Diagnostic techniques for cultural heritage: applications of Synchrotron FourierTransform Infrared (FT-IR) spectroscopy

Mariangela Cestelli Guidi
Sinbad IR beamline @ DaΦne

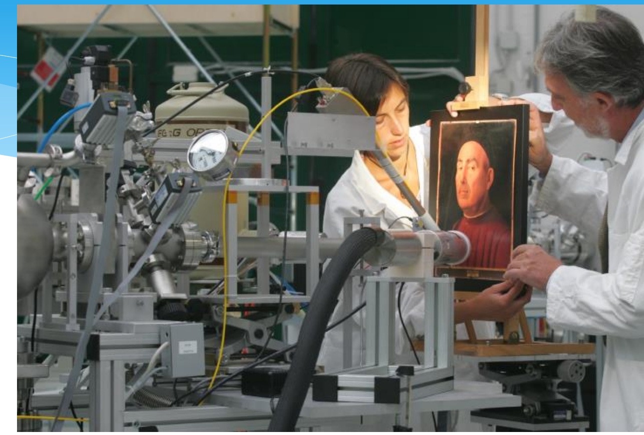
INFN-International Masterclass 2017

Layout

* The scientific approach to conservation
* Principles of FT-IR spectroscopy
* Sampling techniques: transmission, reflection, Attenuated total reflection (ATR) and Diffuse reflection (DRIFT)
* Infrared imaging and microscopy: chemical images
* FT-IR Analysis of a painting cross section

The scientific approach to conservation

* Material ageing, climate change, atmospheric pollution, anthropic pressure…
* Inappropriate conservation and restoration procedures have also contributed to degradation of artworks
* The modern approach to conservation requires a **deep scientific investigation** before any treatment

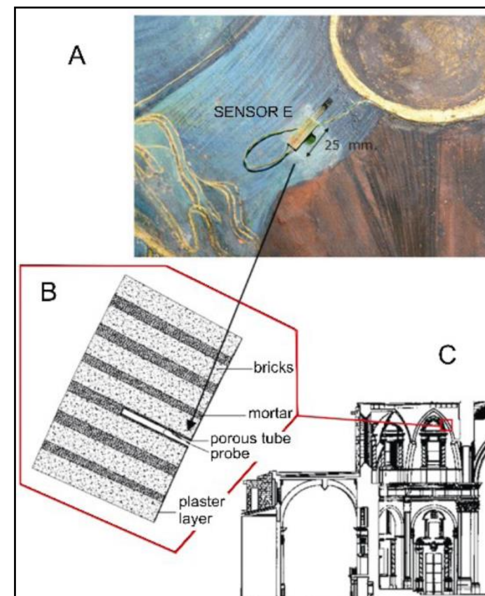


In situ diagnostic

Laboratory diagnostic

Conservation

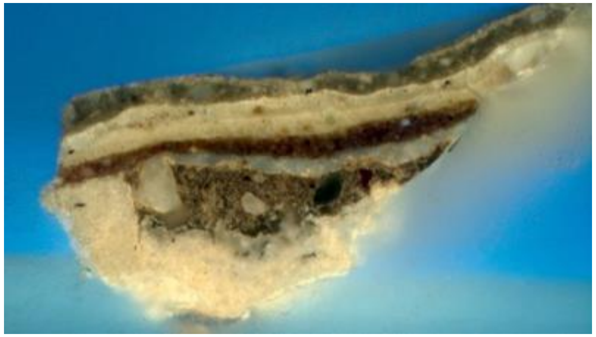
Monitoring

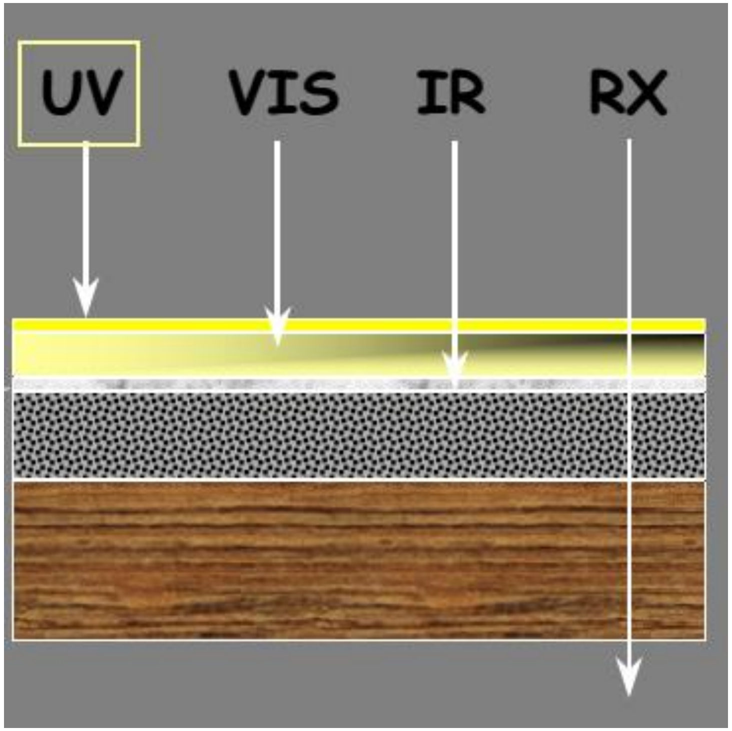


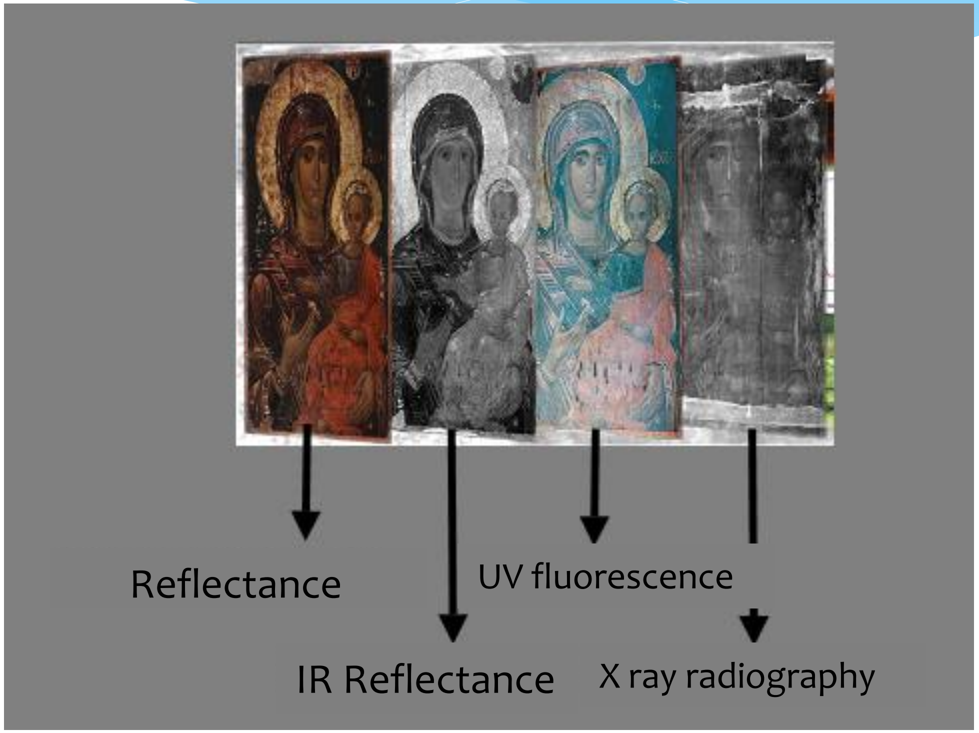
Sampling techniques

* Non destructive

* Micro destructive

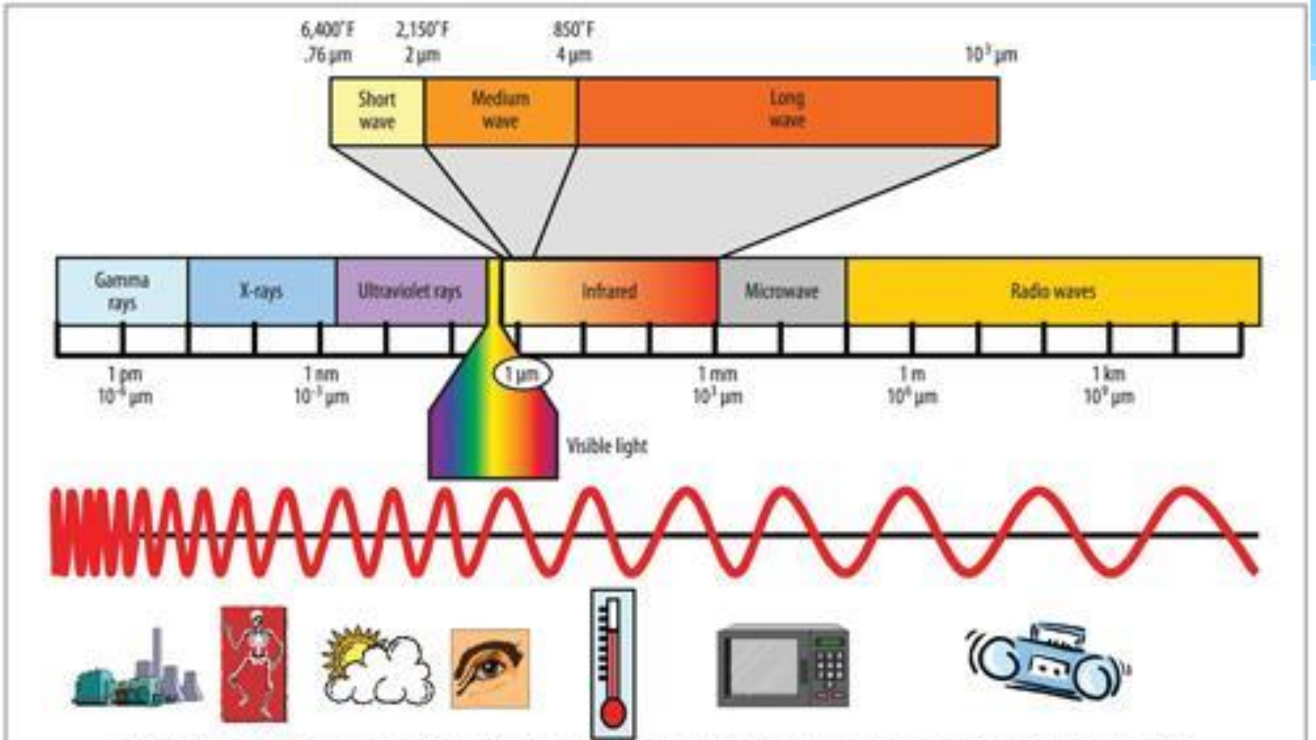



UV
VIS
IR
RX

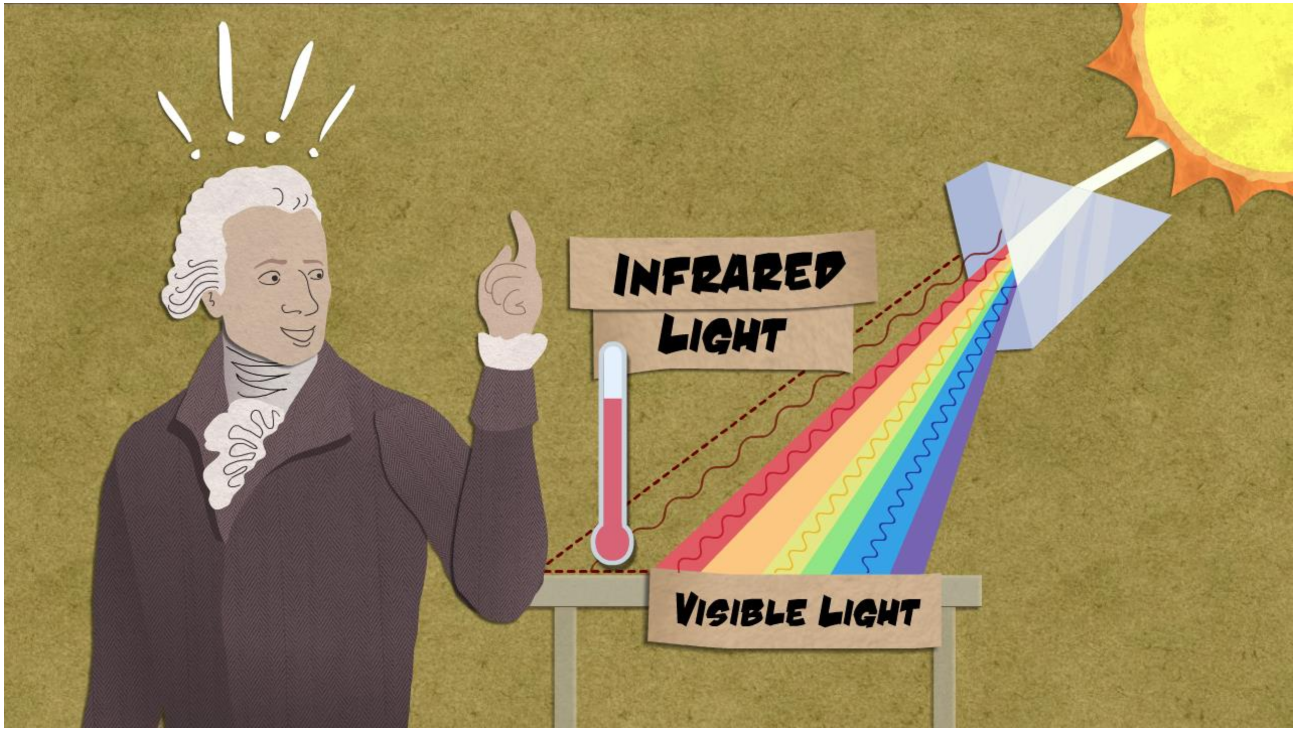

Reflectance
UV fluorescence
IR Reflectance
X ray radiography

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

Electromagnetic spectrum and IR



The electromagnetic spectrum describes the various types of electromagnetic energy based on wavelength.



