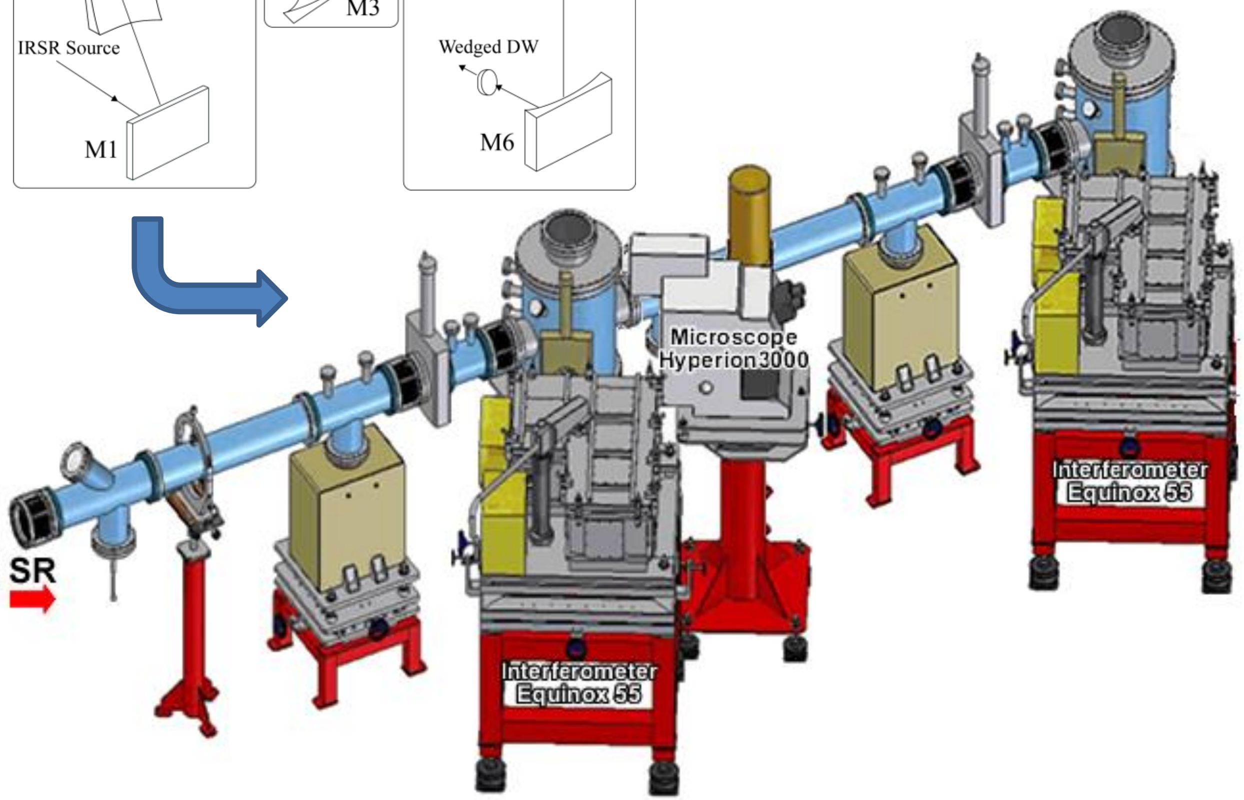
Infrared domain

from 10 to 10^3 cm^{-1}

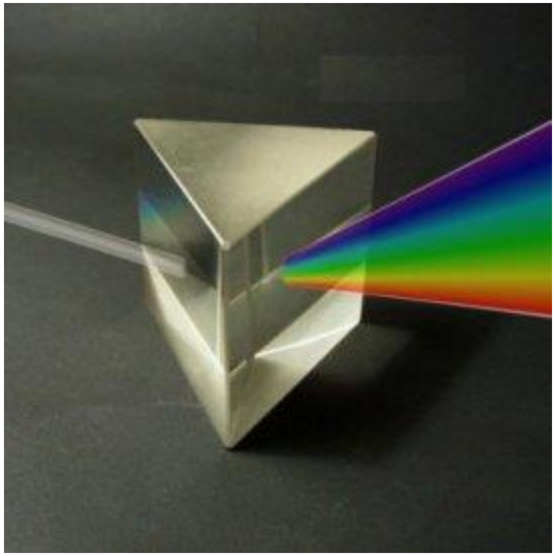
1.24meV to 1.24 eV

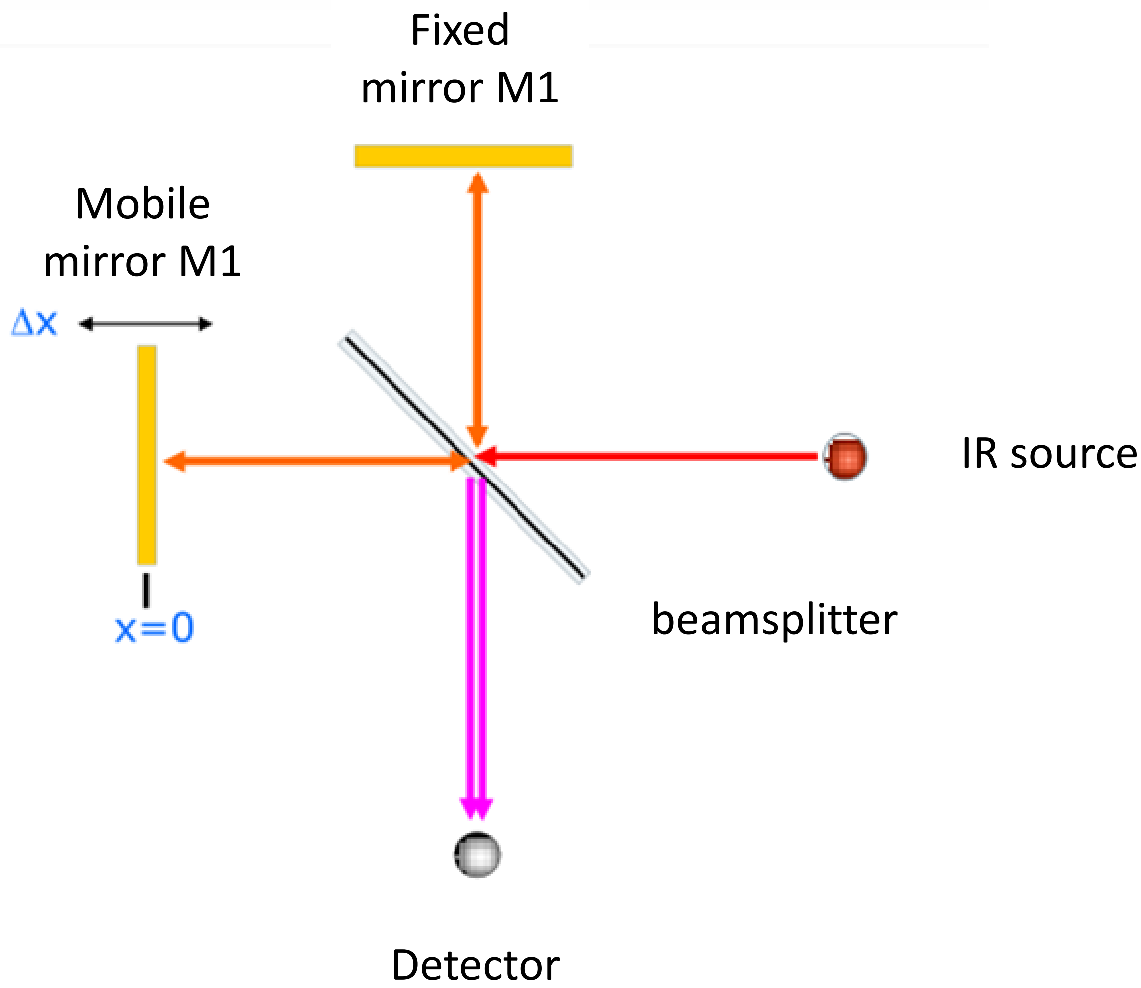




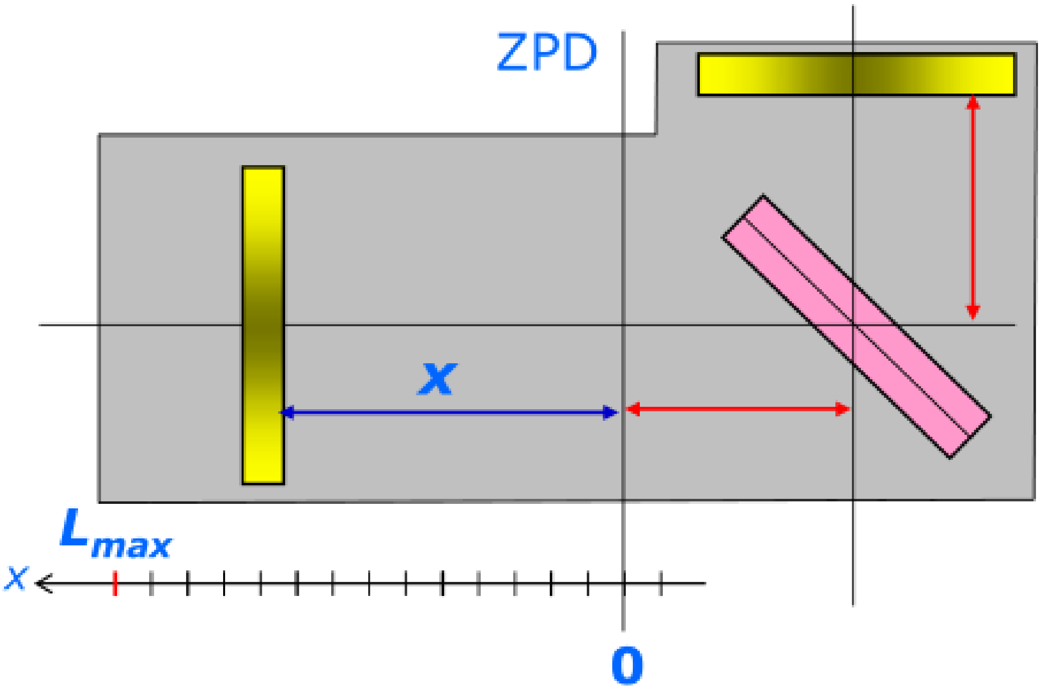


Michelson interferometer



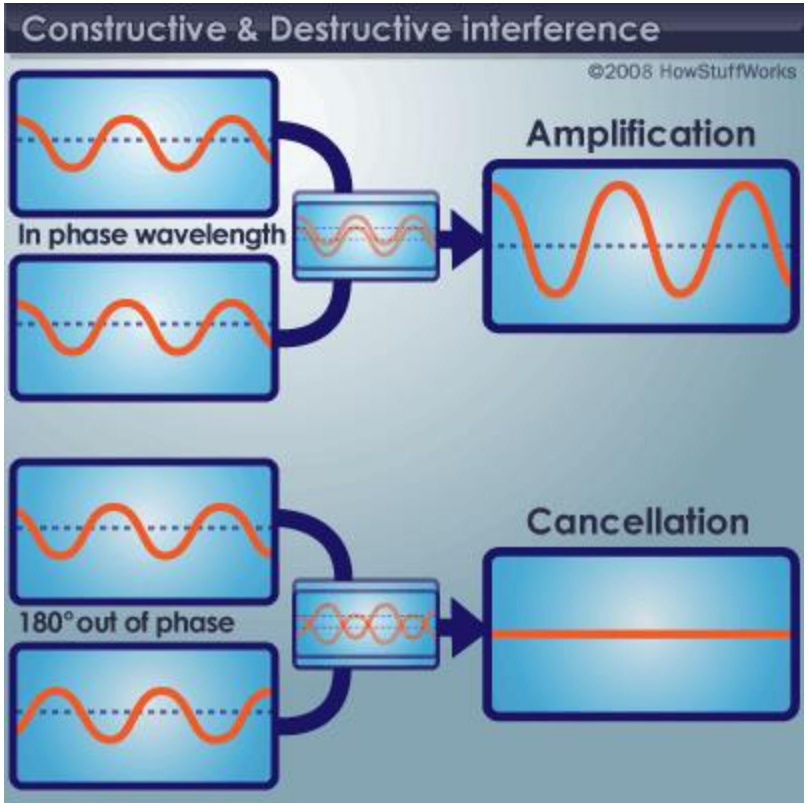

Fixed
mirror M1
Mobile
mirror M1
Δx
x=0
IR source
beamsplitter
Detector

The interferogram depends on the optical path difference (OPD) between the two beams