William Herschel (1738-1822)

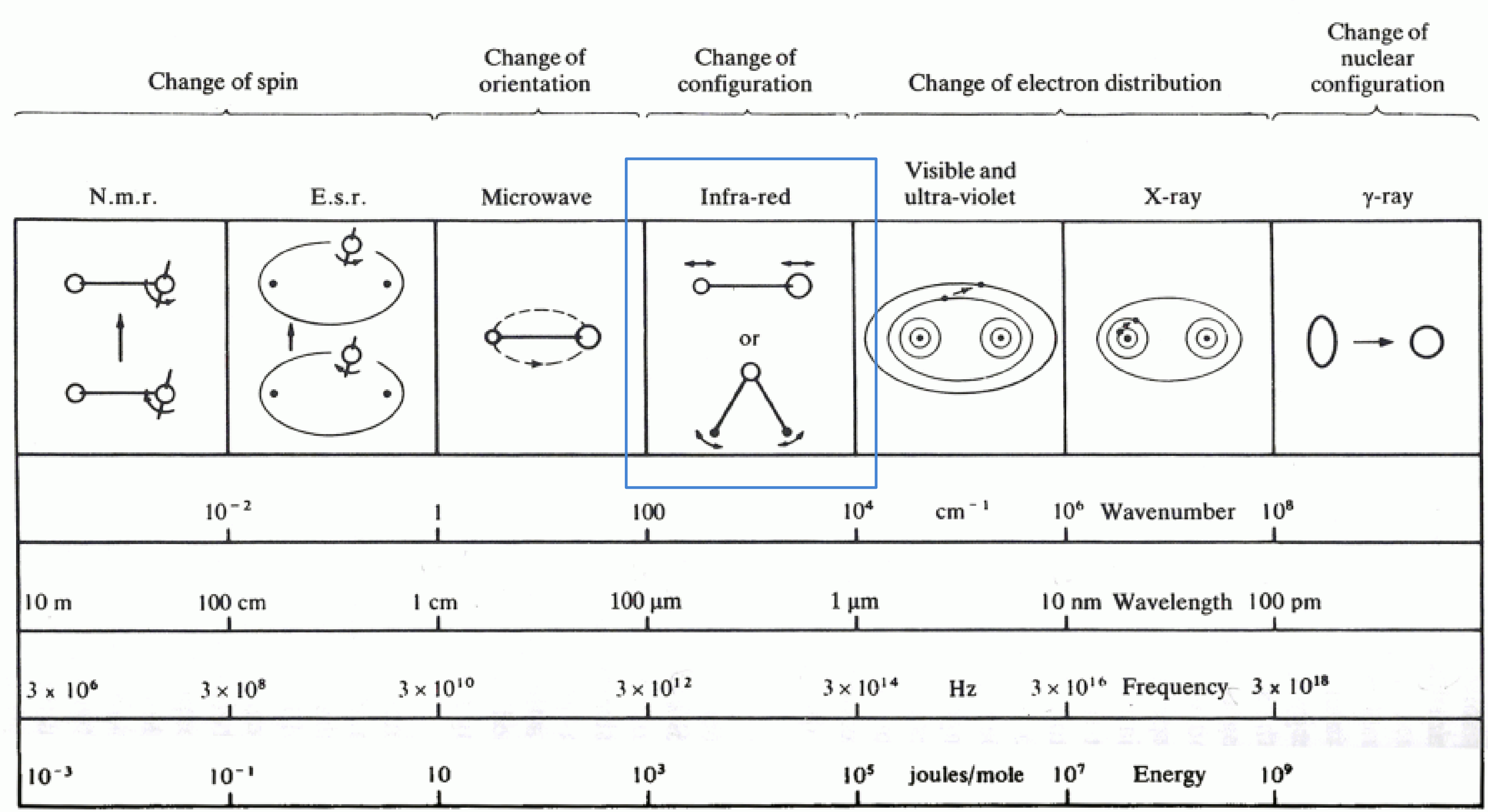
IR Units

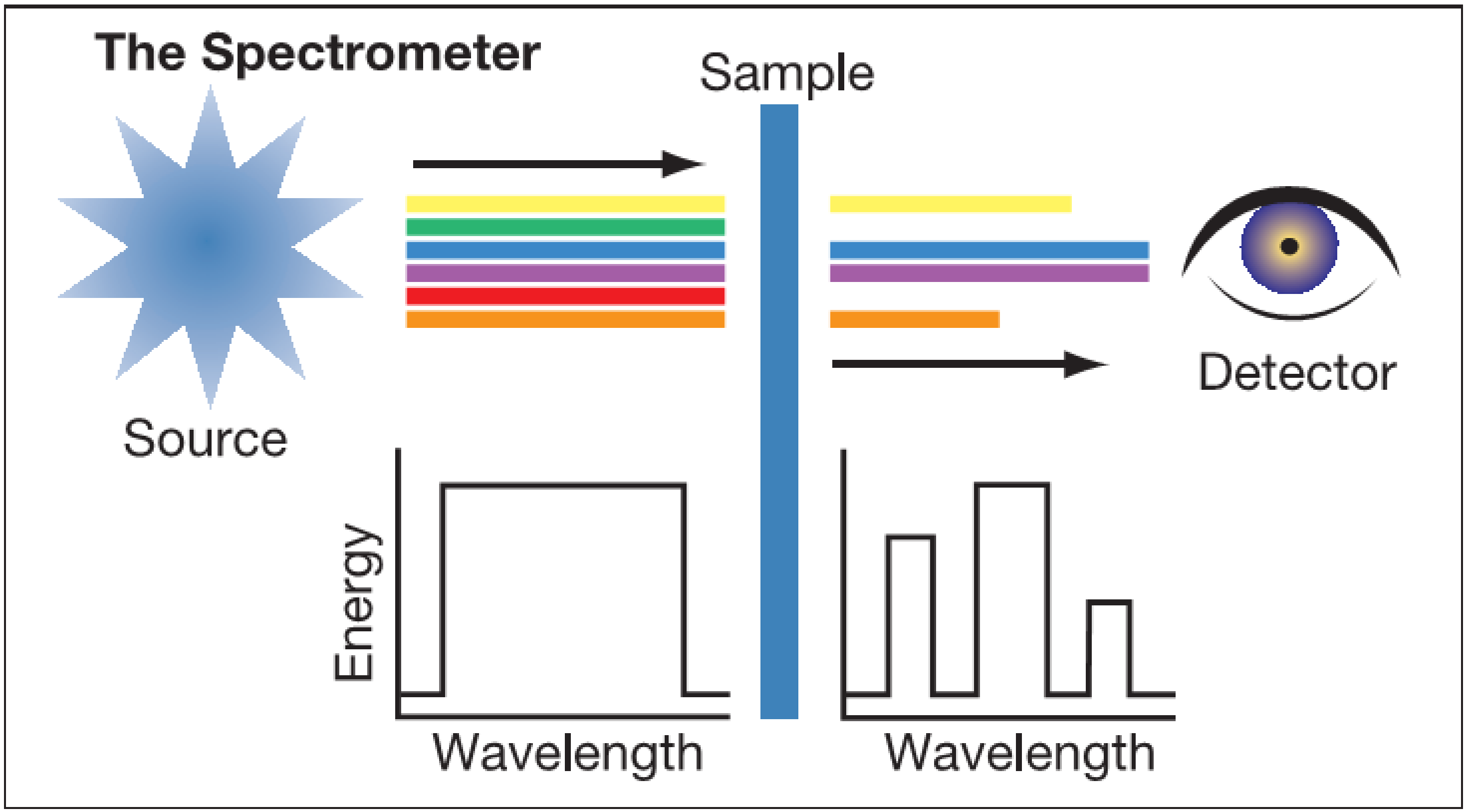
- Visible and IR light are both EM radiation, differing only for the wavelegth. They both propagate in vacuum at the light speed c.

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

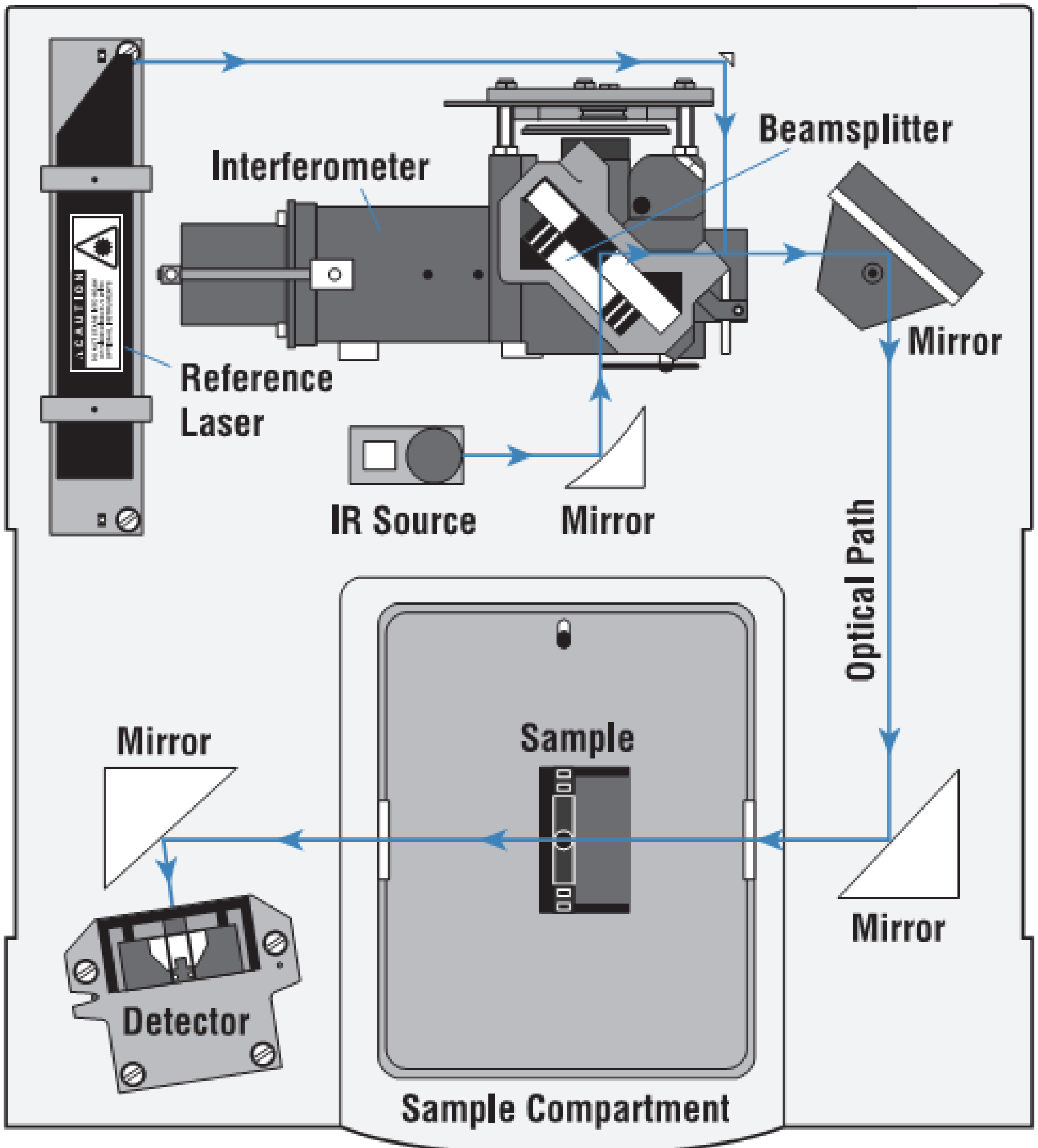
$$\tilde{\nu}\ (\mathrm{cm}^{-1}) = 1/\lambda\ (\mathrm{cm})$$

What happens when «light» interacts with matter




The Spectrometer
Sample
Source
Detector
Energy
Wavelength
Wavelength

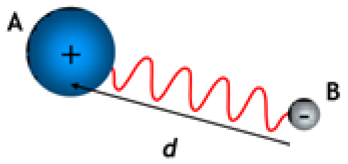

Optical Beampath
HYPERION 1000/2000
www.brukeroptics.com
VERTEX 70
Infrared correlation cha
HYPERION
VERTEX 70


Interferometer
Beamsplitter
Mirror
Reference
Laser
IR Source
Mirror
Optical Path
Sample
Mirror
Mirror
Detector
Sample Compartment

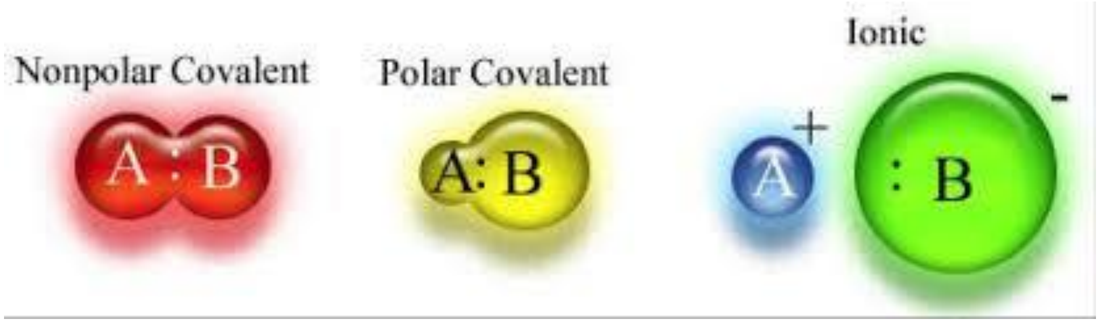
Every molecule interacts with the IR EM field?

* In the simple case of two point charges, one with charge $+q$ and the other one with charge $-q$, the electric dipole moment **p** is:

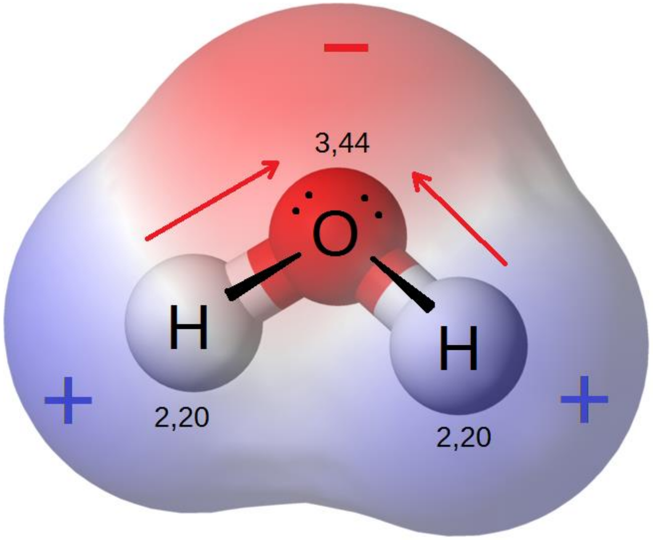
$$\mathbf{p} = q\mathbf{d}$$



* **d** is the displacement vector pointing from the negative charge to the positive charge. Thus, the electric dipole moment vector **p** points from the negative charge to the positive charge.


Nonpolar Covalent
A : B
Polar Covalent
A: B
Ionic
A
+
: B
-

Polar molecules



When one end of the molecule is slightly positive and one end is slightly negative

Non polar molecules

Common examples of non-polar gases are the noble or inert gases, including:

* Helium (**He**)
* Neon (**Ne**)
* Krypton (**Kr**)
* Xenon (**Xe**)

Other non-polar gases include:

* Hydrogen ($\mathbf{H_2}$)
* Nitrogen ($\mathbf{N_2}$)
* Oxygen ($\mathbf{O_2}$)

IR active modes

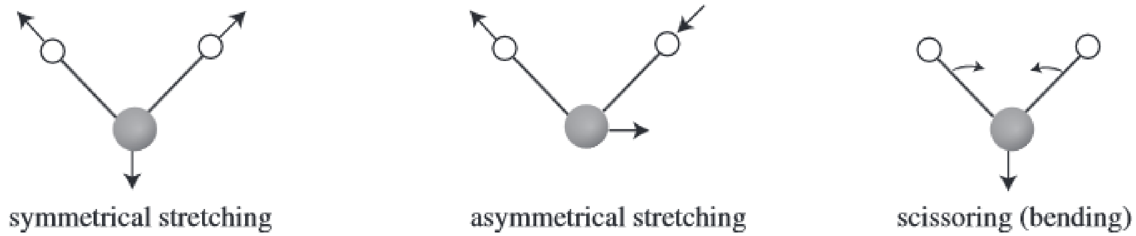


Figure : Stretching and bending vibrational modes for H_2O

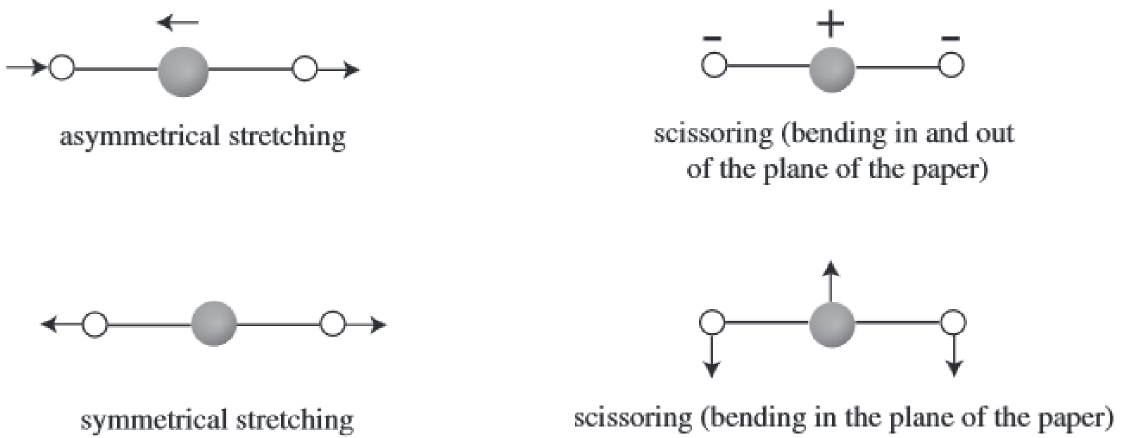
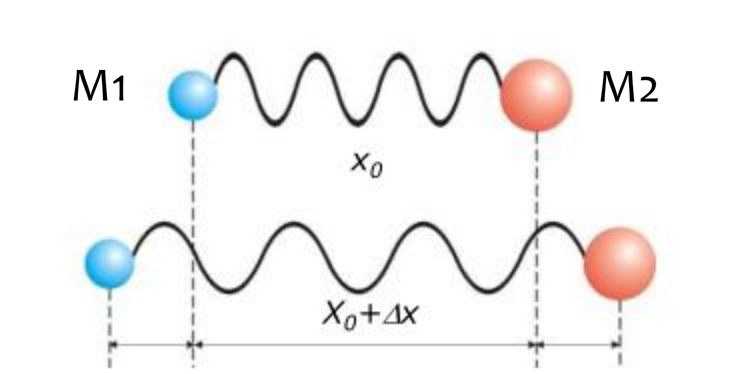


Figure : Stretching and bending vibrational modes for CO_2

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



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

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

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

Normal modes of vibration

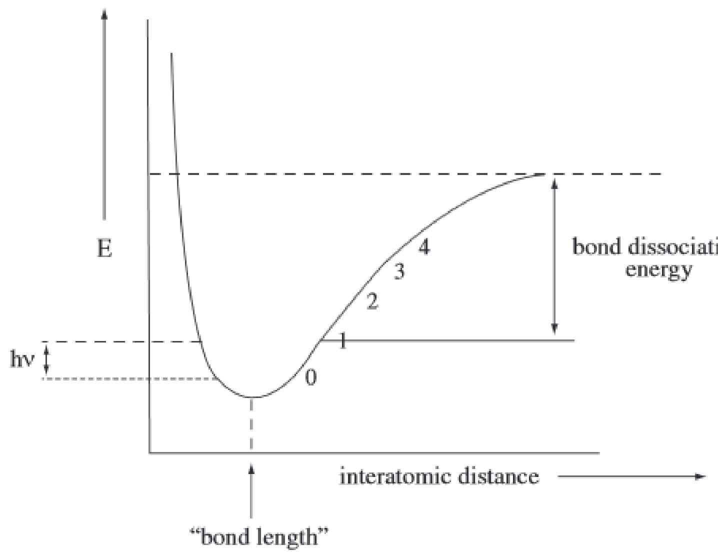
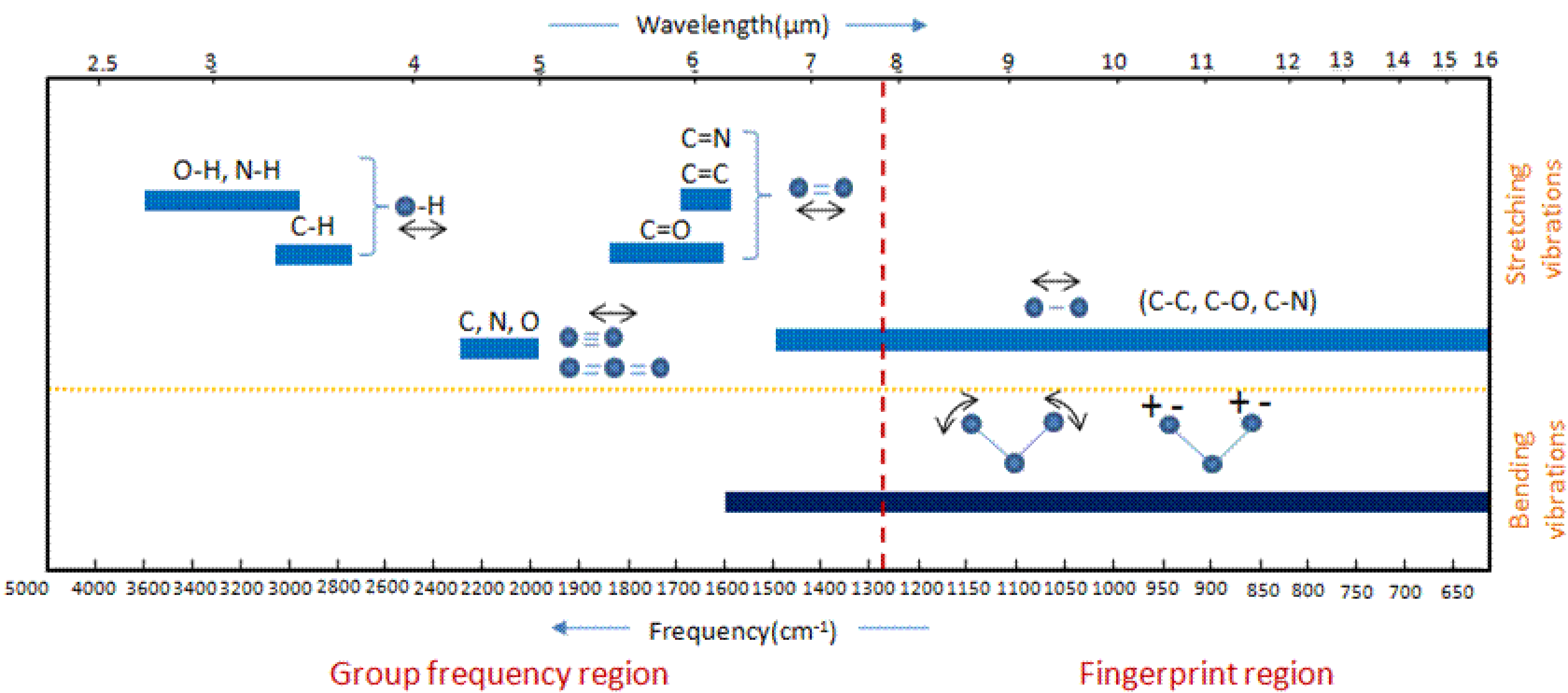


Figure 15.8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

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

(quantized energy levels)

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



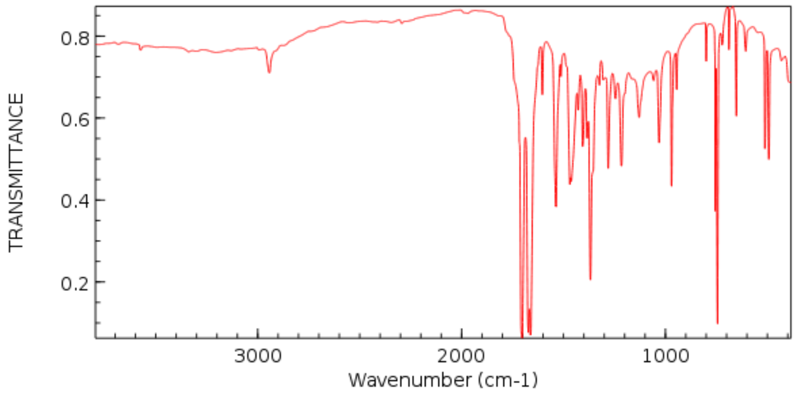
Single bonds: C-C, C-O, C-N → 800 - 1300 cm^{-1}

Double bonds: C=C, C=O, C=N → 1700-1900 cm^{-1}

Triple bonds: C≡C, C ≡N → 2000-2300 cm^{-1}

C-H, N-H, O-H → 2700-3800 cm^{-1}

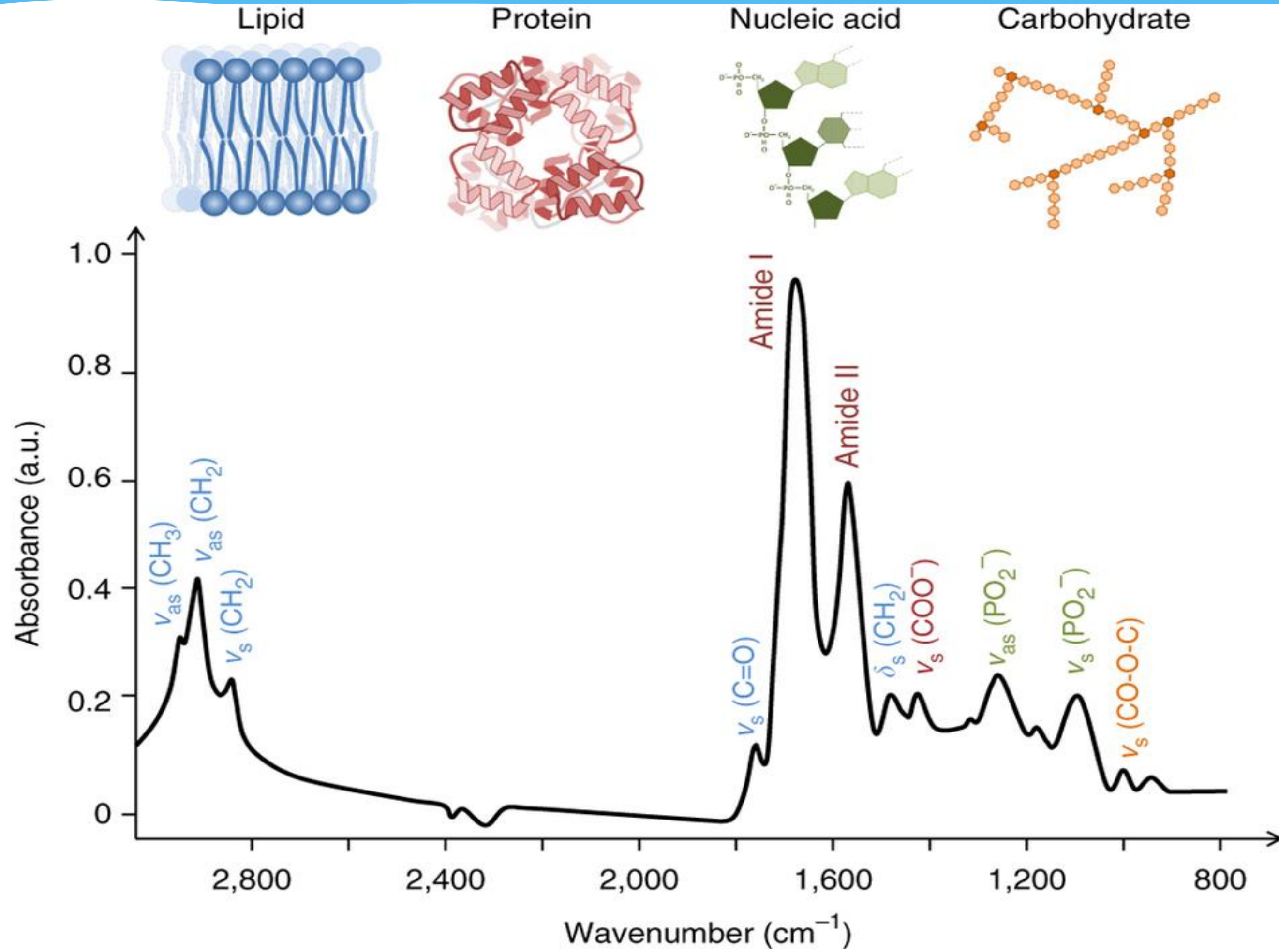
Every molecule has its unique IR spectrum