The OPD is twice the mirror excursion x. Since the mirror speed *v* is constant:

$$2x=2vt$$

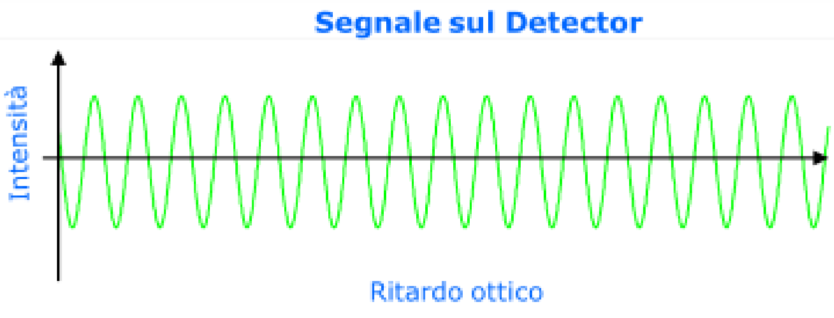


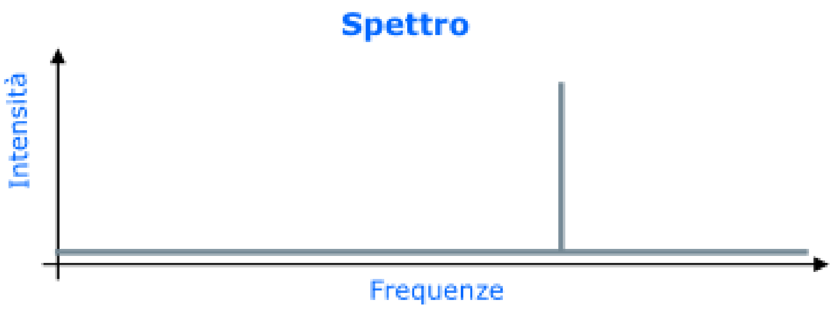
OPD= $2n\frac{\lambda}{2}\ (n = 0, \pm 1, \pm 2, \ldots)$

OPD= $(2n+1)\frac{\lambda}{2}\ (n = 0, \pm 1, \pm 2, \ldots)$

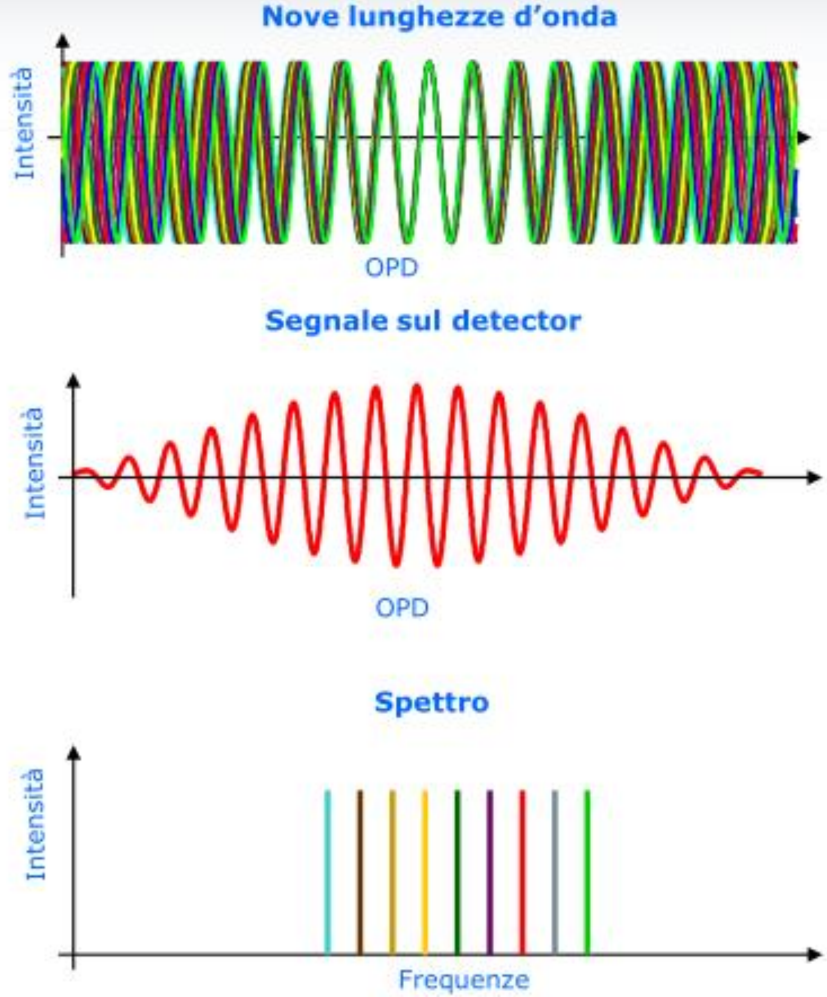
$$I(t) = S(\tilde{\nu}) \cdot \cos(2\pi \underbrace{2\tilde{\nu}\upsilon}_{\text{Modulation frequency}} t)$$

- Origine dell'interferogramma: l'onda monocromatica

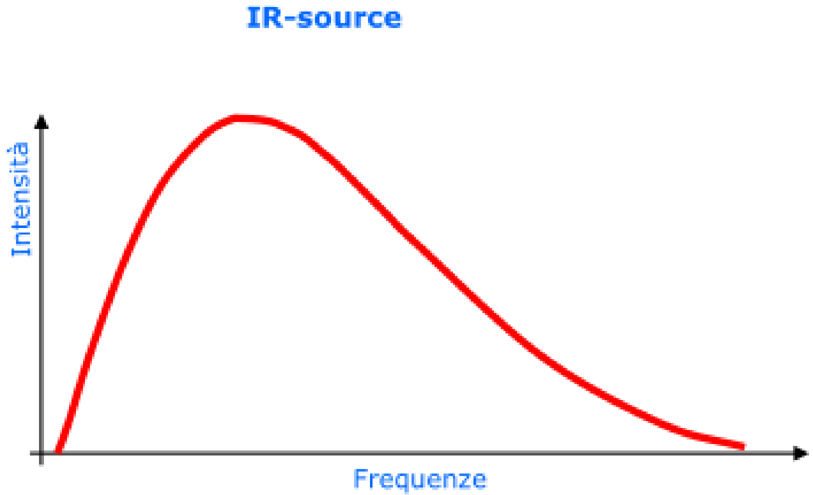




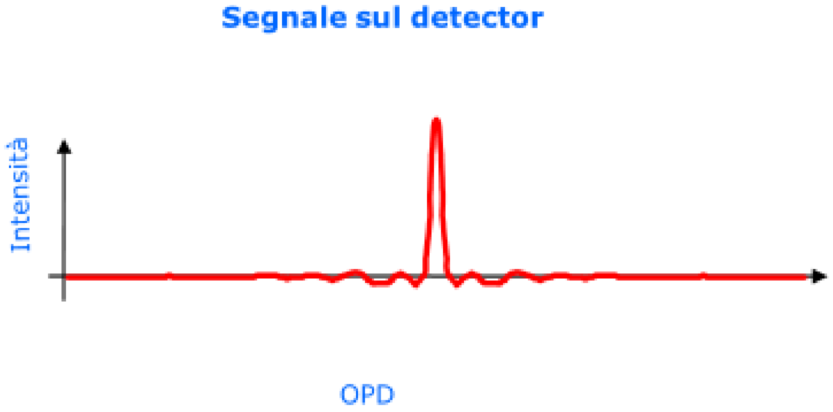
- Origine dell'interferogramma: onda policromatica a componenti discrete

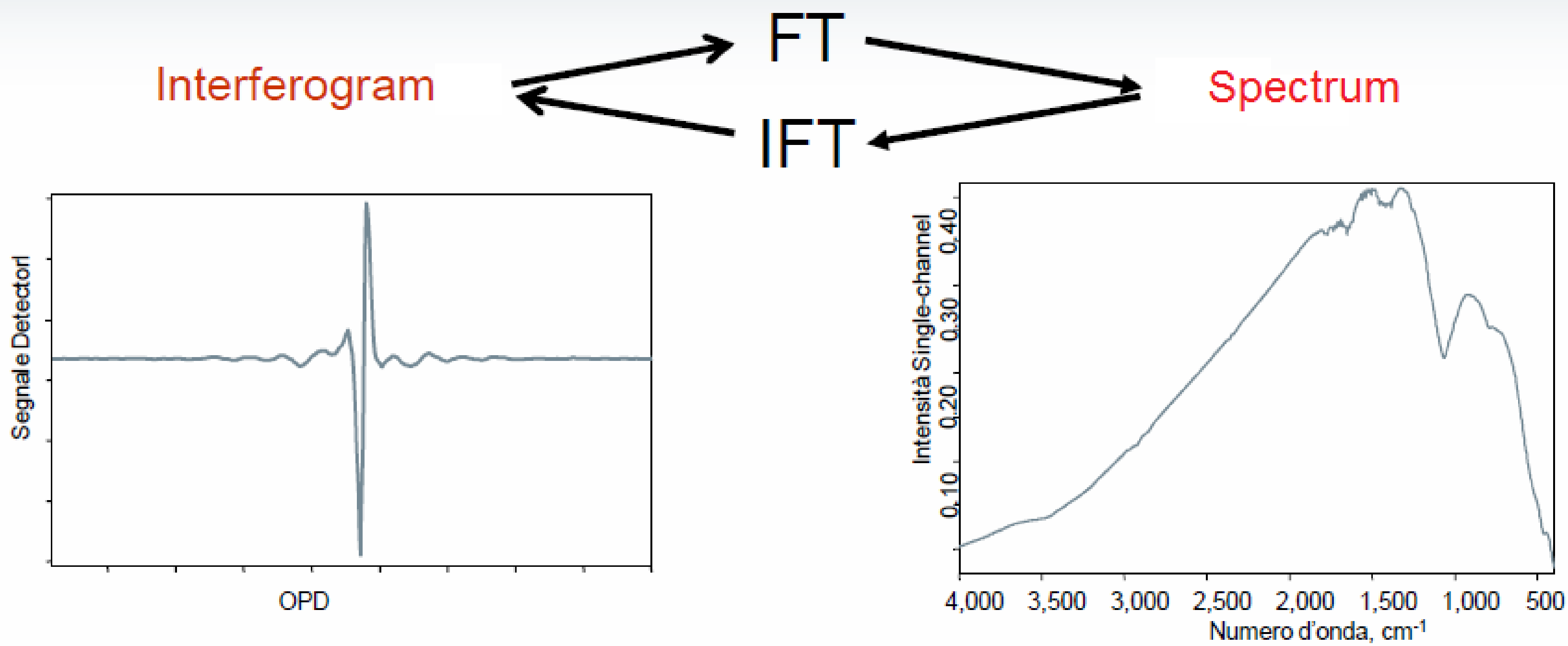


- Origine dell’interferogramma:
  sorgenti a spettro esteso



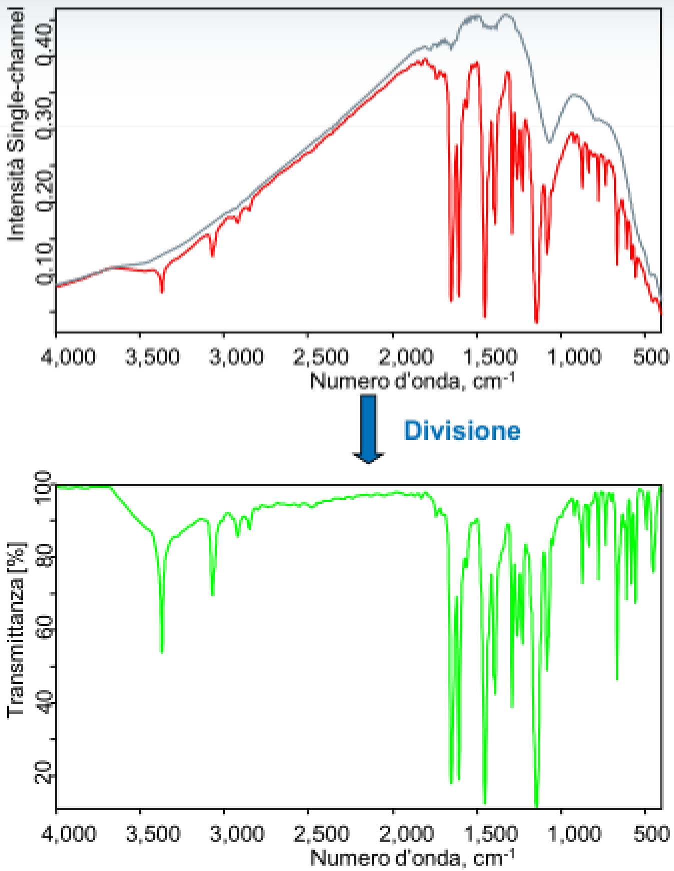
Distribuzione di frequenze di una sorgente di corpo nero