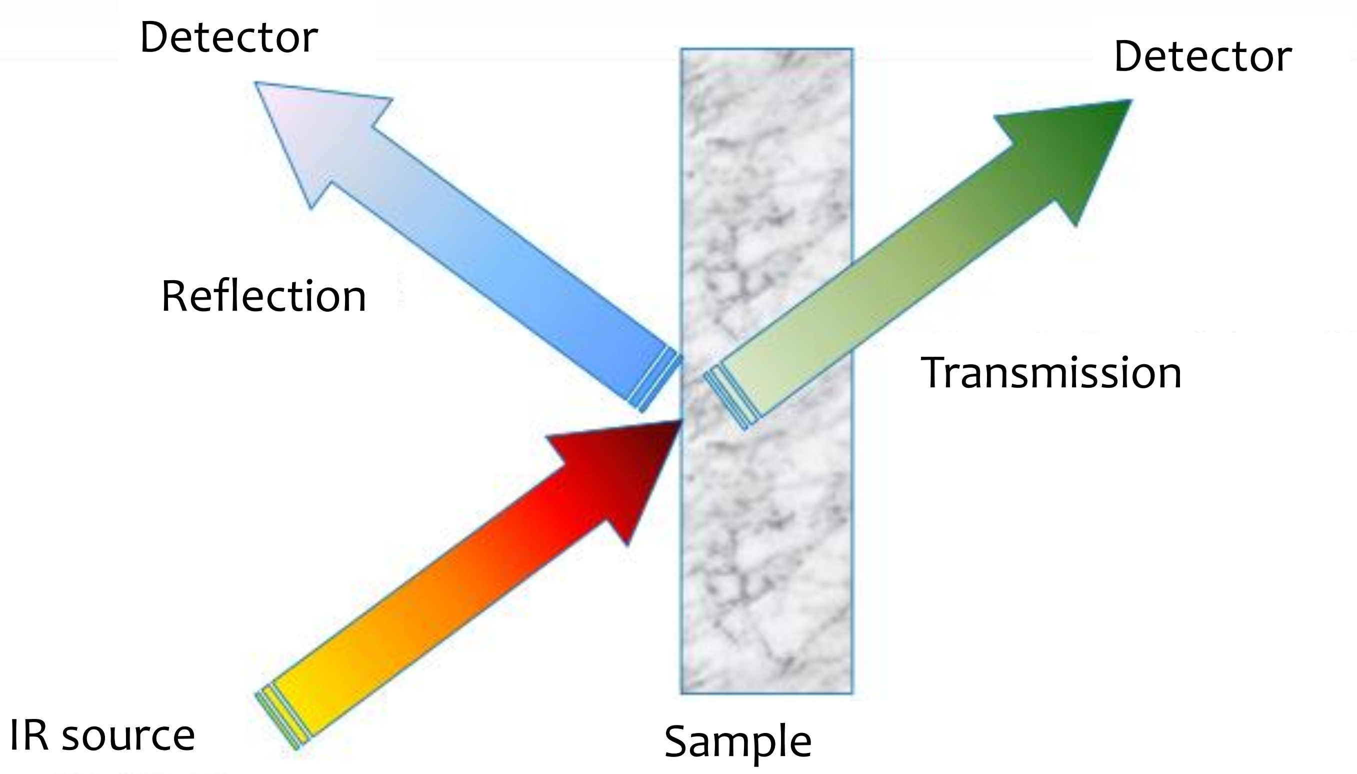
So, what Information can FT-IR Provide?

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

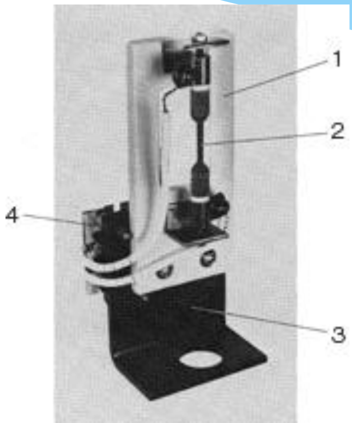
Also very complex molecules…

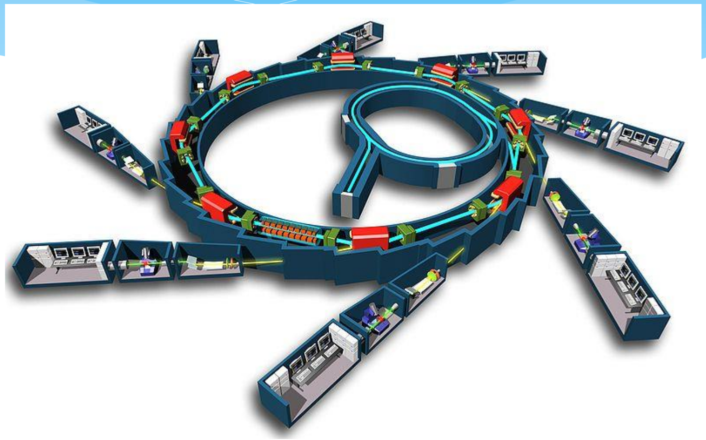


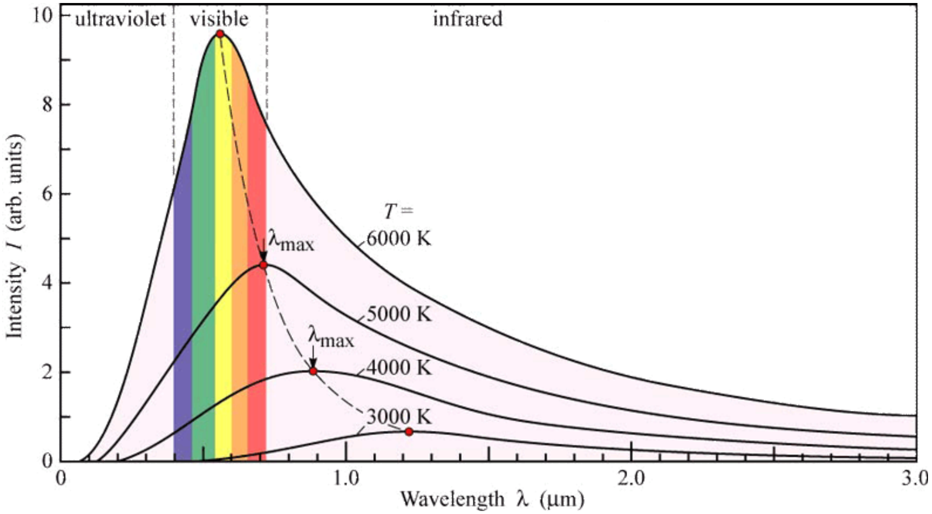
Fourier Transform Infrared Spectroscopy (FT-IR)


Detector
Detector
Reflection
Transmission
IR source
Sample

IR sources

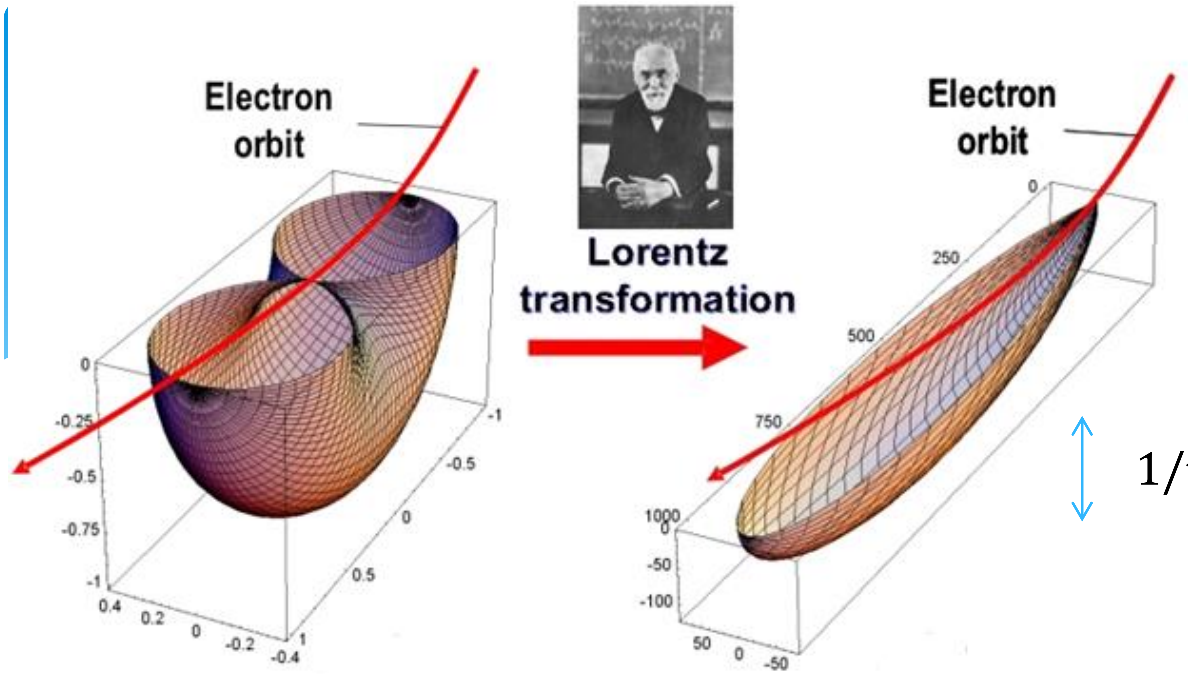

1
2
3
4




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

Synchrotron radiation

The electromagnetic radiation emitted when charged particles are accelerated radially (**a** ⊥ **v**) is called **synchrotron radiation**



$1/\gamma$

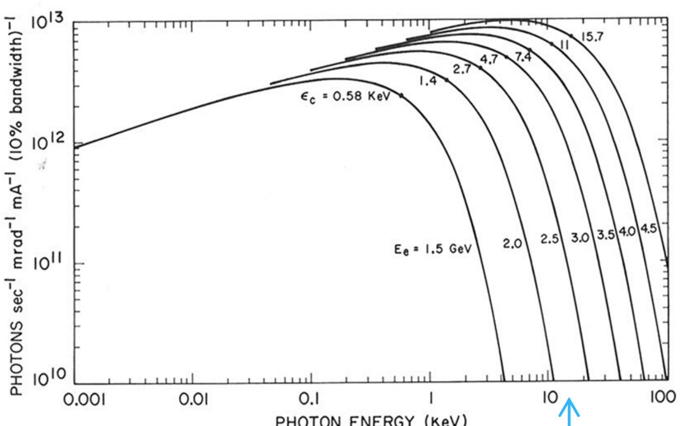
Classic (v<<c)
(c= speed of light)

Relativistic (v≈c)

$$\beta = v/c$$

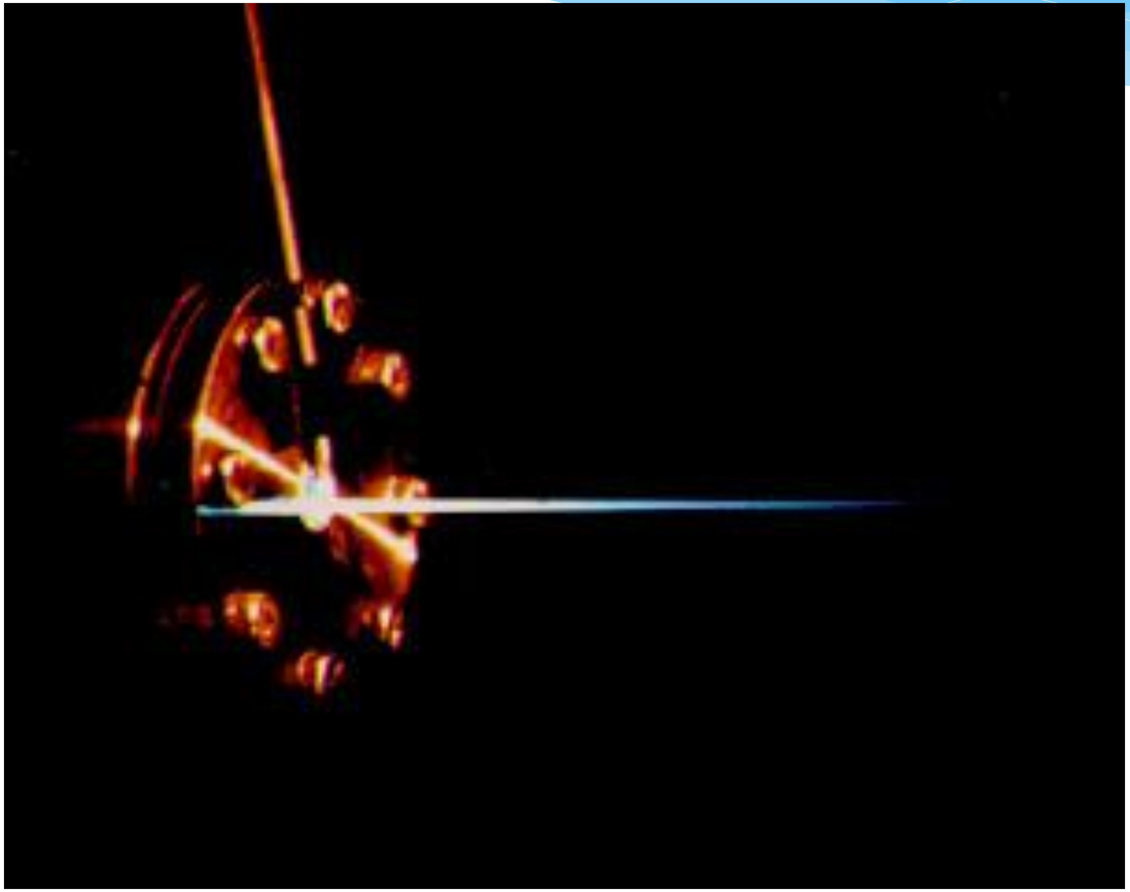
$$\gamma = \frac{1}{\sqrt{1-\beta^2}}$$

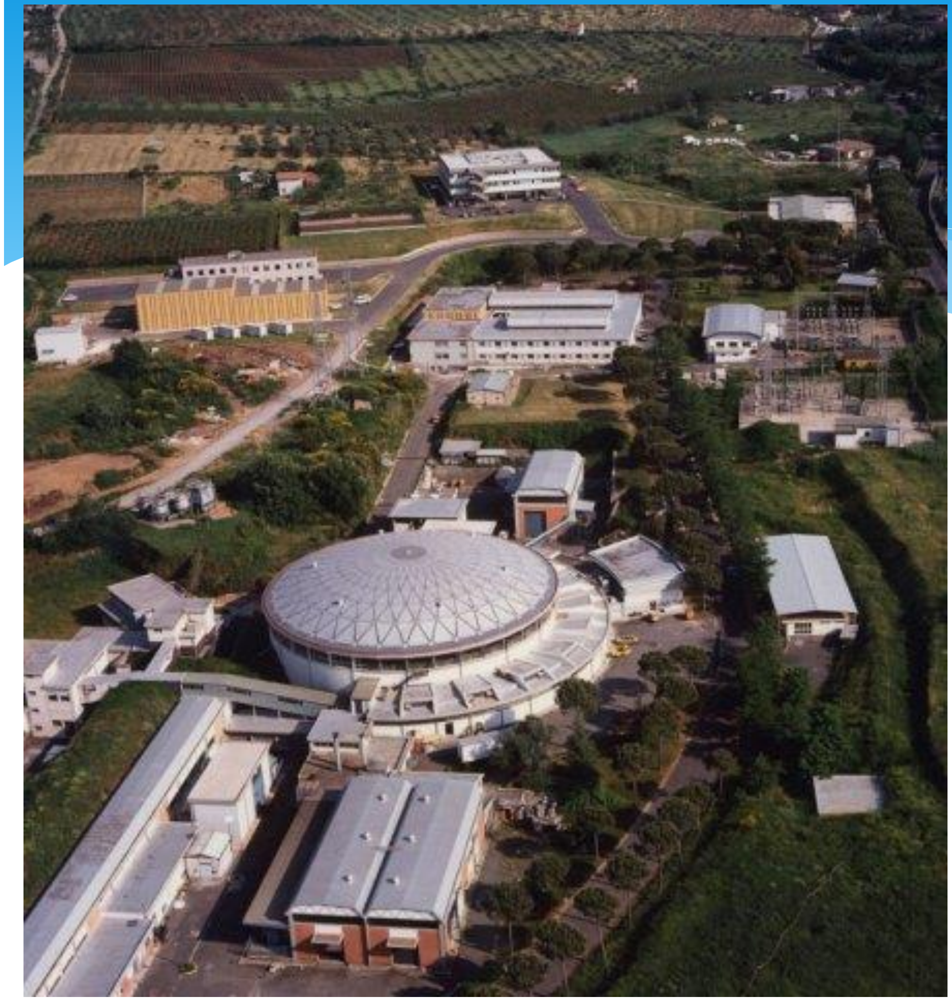
Per β=0.99 1/γ= 10 mrad

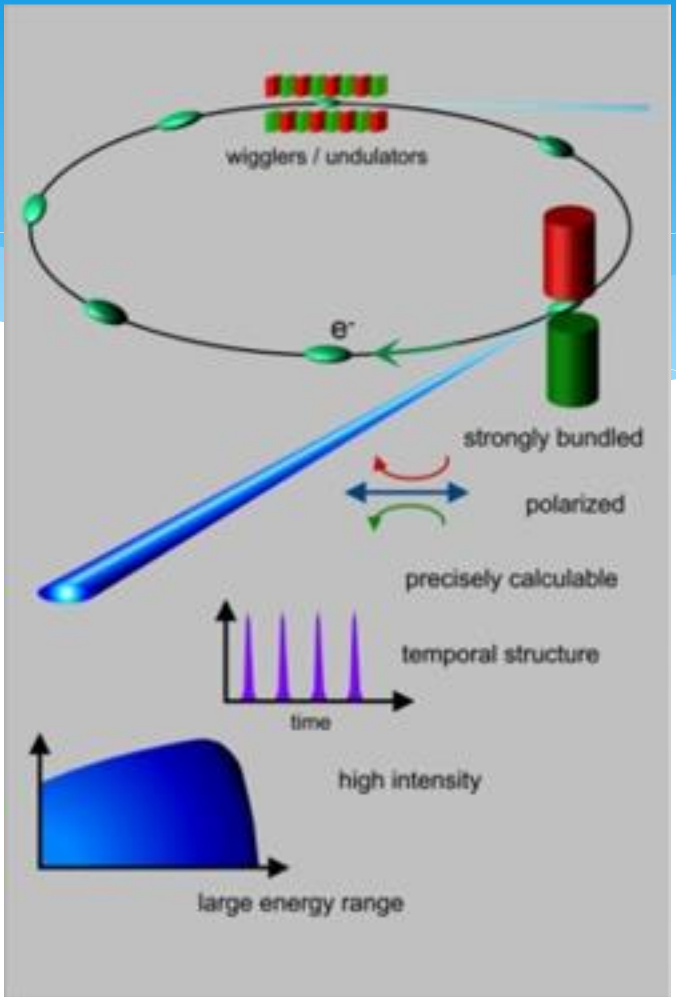


Critical energy

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

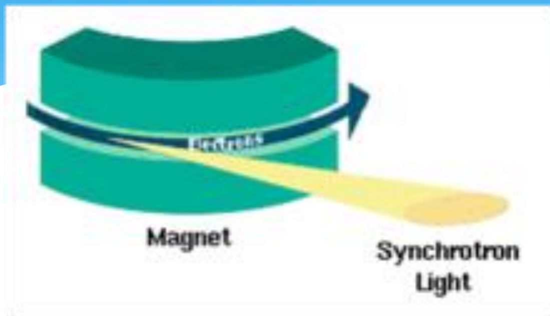


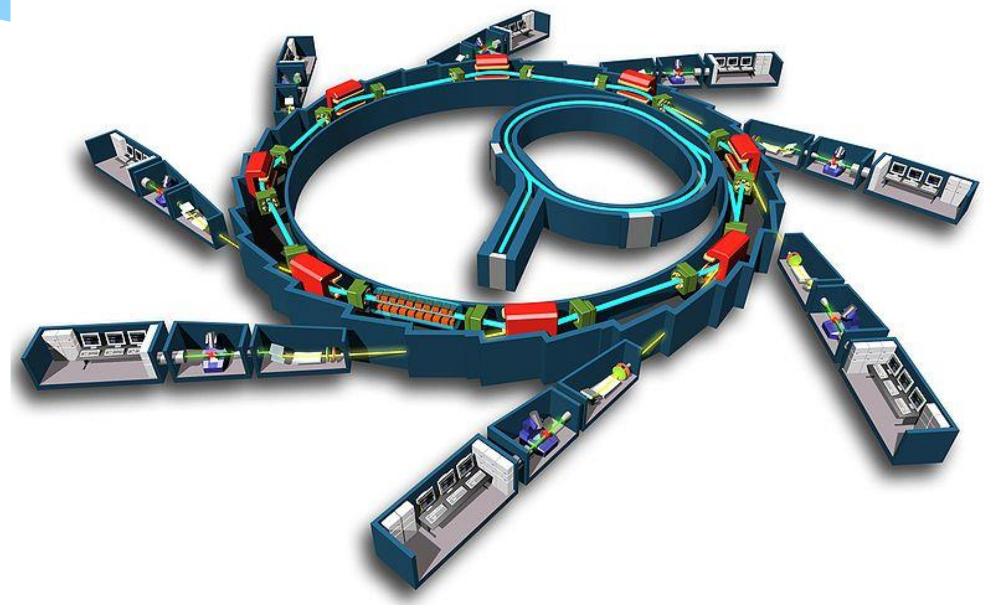


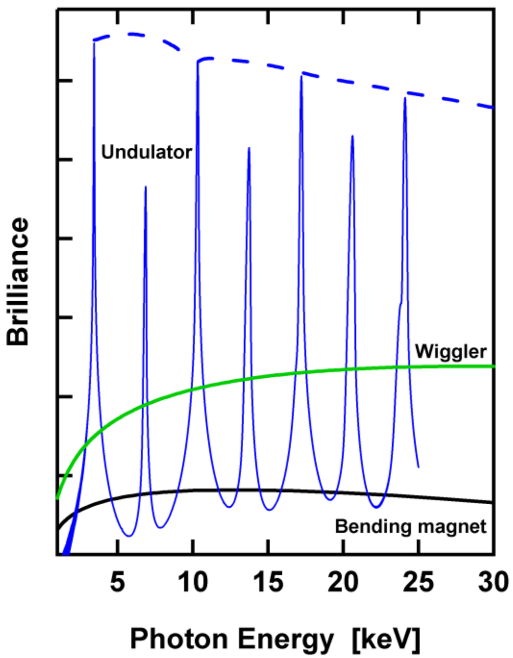


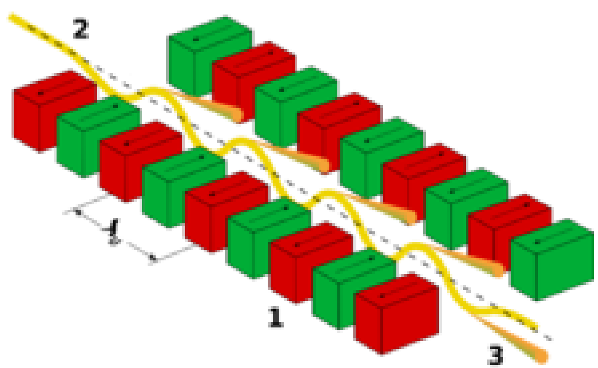
INFN
Istituto Nazionale
di Fisica Nucleare