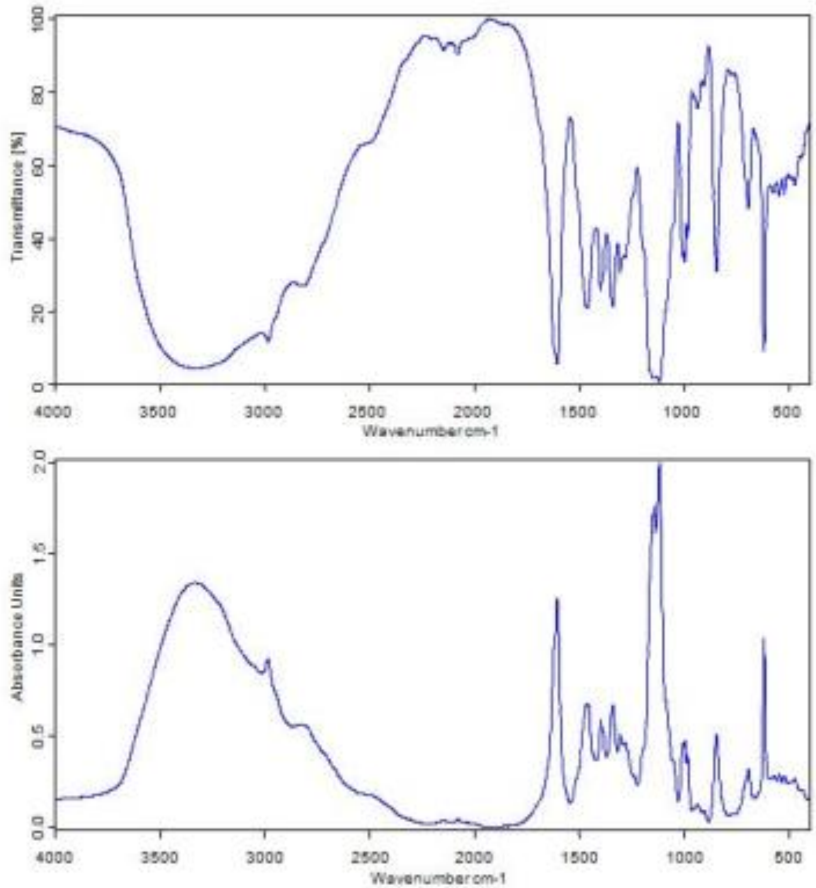
$$S(\nu) = \int_{-\infty}^{\infty} I(x) e^{i2\pi\nu x} dx$$

Measuring an IR spectrum



TRANSMITTANCE

$T(\nu) = SSC/RSC$



$$A = -Log\ T$$

ABSORBANCE

Sampling techniques

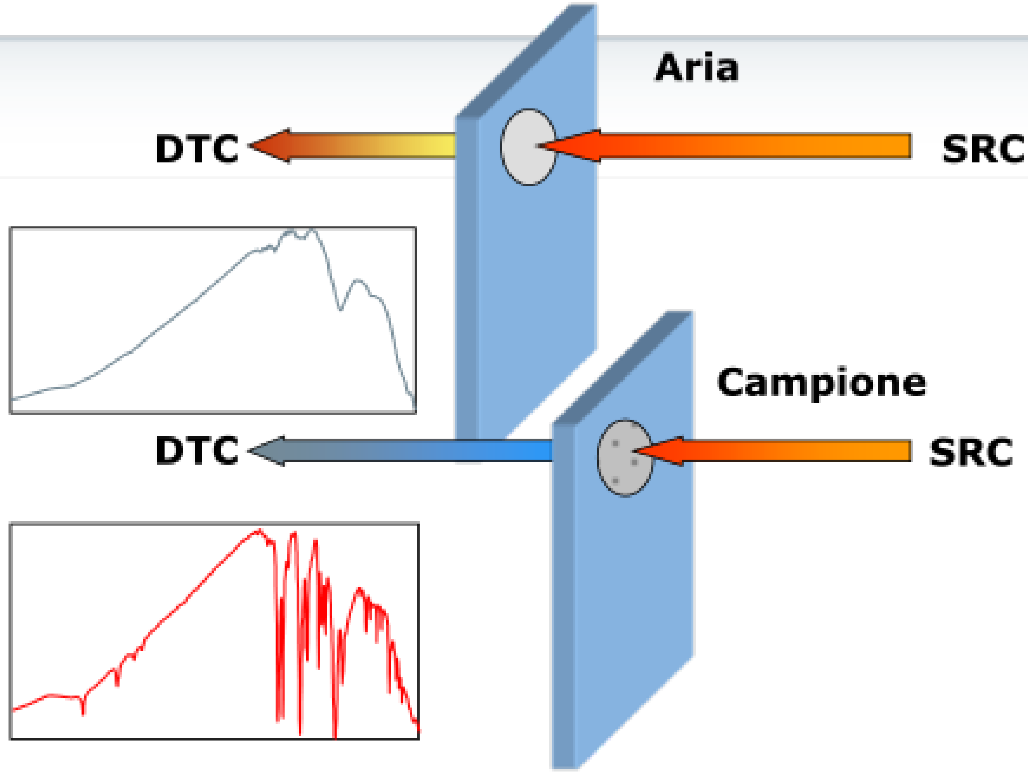
- Depending on the sample form (solid, liquid, powder, film) and which characteristics you want to mantain, it is possible to use different sampling techniques, distructive or non distructive:

- Transmission (liquids, powders, thin sections)
- Specular reflection (crystals, polished sections)
- Diffuse reflectance (powders)
- Attenuated Total Reflection (ATR) (thick samples, non reflecting surfaces)

Transmission
KBr powder pellets

- Invasiva
- Distruttiva
- Laboriosa
- Molto precisa (misura assoluta)
- Creazione di spettri di riferimento

- Background (I_0)

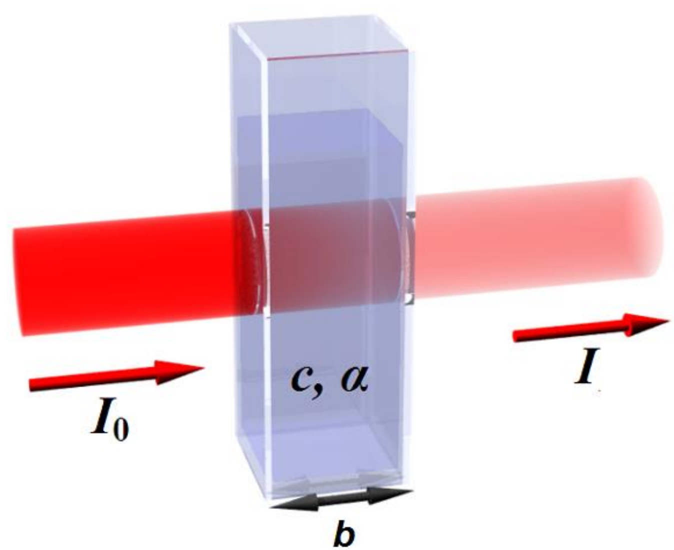


- Sample (I)

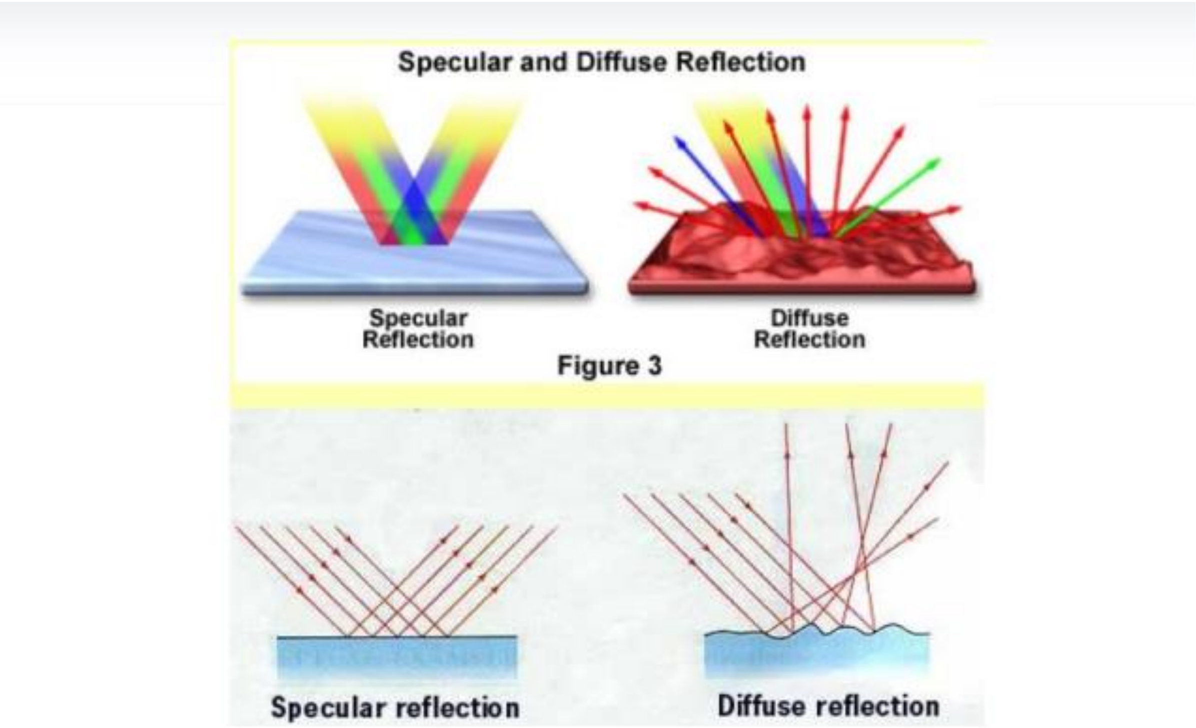
$$T = \frac{I}{I_0} \qquad A = \log\frac{1}{T} = -\log T$$

Beer-Lambert law

$$A=\alpha bC$$



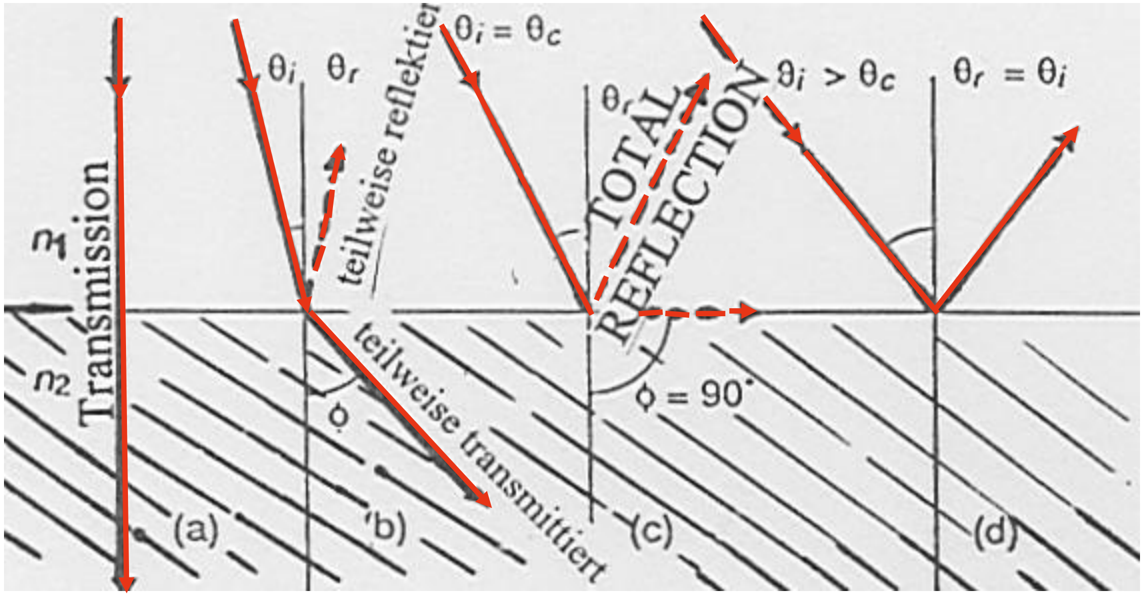
Reflection spectroscopy



Preparation of the surface – polishing ☹
Thick samples ☺

Attenuated Total Reflection (ATR)

Principles of Attenuated Total Reflection spectroscopy (ATR)