The beamlines







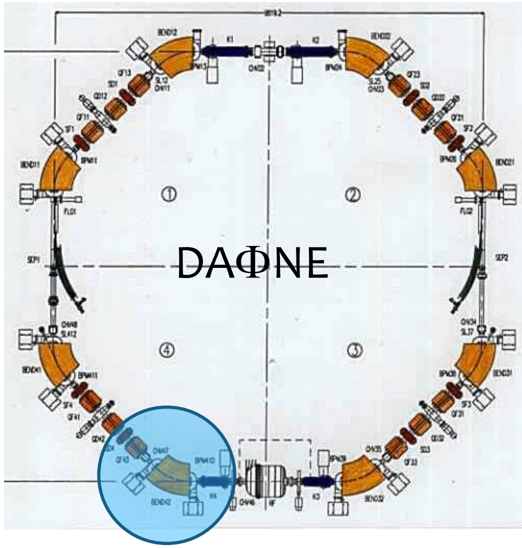


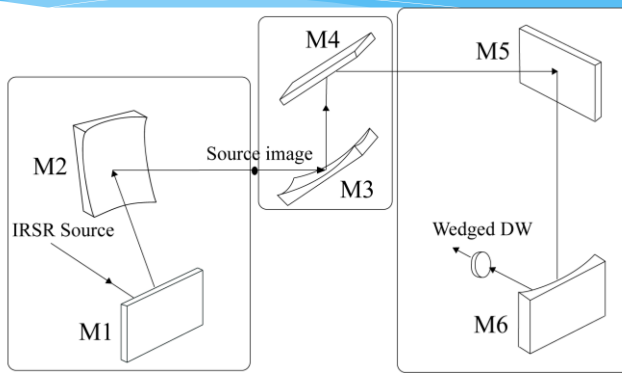
The IR SINBAD beamline

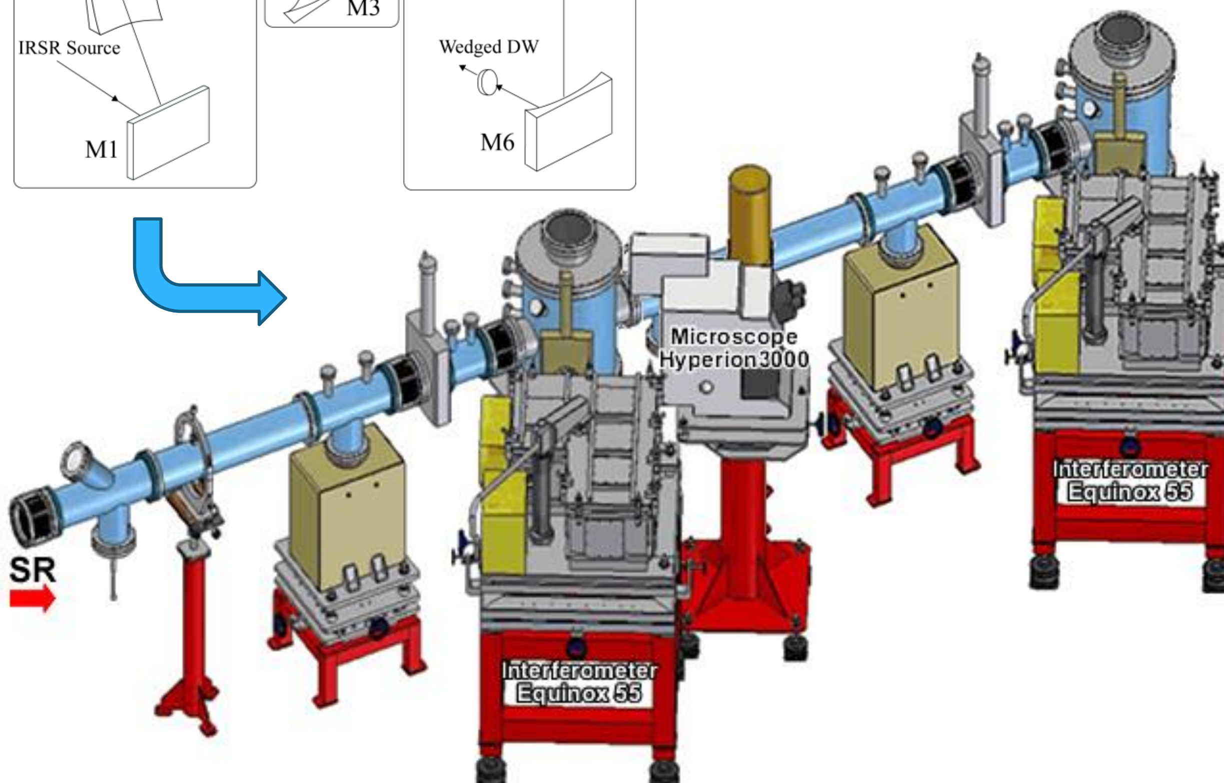
Infrared domain

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

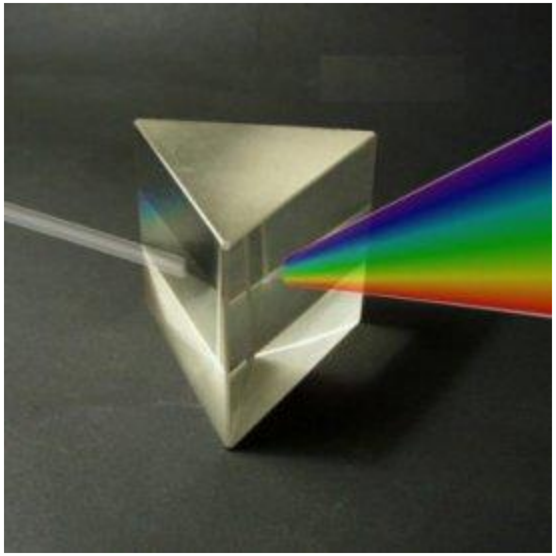
1.24meV to 1.24 eV

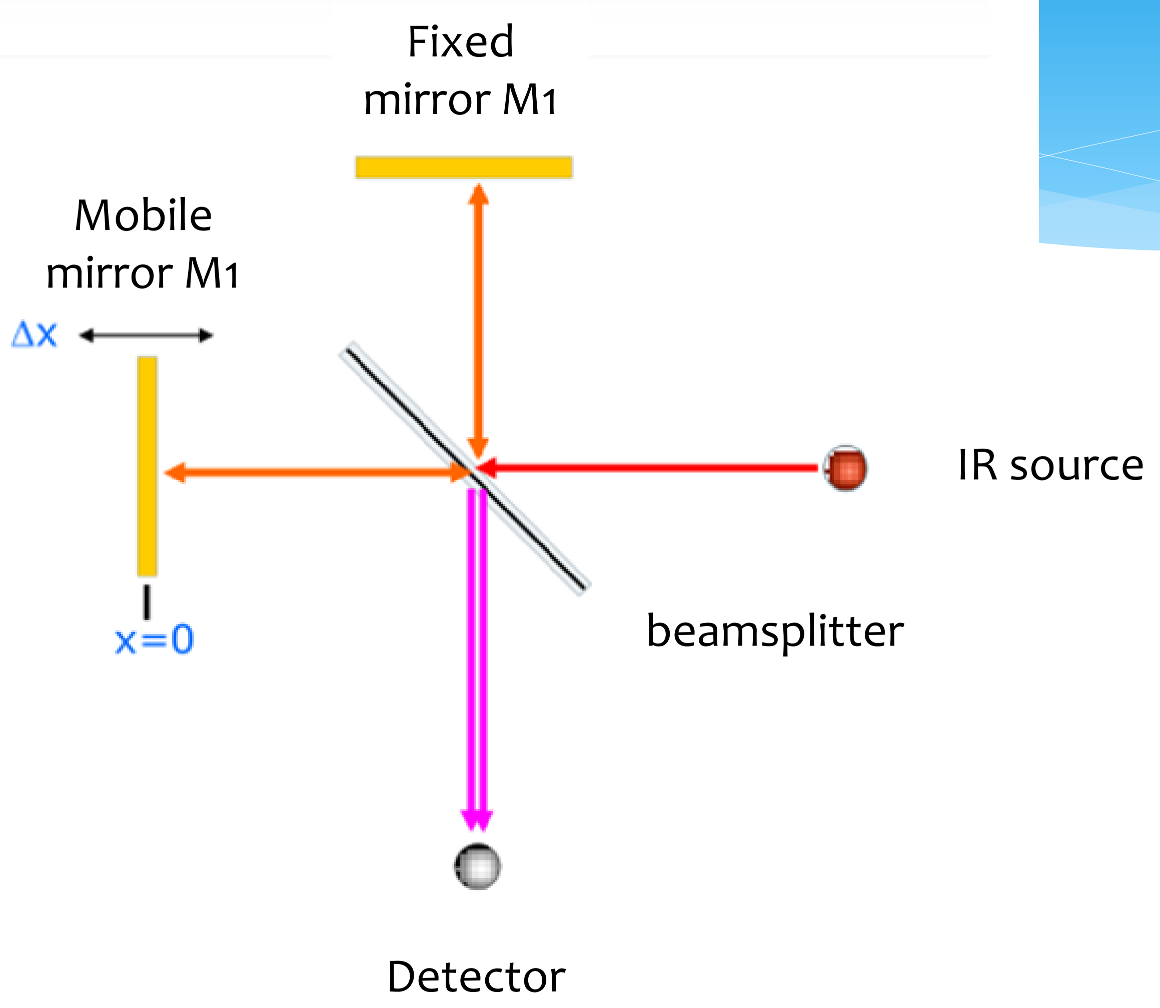




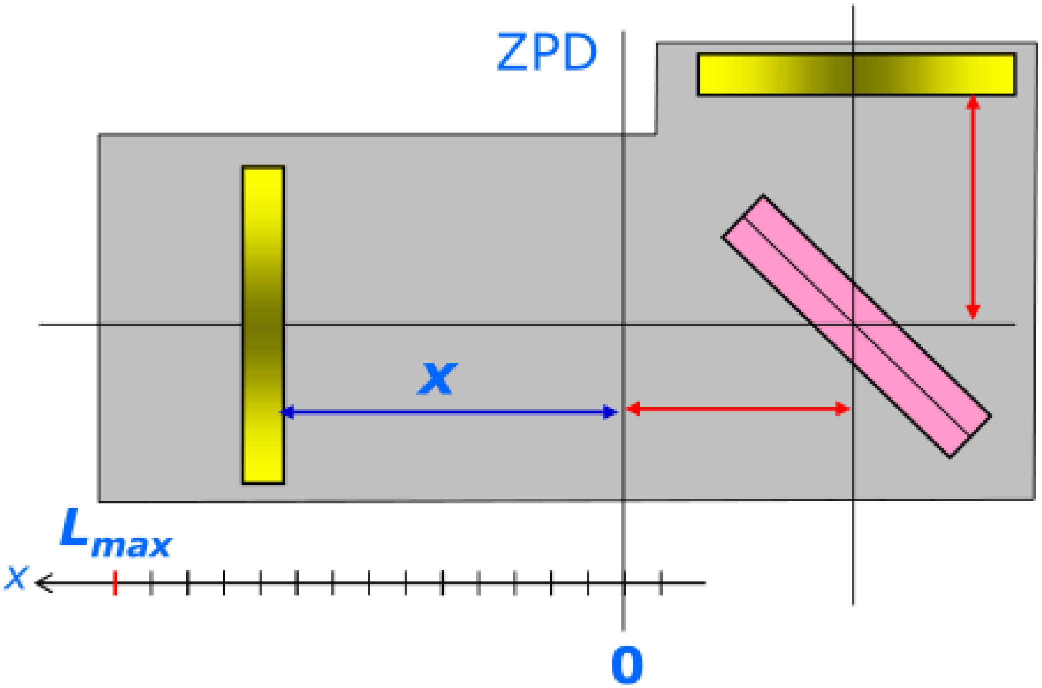


Michelson interferometer



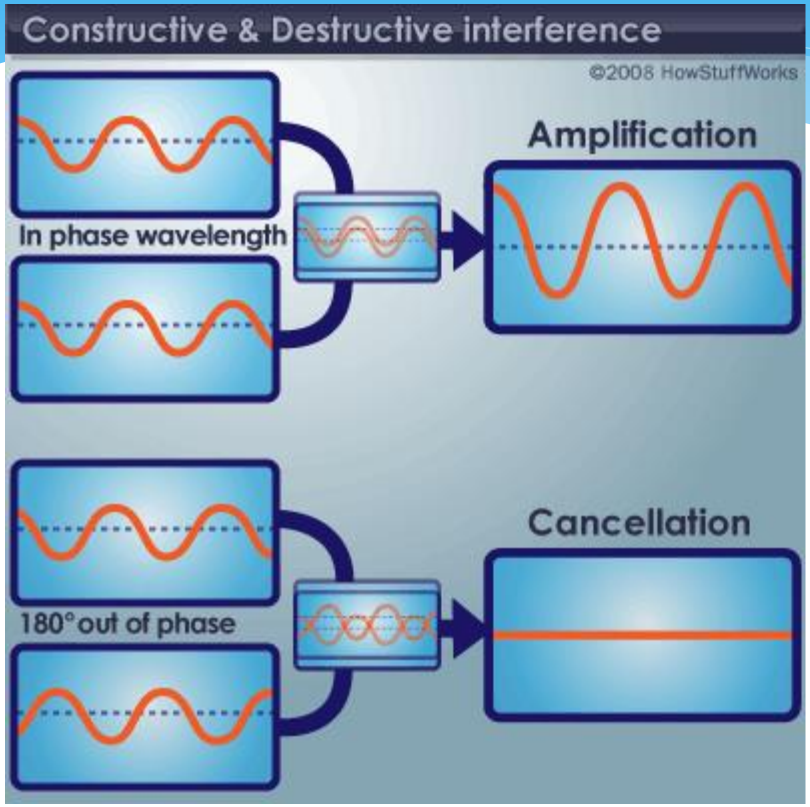

Fixed
mirror M1
Mobile
mirror M1
Δx
x=0
IR source
beamsplitter
Detector

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



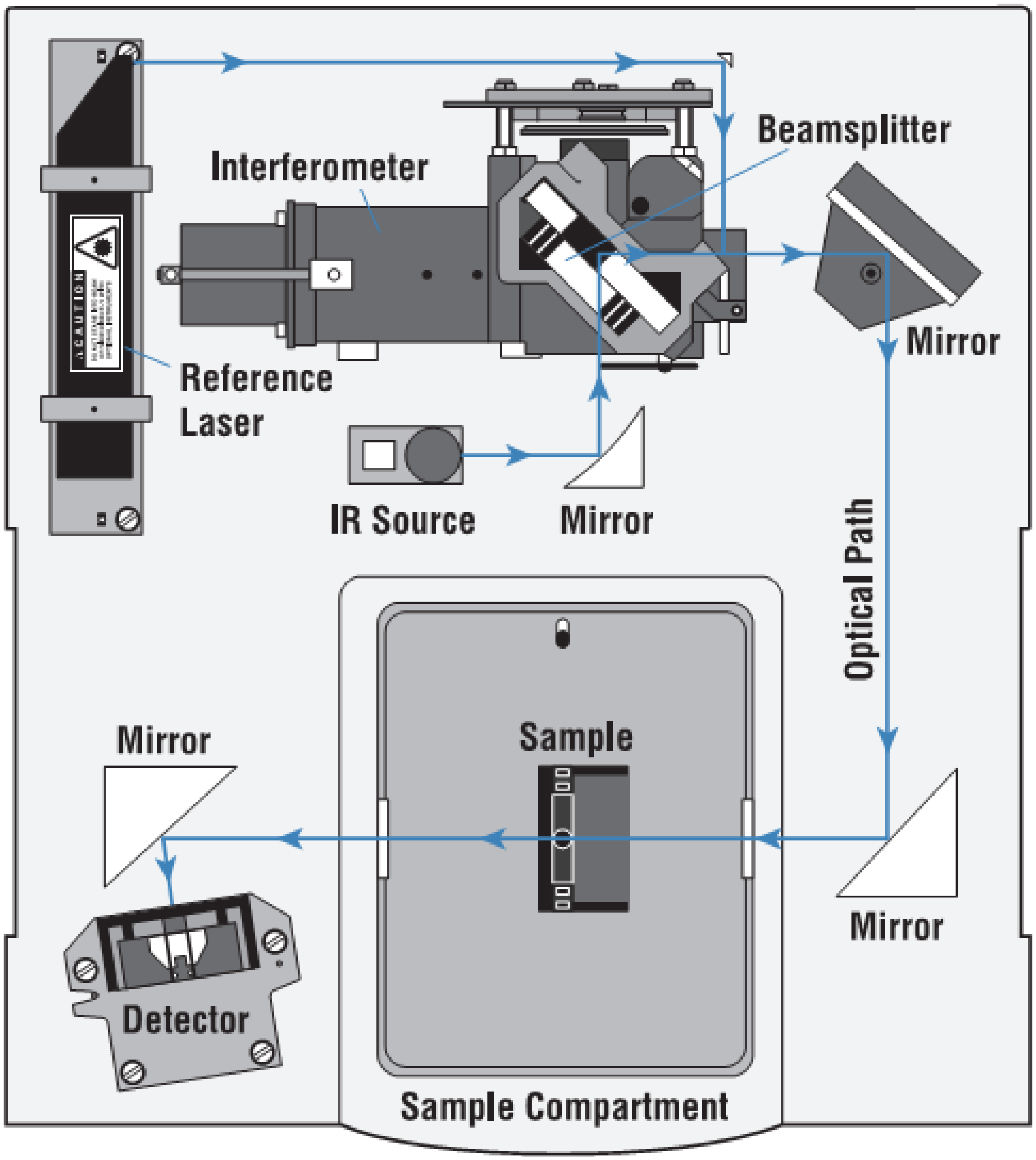
The OPD is twice the mirror excursion x. Since the mirror speed *v* is constant:

$$2x=2vt$$



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

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



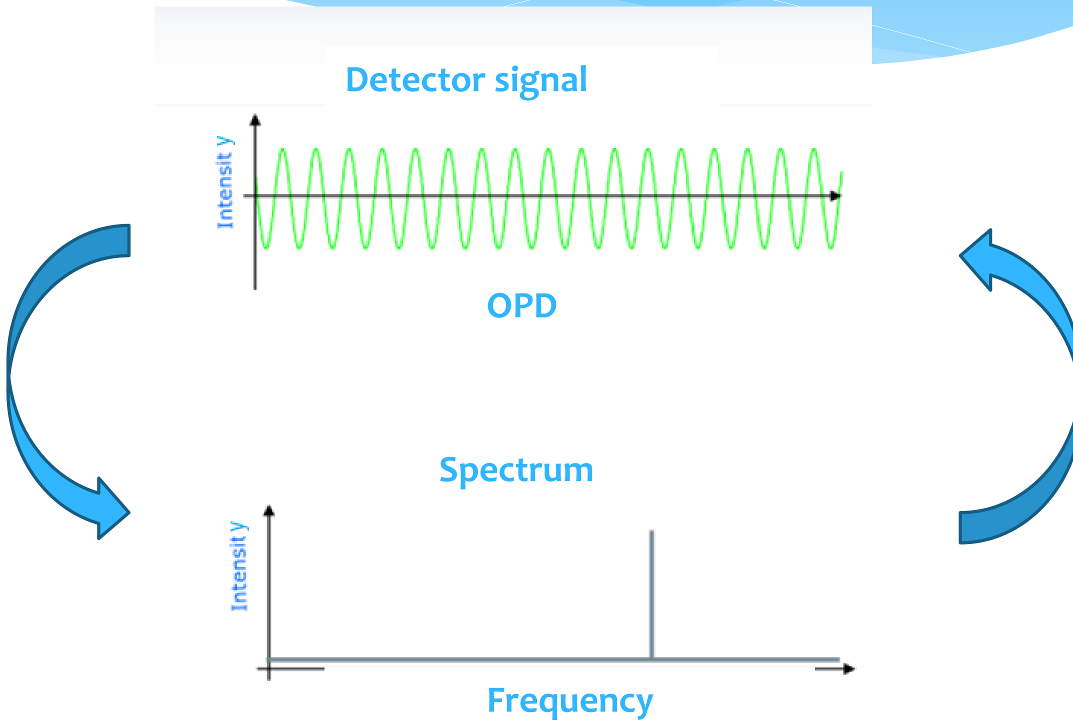
Interferometer
Beamsplitter
Mirror
Reference
Laser
IR Source
Mirror
Optical Path
Sample
Mirror
Mirror
Detector
Sample Compartment

The Fourier Transformation

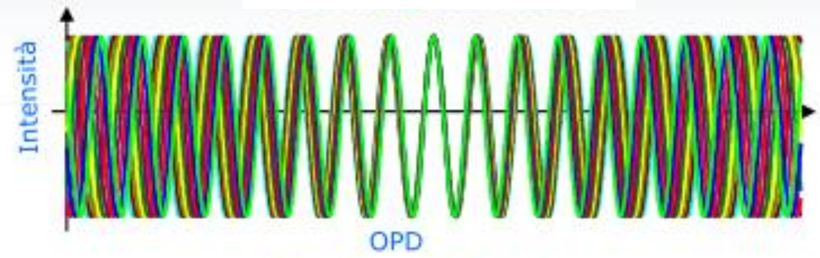
Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation**. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

Origin of the interferogram: the momocromatic wave

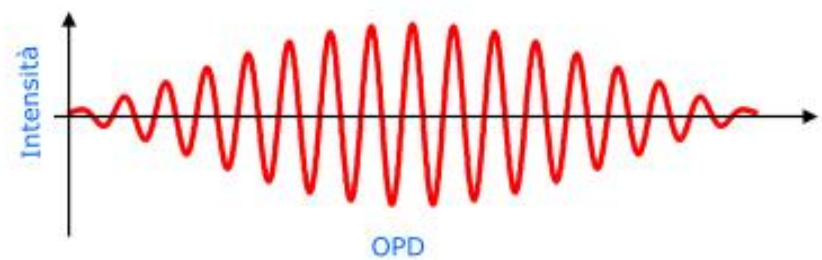
FOURIER TRANSFORMATION



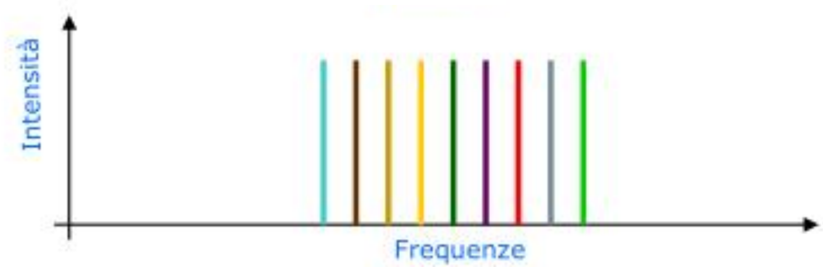
Origin of the interferogram: the policromatic wave (disccrete frequencies)



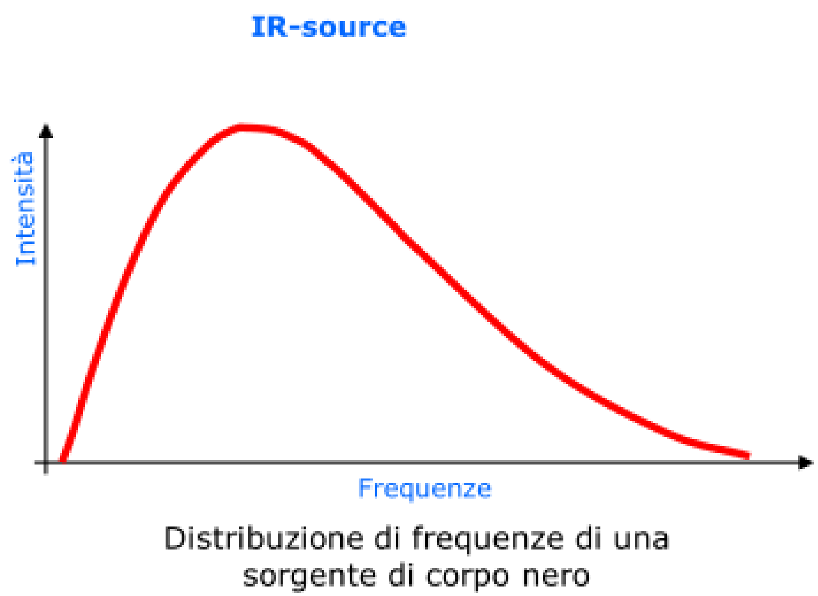
Detector signal

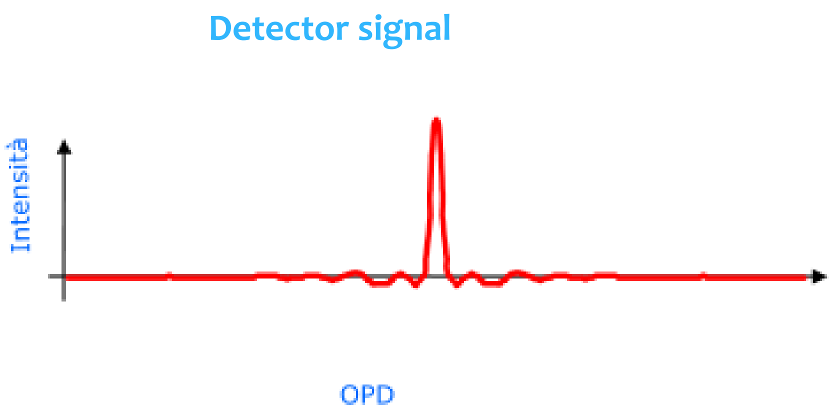


Spectrum

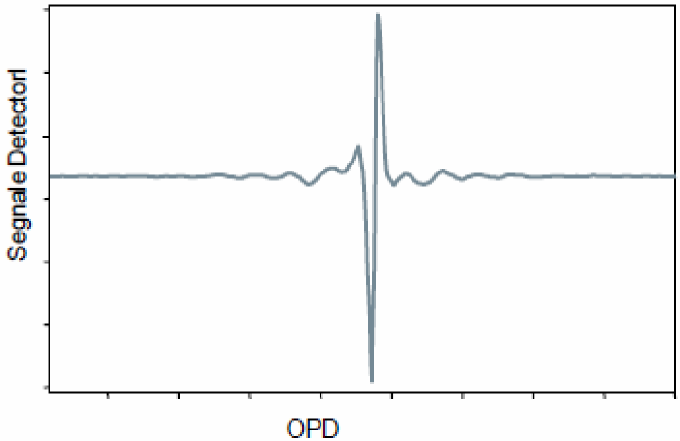


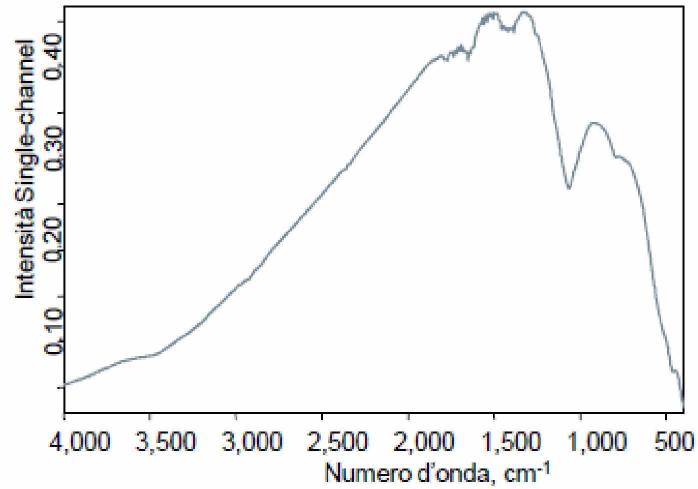
Origin of the interferogram: the policromatic wave (continuous frequencies)





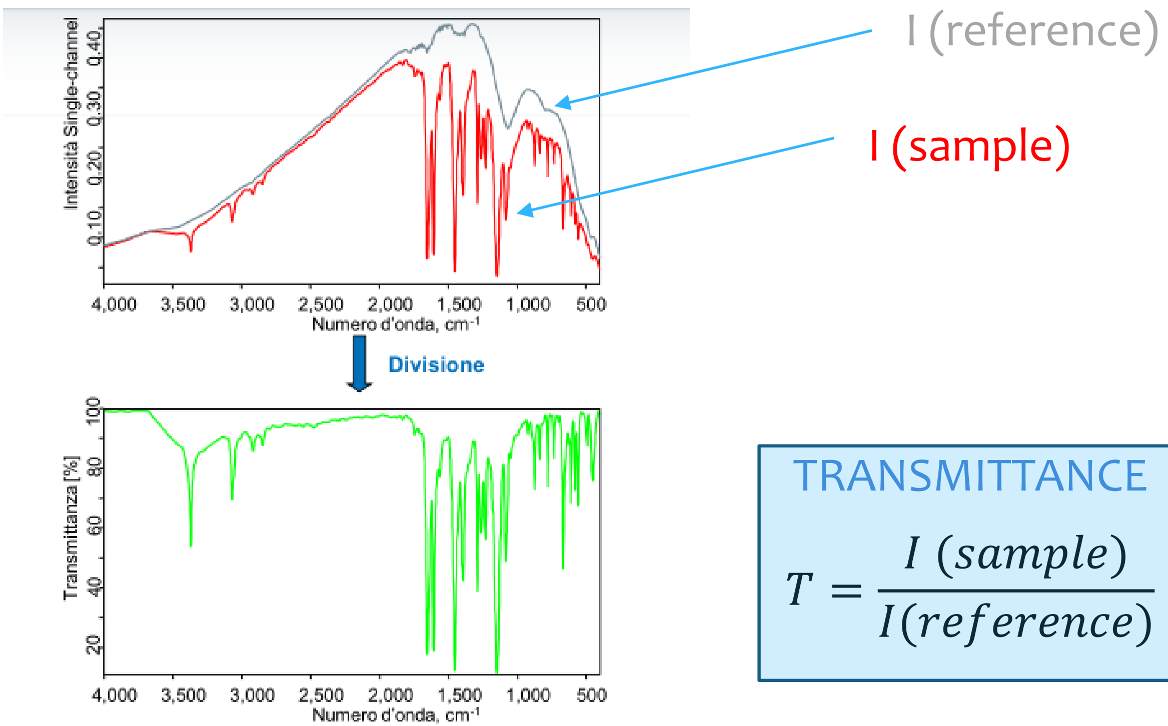
Interferogram ⇄ FT / IFT ⇄ Spectrum





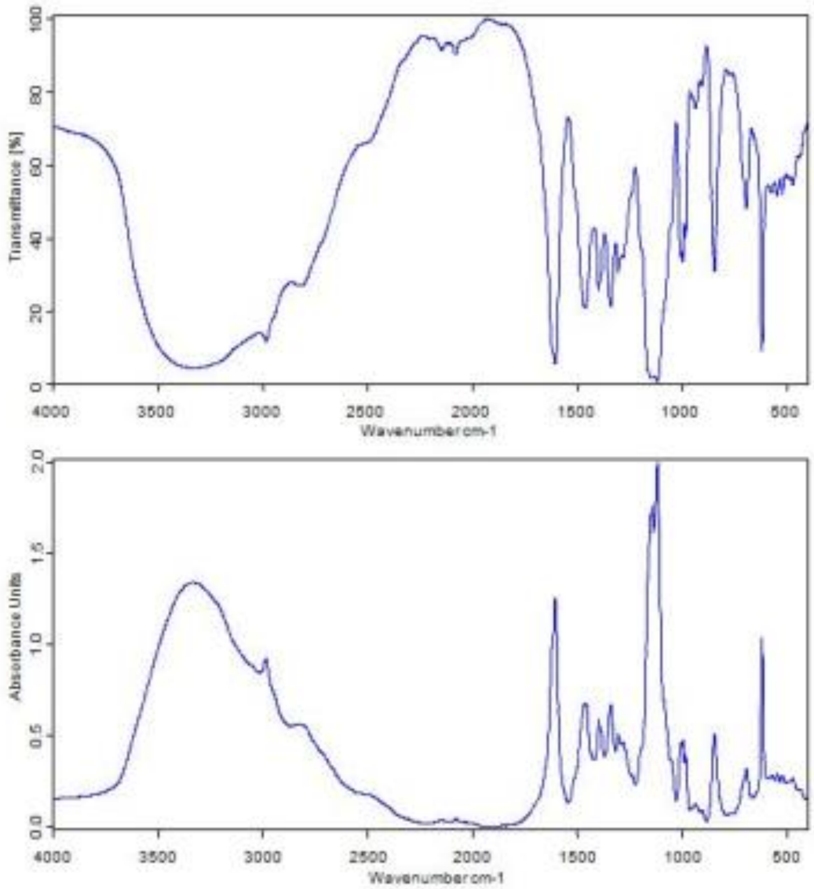
$$S(\nu) = \int_{-\infty}^{\infty} I(x) e^{i2\pi\nu x} dx$$