Crystal n_1

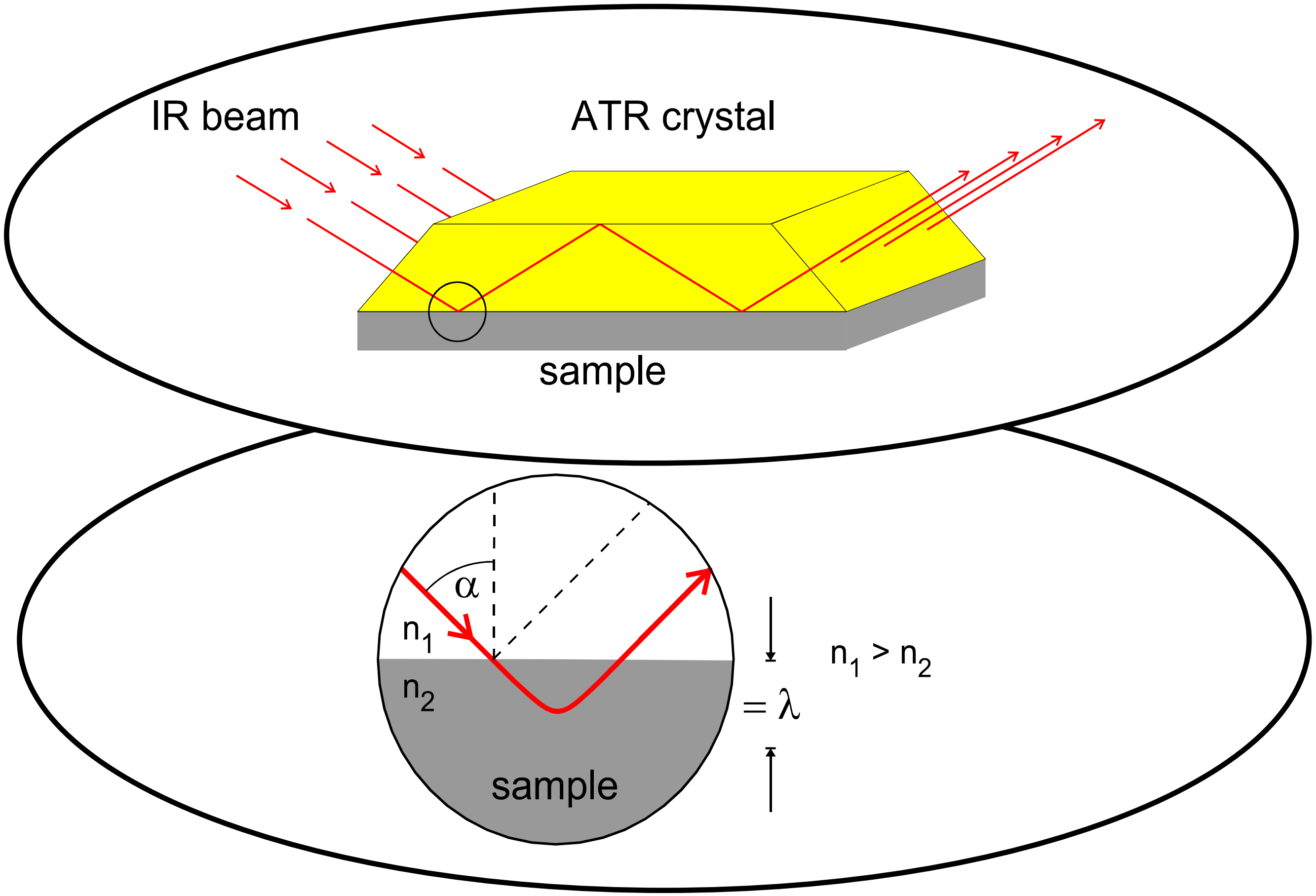
Sample n_2

Snell's law: $n_1 \times \sin\Theta_i = n_2 \times \sin\Theta_r$

Critical angle: $\Theta_r = 90°$

$$\sin\Theta_c = n_2 / n_1$$

(es. 38° for ZnSe for a sample with n=1.5)

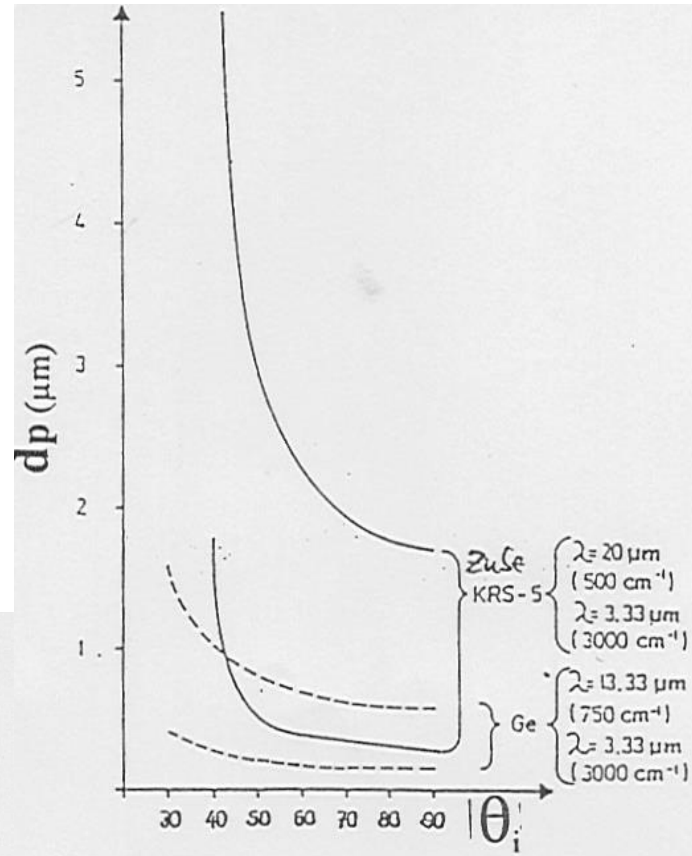

IR beam
ATR crystal
sample
α
n_1
n_2
sample
$= \lambda$
$n_1 > n_2$

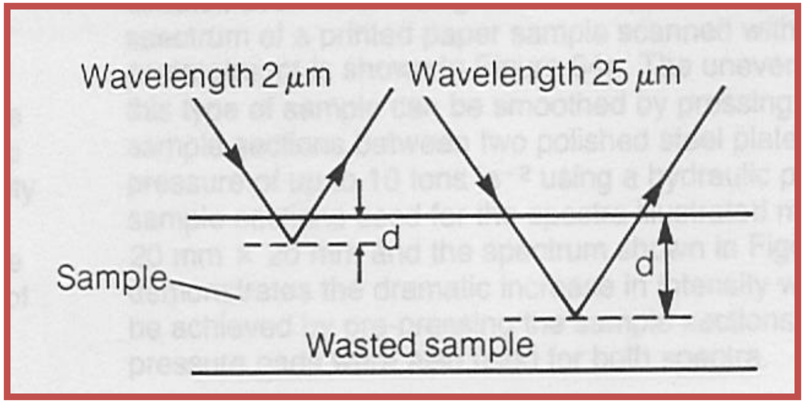
Penetration depth

$$d_p = \frac{\lambda}{2\pi n_1 \left(\sin^2\theta_i - n_{21}^2\right)^{1/2}}$$

θ_i	30°	45°	60°
KRS-5	iλ	0.290λ	0.113λ
Ge	0.091λ	0.041λ	0.002λ

(i = total transmission, sample index = 1.5)

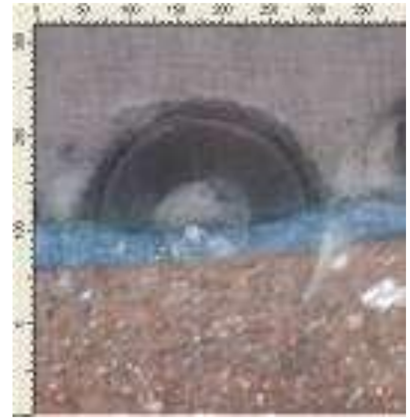




d_p prop λ

$$ATR = AB * \nu \, [cm^{-1}] \,/\, 1000 \, [cm^{-1}]$$

- Quick
- Non invasive
- (semi)destructive



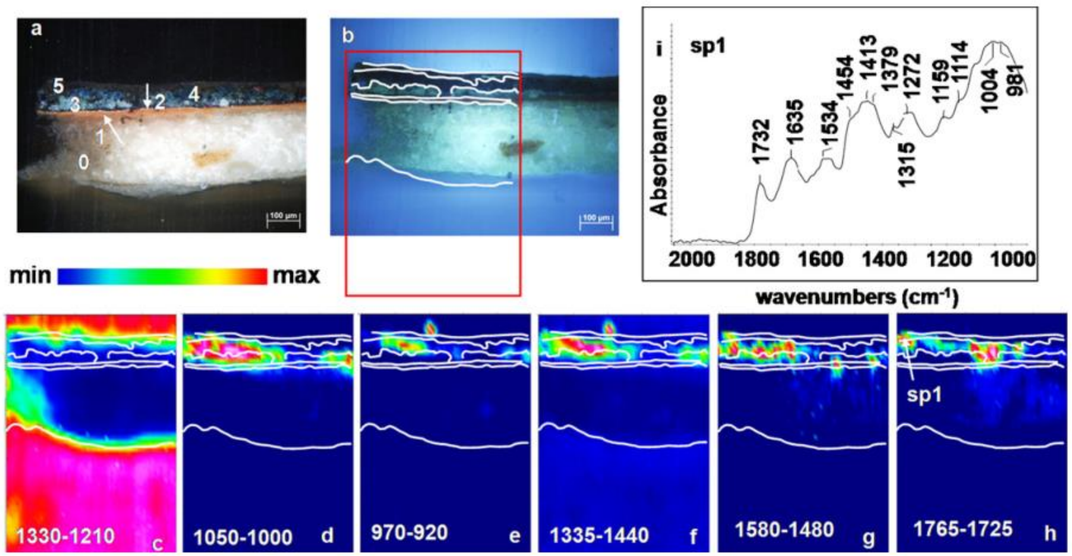
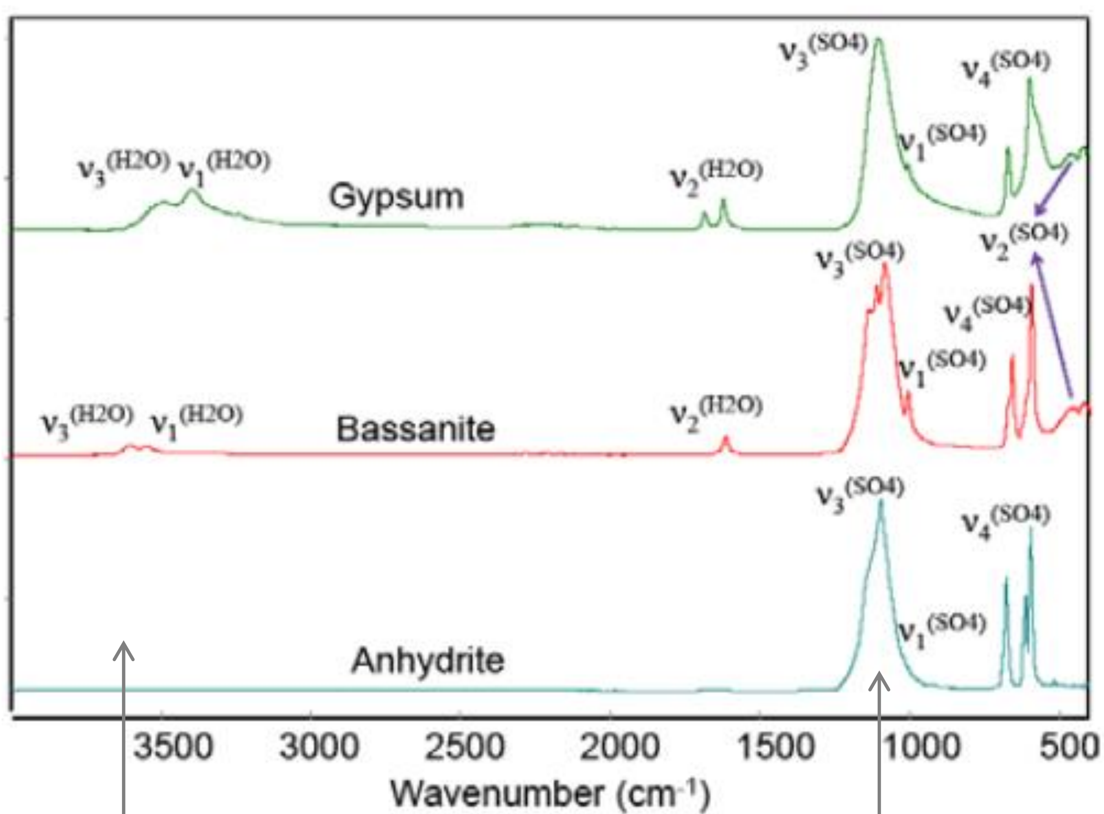


Fig. 2. Detail of a cross-section from the polychrome sculpture (Fe2): (a) visible microscopic image; (b) image of sample under ultraviolet light; (c) FT-IR image created by plotting the integrated absorbance of the embedding resin band between 1330 and 1200 cm^{-1}; (d) FT-IR image showing the distribution of the silicate integrated absorbance between 1050 and 1000 cm^{-1}; (e) FT-IR image showing the distribution of the azurite integrated absorbance between 970 and 920 cm^{-1}; (f) FT-IR image showing the distribution of the carbonate integrated absorbance between 1335 and 1440 cm^{-1}; (g) FT-IR image showing the distribution of the amide II integrated absorbance between 1580 and 1480 cm^{-1}; (h) FT-IR image showing the distribution of the triglycerides integrated absorbance between 1765 and 1725 cm^{-1}; (i) FT-IR spectrum extracted from the right area of h, marked sp1. The size of the FT-IR images is 700 μm × 500 μm. The figure is available in colour in the online version via Science Direct.

Kazarian et al, Vibrational Spectroscopy 53 (2010) 274–278

ATR spectrum of gypsum



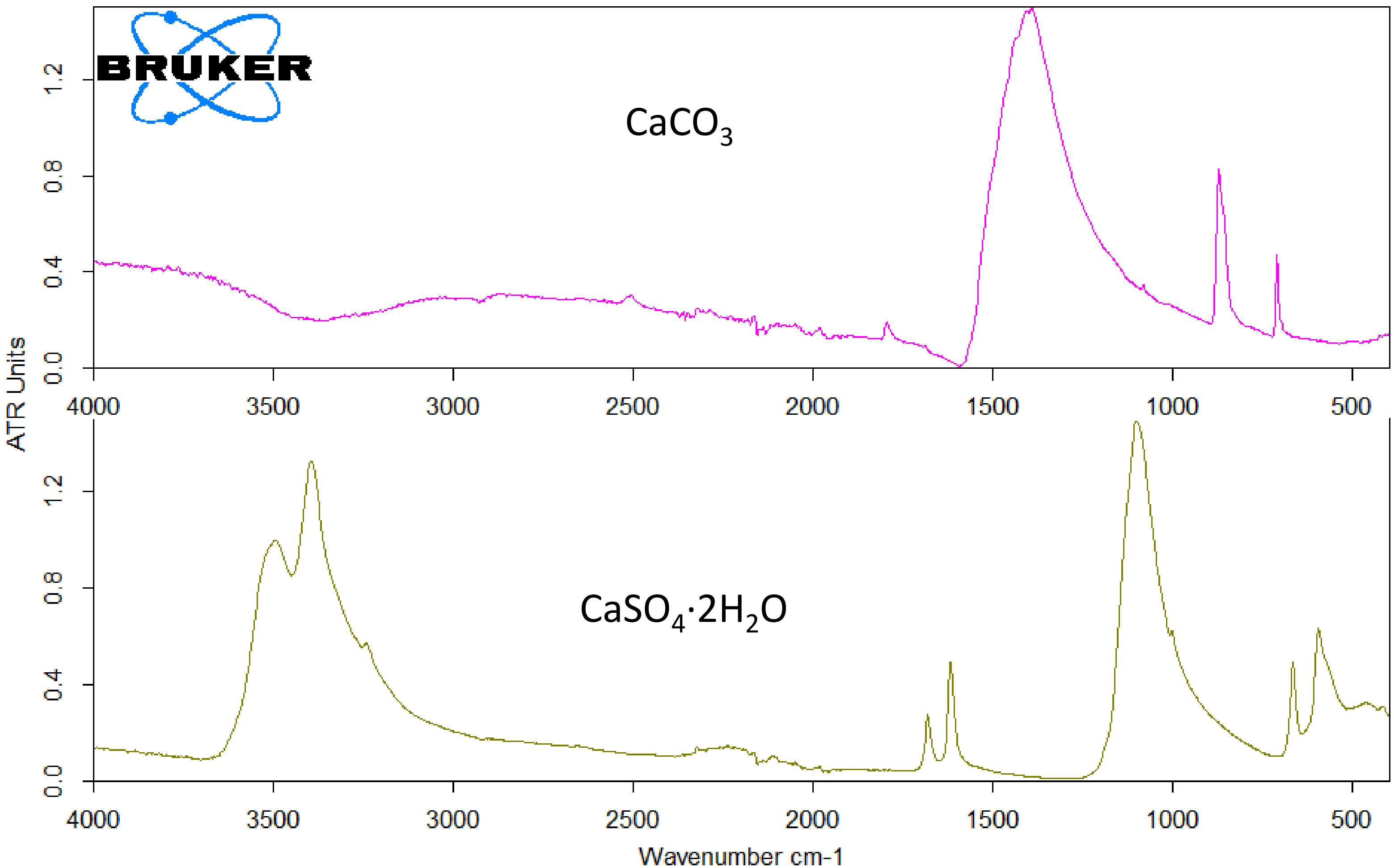
$CaSO_4 \cdot 2H_2O$

$CaSO_4.0.5H_2O$

$CaSO_4$

Water molecule:
Stretching symmetric
and antisymmetric of H_2O

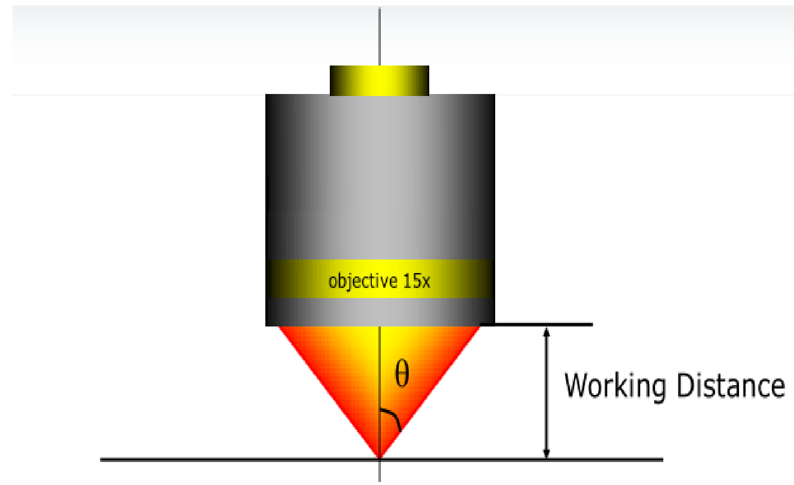
ν_3 Stretching antisymmetric of SO_4 tetrahedra
ν_1 Stretching symmetric of SO_4 tetrahedra



C:\Users\Mariangela\Documents\AAA-Misure, Analisi dati\mb	\Libreria BOPT Beni Culturali\Calcium Carbonate CaCO3 P-ATR.0	28/04/2010
C:\Users\Mariangela\Documents\AAA-Misure, Analisi dati\mb	\Libreria BOPT Beni Culturali\Calcium Sulfate CaSO4 P-ATR.0	28/04/2010

Page 1/1

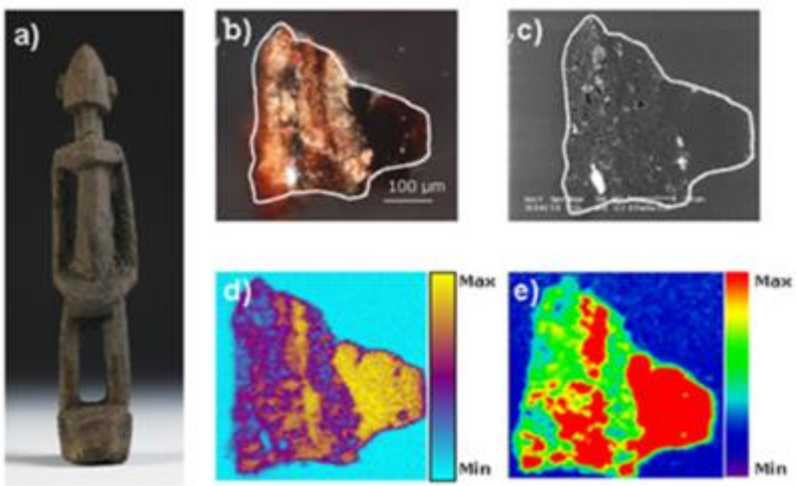
Microscopy and Imaging



$$NA = n \cdot \sin 2\theta$$

The IR microscope is essentially a beam condenser

FTIR imaging



Study of the patina sample from a Dogon statuette:

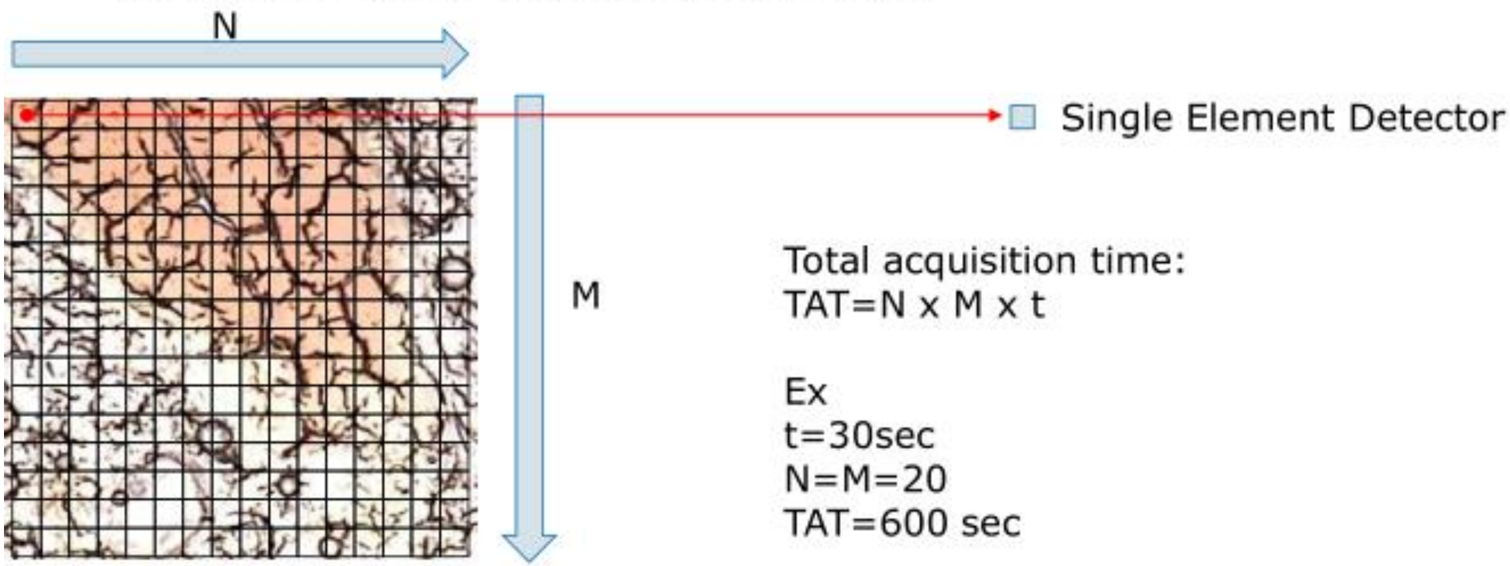
a) Photograph of the object, Quai Branly Museum, inventory no 71.1935.105.169, (copyright C2RMF, D. Vigears);
b) Dark field microscopic view of the cross-section of the sample;
c) Backscattered electron micrograph;
d) ToF-SIMS image of protein fragment ions;
e) SR-µFTIR image of proteins.

Vincent Mazel et al, (2007).
Analytical Chemistry. DOI : 10.1021/ac070993k

Mapping vs imaging

Mapping:

- Campione
- Stage portacampioni automatico gestito da PC
- Rivelatore a singolo elemento (MCT, 250μm)



Total acquisition time:
TAT=N x M x t

Ex
t=30sec
N=M=20
TAT=600 sec

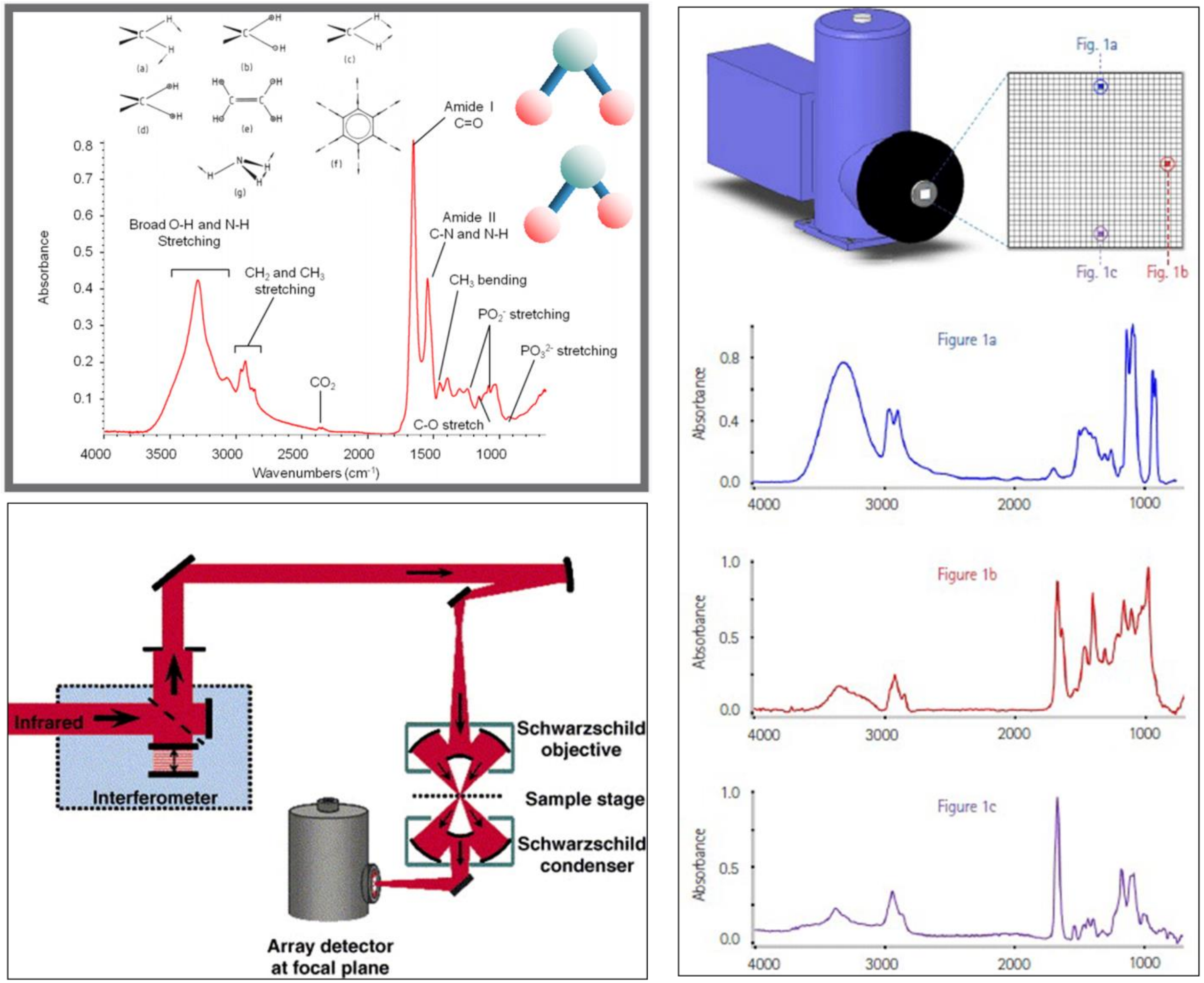
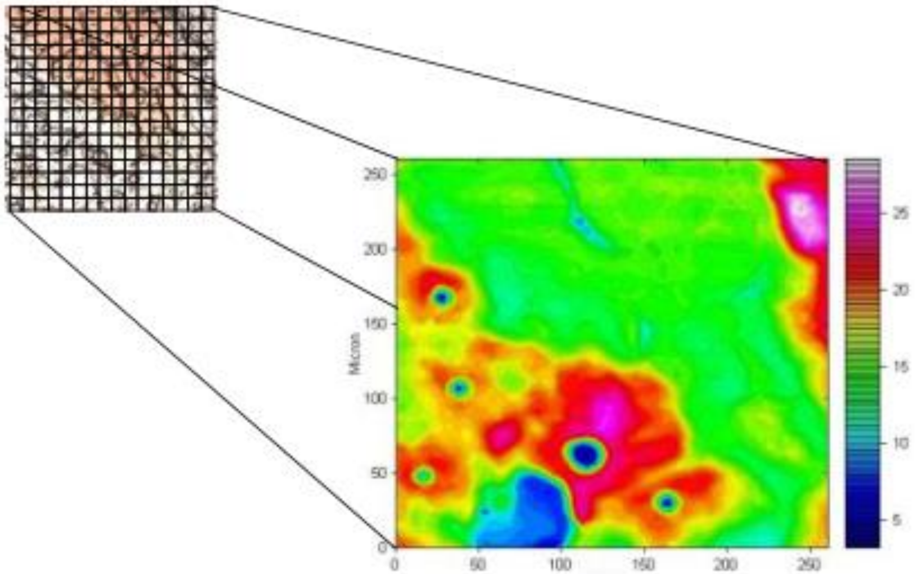


Figura 2: (a) Lo spettro IR di un composto organico mostra gli assorbimenti dovuti alle vibrazioni molecolari. (b) Schema ottico del microscopio IR accoppiato allo spettrometro ed al detector FPA. (c) Schema di funzionamento di un detector FPA.

Imaging:

- Campione
- Stage portacampioni non necessariamente automatico
- Focal Plane Array Detector (64x64, 128x128, 256x256 – pixel da 40μm)



Total acquisition time:
TAT=t

In t we are acquiring a NxN matrix of spectra

APPLICATION TO THE STUDY OF PAINTING CROSS SECTIONS

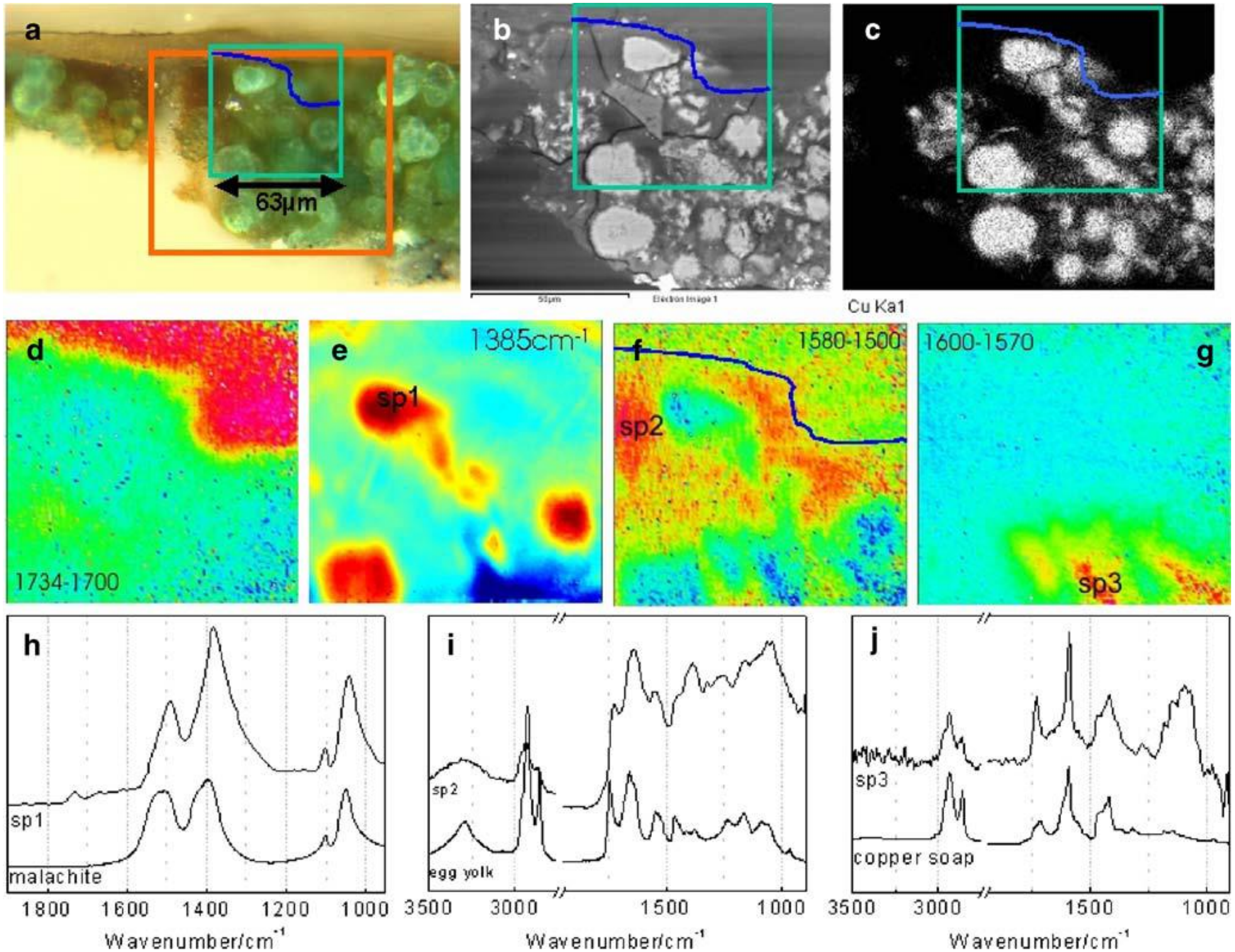


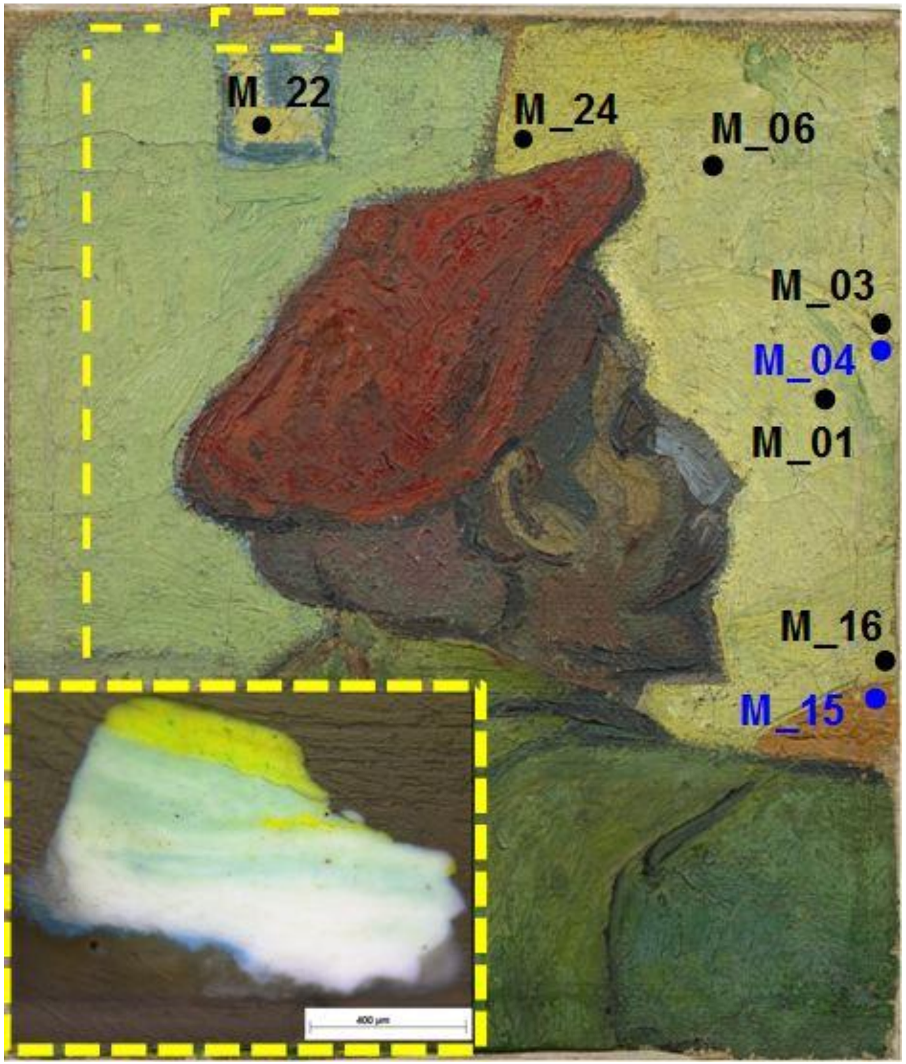
Figura 1. Sezione stratigrafica di un frammento prelevato dalla veste verde di un dipinto raffigurante la Madonna col Bambino: a) sezione stratigrafia al microscopio ottico in luce visibile; b) immagine ottenuta al microscopio elettronico (SEM); c) mappatura dell'elemento rame (Cu) eseguita mediante spettrometro a raggi X al microscopio elettronico (SEM-EDS); d) distribuzione della resina poliestere ottenuta mediante FTIR FPA-imaging; e) distribuzione del pigmento verde malachite, ottenuta mediante FTIR FPA-imaging; f) distribuzione di legante proteico, ottenuta mediante FTIR FPA-imaging; g) distribuzione di olio siccativo ottenuta mediante FTIR FPA-imaging; h) spettro di assorbenza della particella verde e del riferimento della malachite; i) spettro della componente proteica e del riferimento del rosso d'uovo; j) spettro ottenuto da una zona contenente olio siccativo e lo spettro di riferimento di una "sapone" formatosi per reazione tra rame e olio siccativo – immagine tratta dal testo citato – nota 3

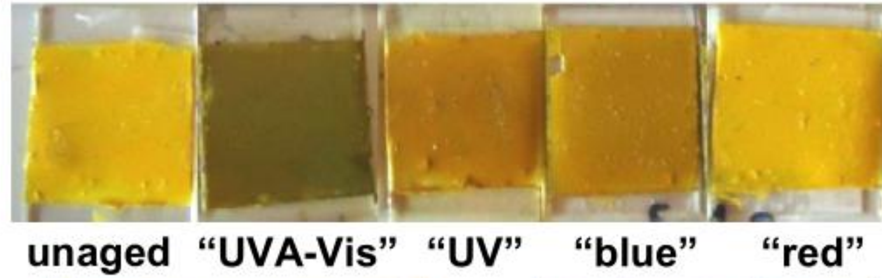
Studio dei processi di degradazione dei pigmenti gialli di Van Gogh

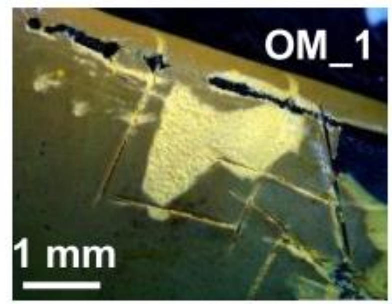
ESRF DESY Universiteit Antwerpen VAN GOGH MUSEUM kröller-müller museum CENTRE DE RECHERCHE ET DE RESTAURATION DES MUSÉES DE FRANCE

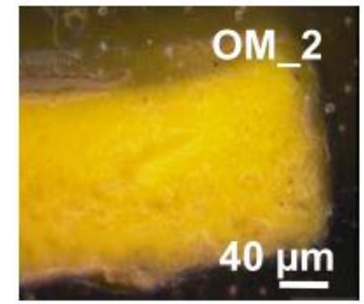
INFN Istituto Nazionale di Fisica Nucleare

http://www.vangogh.ua.ac.be/









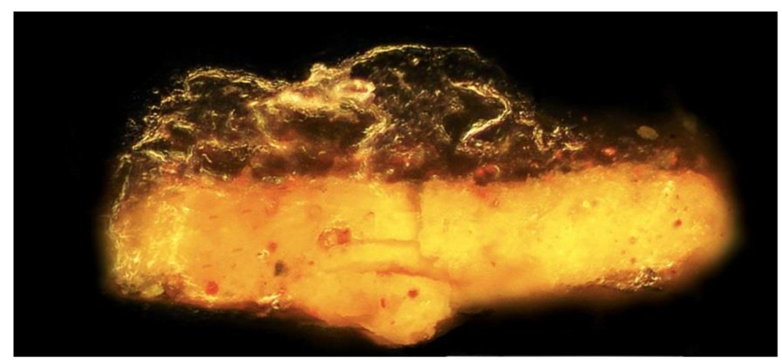


Image courtesy of http://www.vangogh.ua.ac.be/

Alcuni spettri di riferimento

Courtesy of Centro Conservazione e Restauro
La Venaria Reale

Centro Conservazione e Restauro
La Venaria Reale

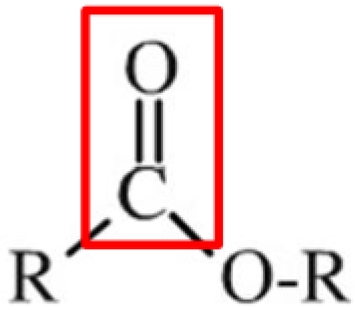
Il carbonile

C-H	2960-2850	stretch
	1470-1350	scissoring and bending
	1380	- Doublet - isopropyl, *t*-butyl
C-H	3080-3020	stretch
	1000-675	bend
C-H	3100-3000	stretch
	870-675	bend
	2000-1600	fingerprint region
C-H	3333-3267	stretch
	700-610	bend
C=C	1680-1640	stretch
C≡C	2260-2100	stretch
C=C	1600, 1500	stretch
C-O	1260-1000	stretch
C=O	1760-1670	stretch
O-H	3640-3160	stretch
	3600-3200	stretch
	3000-2500	stretch
N-H	3500-3300	stretch
	1650-1580	bend
C-N	1340-1020	stretch
C≡N	2260-2220	stretch

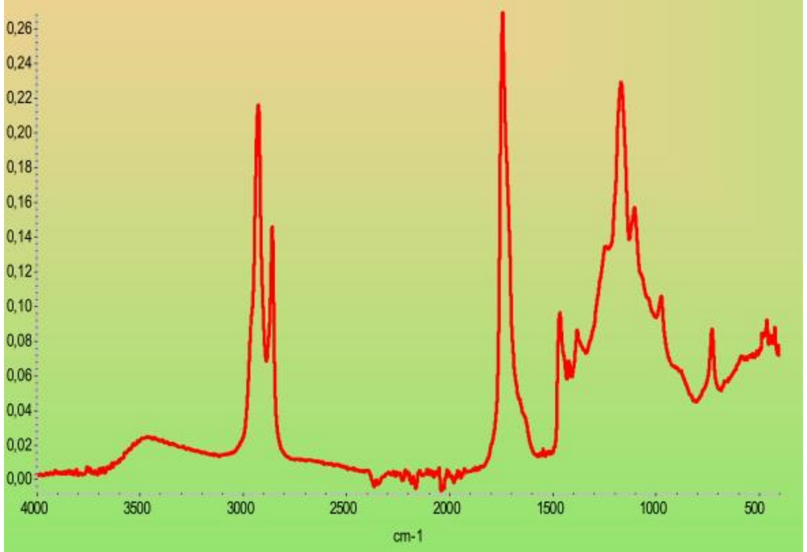
Solventi
Leganti
Vernici
Fibre

Ma anche in alcuni pigmenti inorganici

Gli esteri

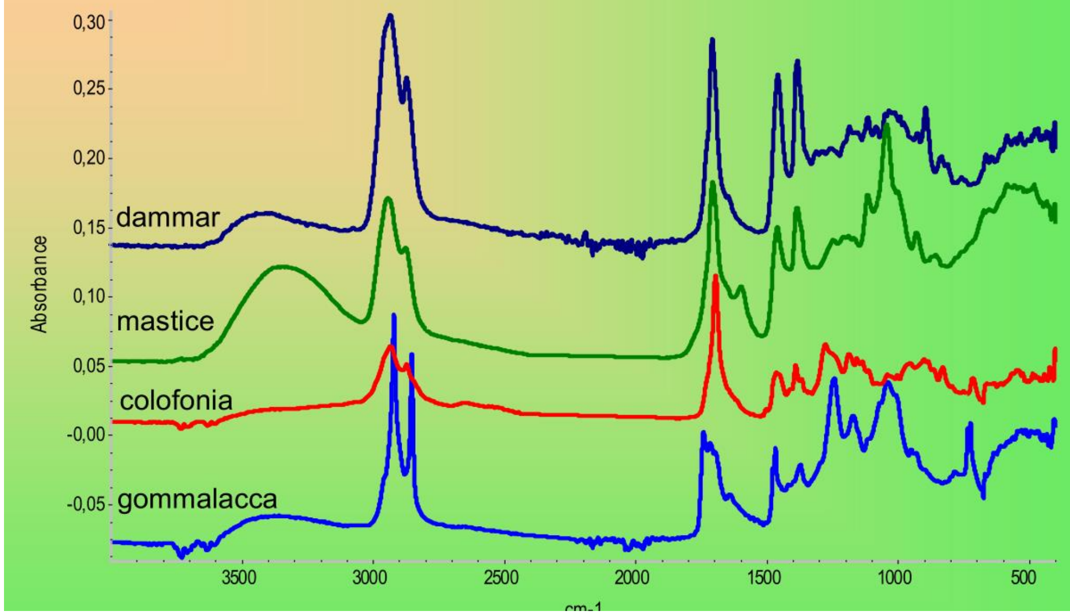


Olii siccativi
Resine naturali
Cere
Resine sintetiche
Additivi
Plastiche

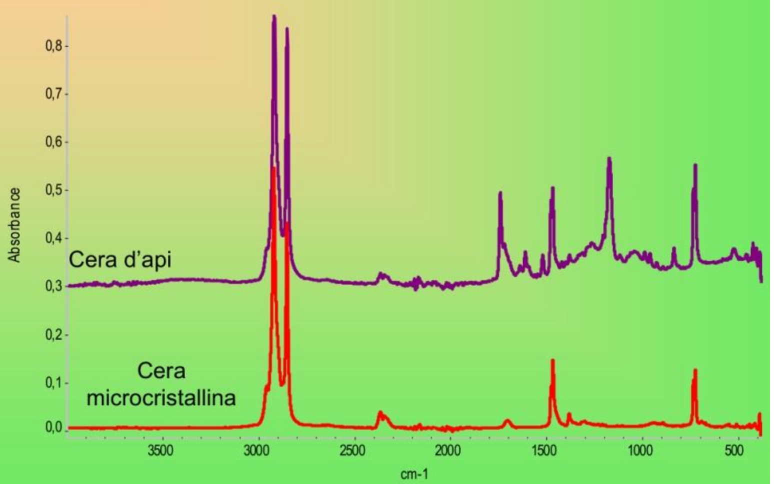


Olio di lino cotto

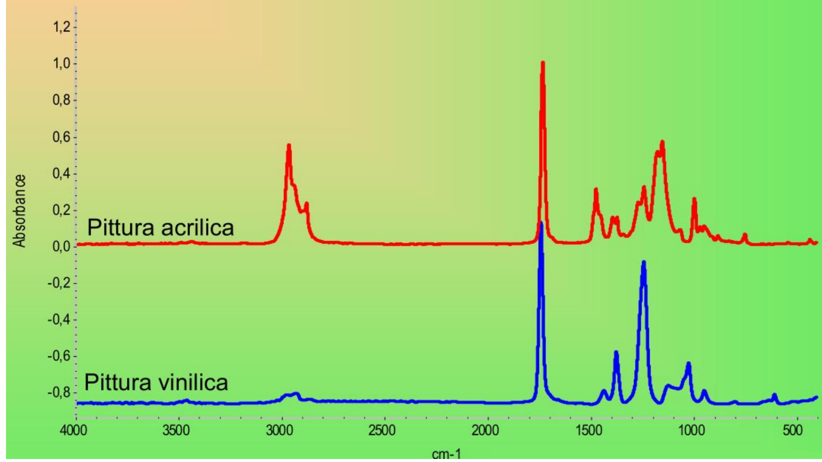
Resine naturali



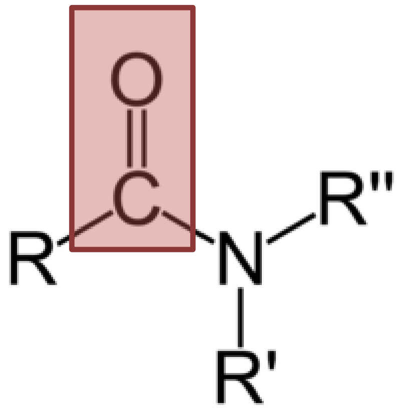
Cere



Resine sintetiche



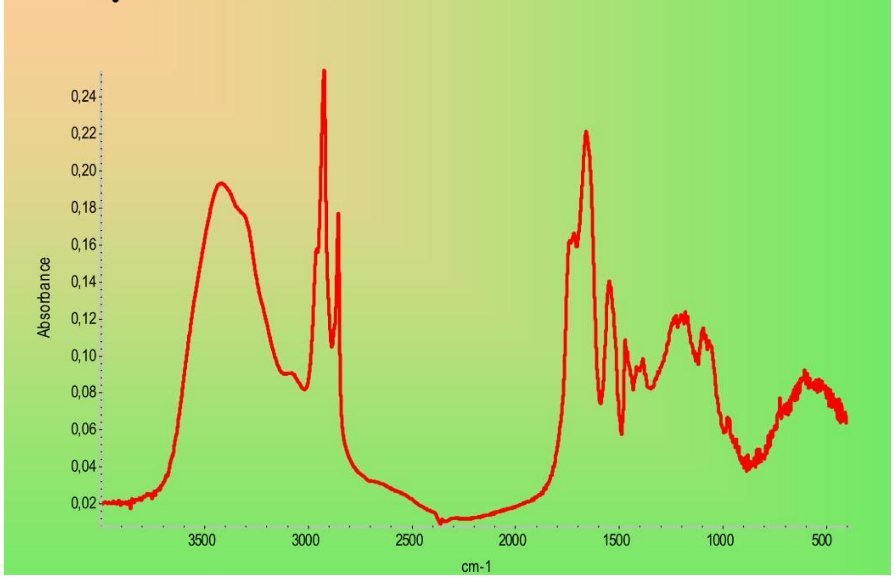
Le ammidi



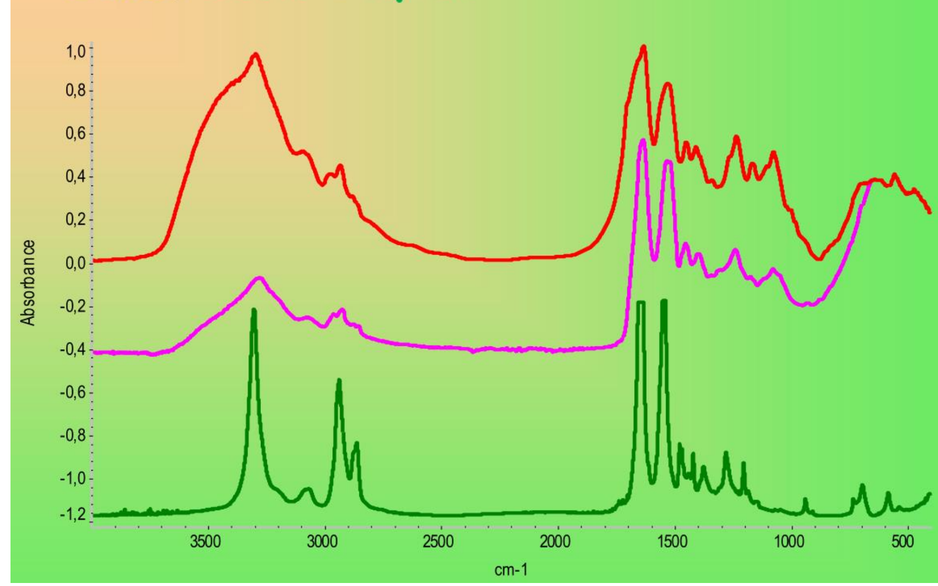
Struttura generale di un'ammide. Se R' e R'' sono idrogeni l'ammide si dice primaria, se solo uno fra R' ed R'' è un H, si dice secondaria, se R' ed R'' non sono idrogeni, l'ammide si dice terziaria

Tempere all'uovo
Tempera grassa
Lana e seta
Colle animali
Cuoio e pelle
Caseina
Plastica

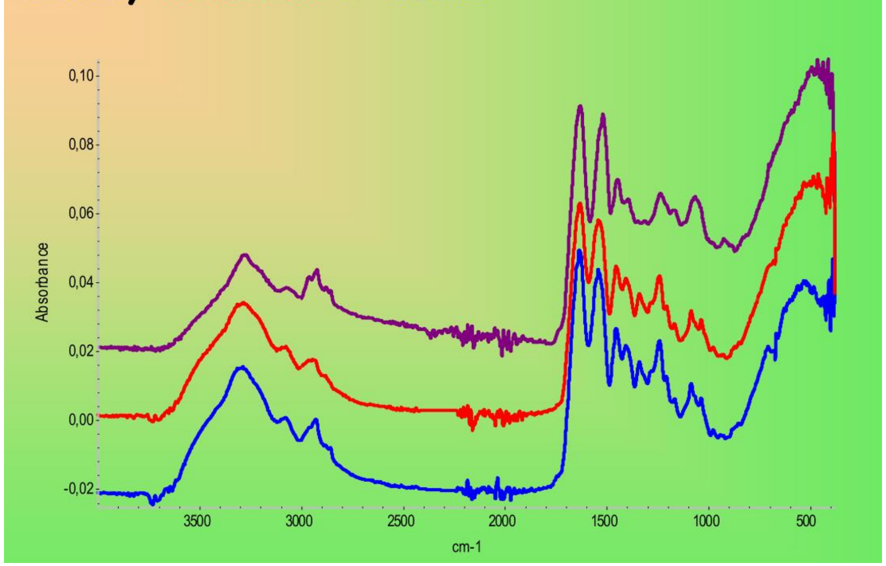
Tempere all'uovo



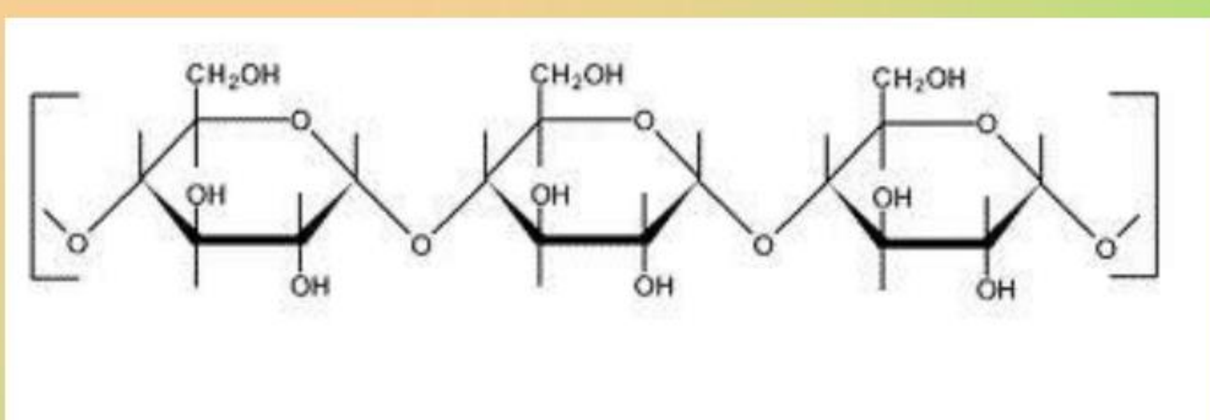
Lana, seta e nylon



Colla, caseina e cuoio



I polisaccaridi



Acquerello

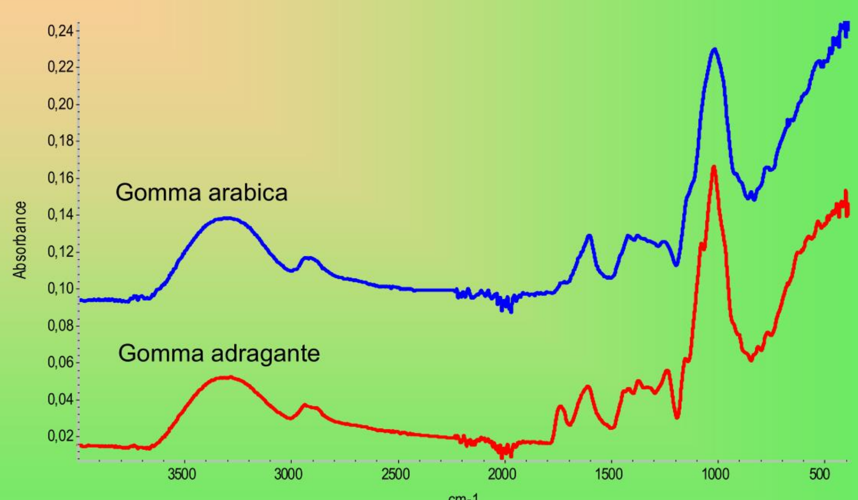
Gomme naturali

Legno

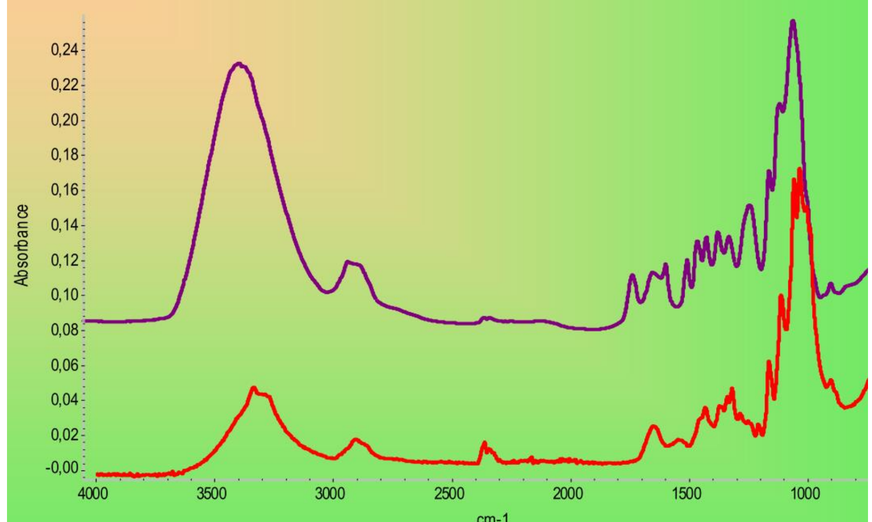
Carta

Fibre vegetali

Acquerello

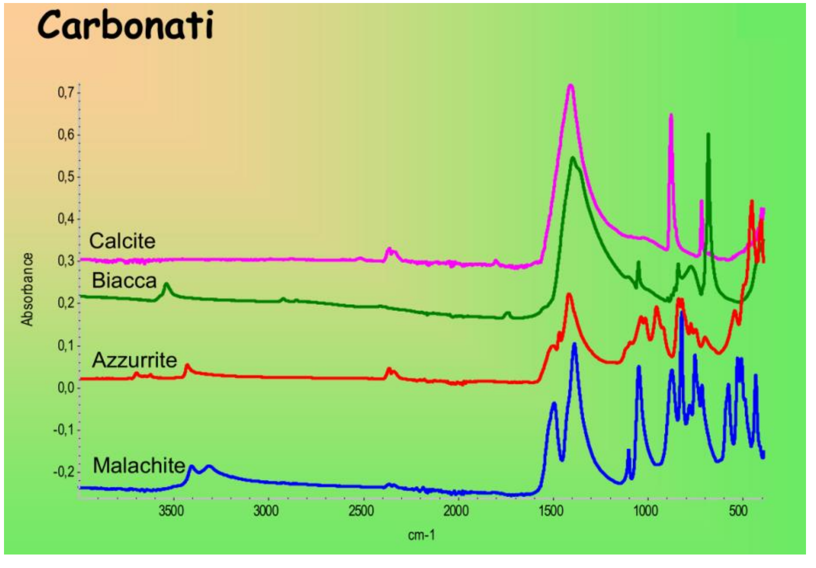


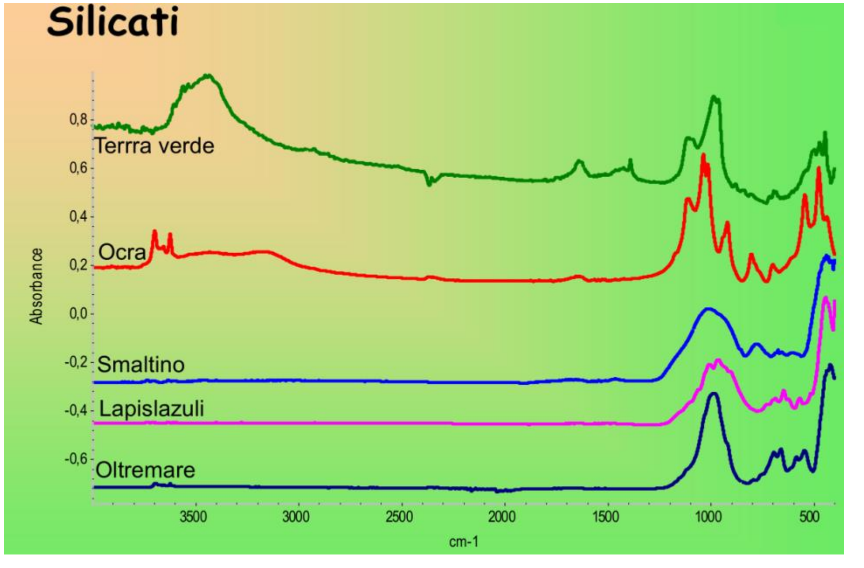
Legno e carta



I pigmenti

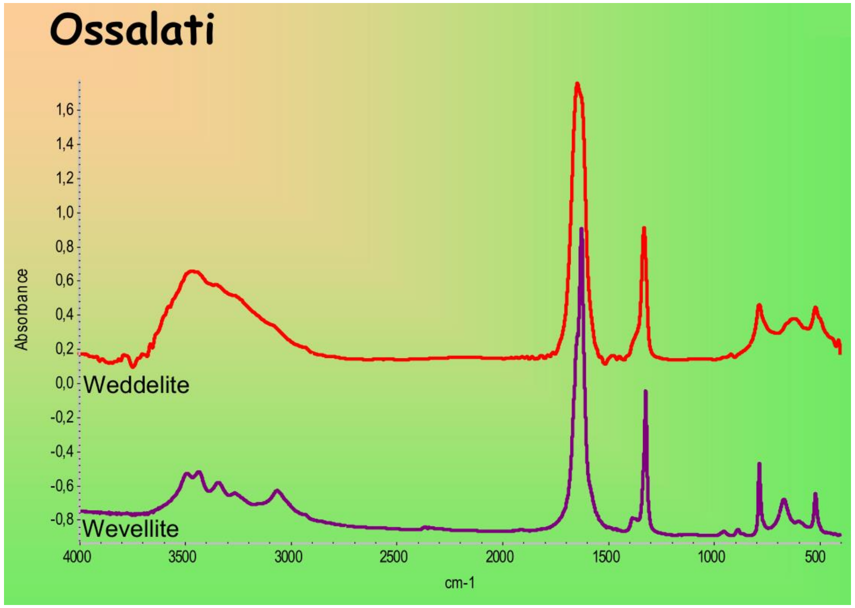
- Carbonati
- Silicati
- Solfati
- Pigmenti organici

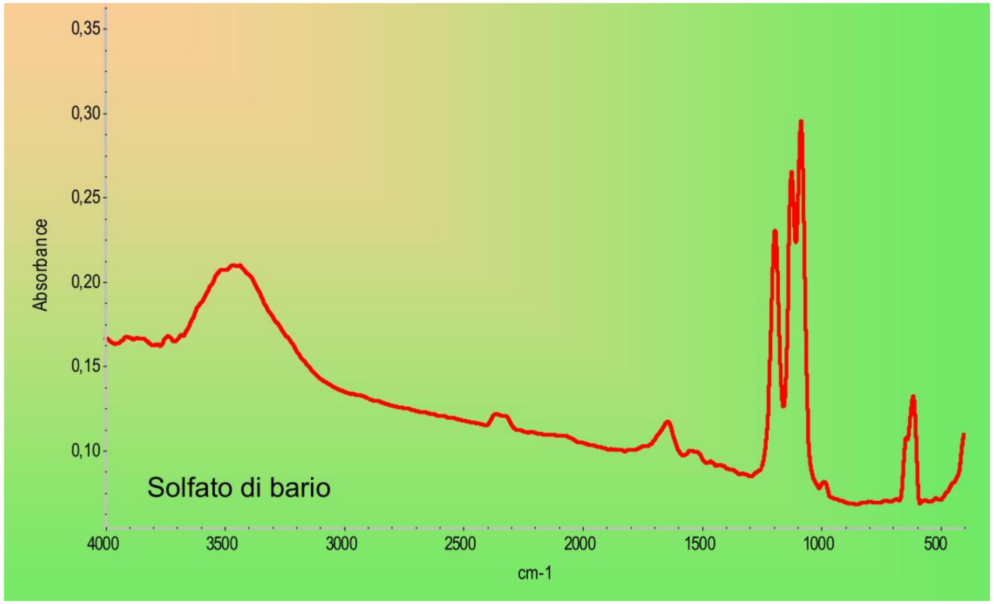




Prodotti di degrado comuni

- Solfati
- Ossalati
- Nitrati
- Saponi





DAFNE-LIGHT

INFN-LNF Synchrotron Radiation Facility

INFN | LNF | DAFNE Storage Ring | DAFNE-Light

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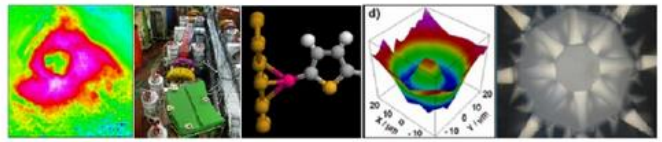

DAFNE-Light

DAFNE-Light is the Synchrotron Radiation Facility at the Laboratori Nazionali di Frascati (LNF).

Three beamlines are operational using, in parasitic and dedicated mode, the intense photon emission of DAFNE, a 0.51 GeV storage ring with a routinely circulating electron current higher than 1 Ampere. Two of these beamlines (DXR1 and DXR2) have one of the DAFNE wiggler magnets as synchrotron radiation source, while the third beamline (SINBAD-IR) collects the radiation from a bending magnet. New XUV bending magnet beamlines are nowadays under construction.

The beamlines DXR1 and SINBAD-IR are open to external users.

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