Measuring an IR spectrum: two ways to look at FTIR data



TRANSMITTANCE

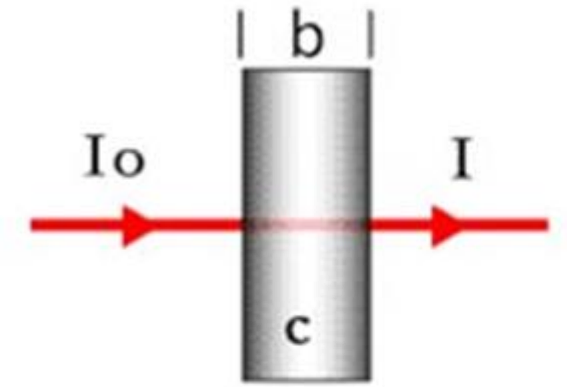
$$T = \frac{I\ (sample)}{I(reference)}$$



ABSORBANCE

$$A = -\log T$$

Beer-Lambert law



$$A = \log I_0/I = \varepsilon\, C\, b$$

ε = absorption coefficient
c = concentration
b = sample thickness

Absorbance is proportional to the concentration

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:

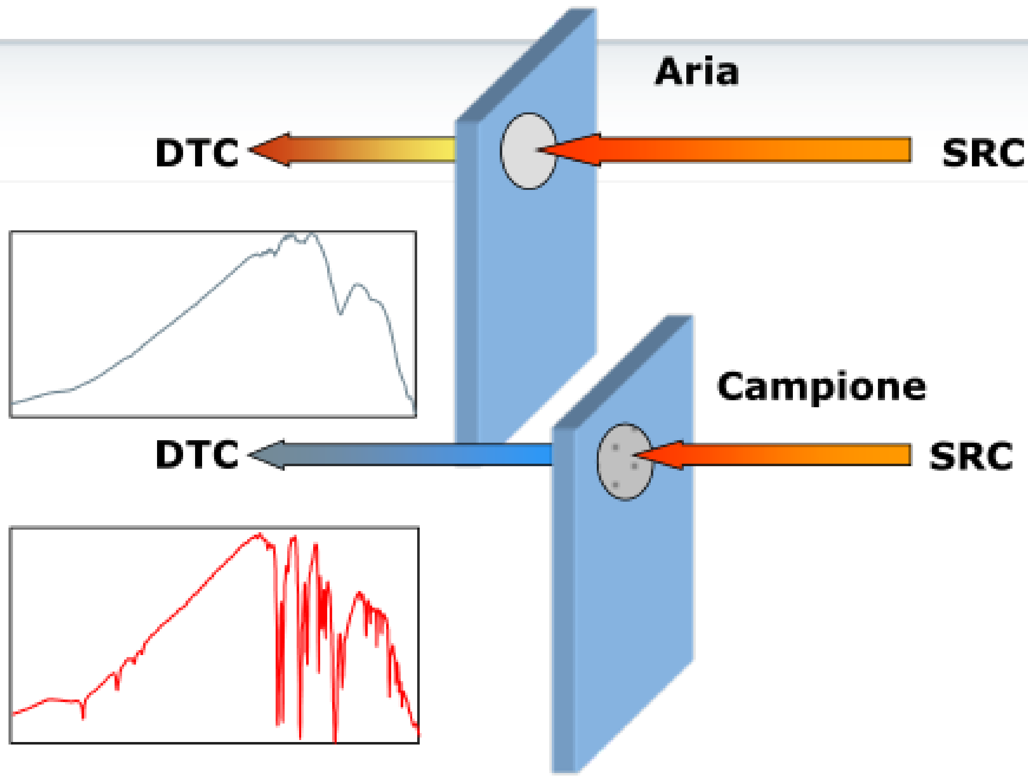
* Transmission (liquids, powders, thin sections)
* Specular reflection (crystals, polished sections)
* Diffuse reflectance (powders)
* Attenuated Total Reflection (ATR) (thick samples, non reflecting surfaces)

Transmission
KBr powder pellets

- Invasive
- Destructive
- Time consuming
- Very precise (absolute measurement)
- Spectral database

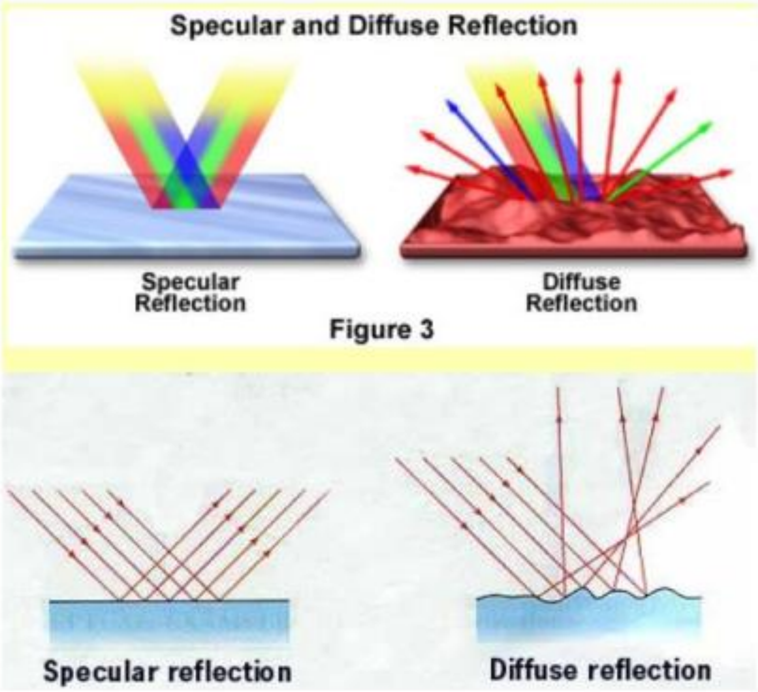
- Background (I_0)

- Sample (I)



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

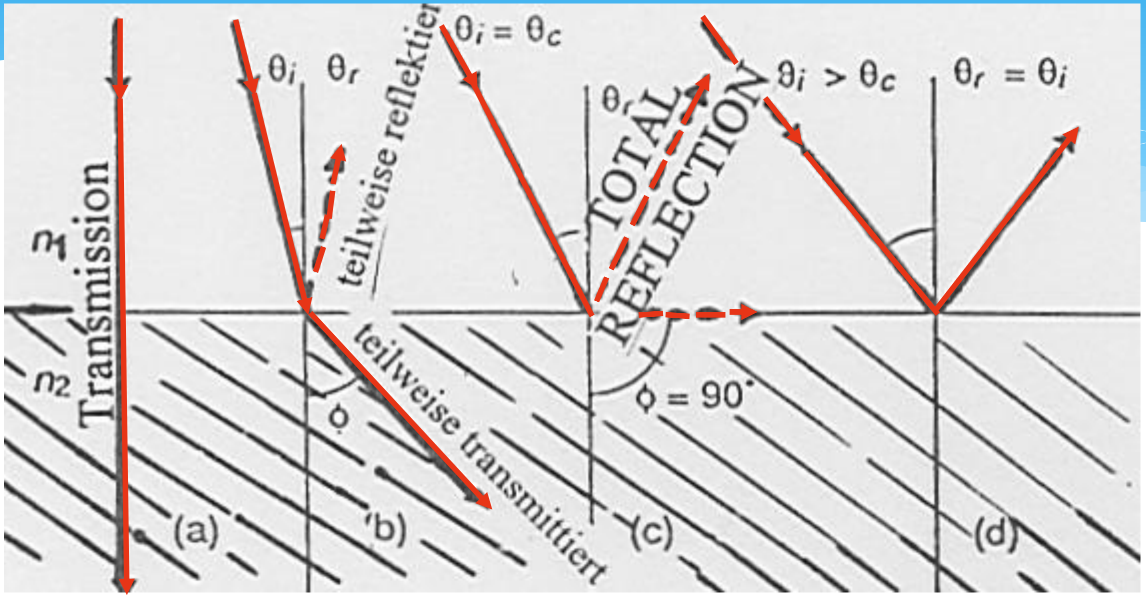
Reflection spectroscopy



Preparation of the surface – polishing ☹
Thick samples ☺

Attenuated Total Reflection (ATR)

Principles of Attenuated Total Reflection spectroscopy (ATR)



Crystal n_1

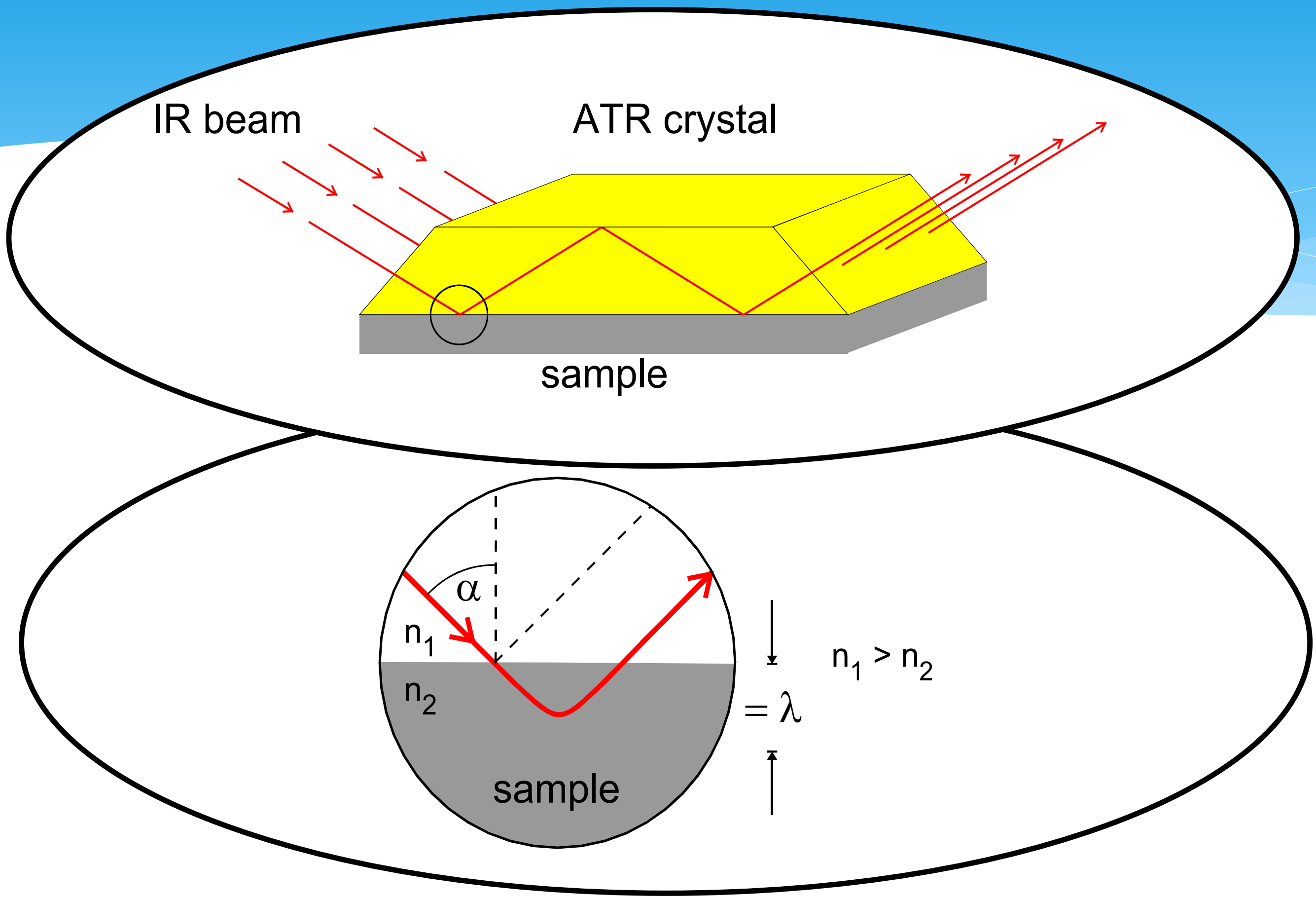
Sample n_2

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)



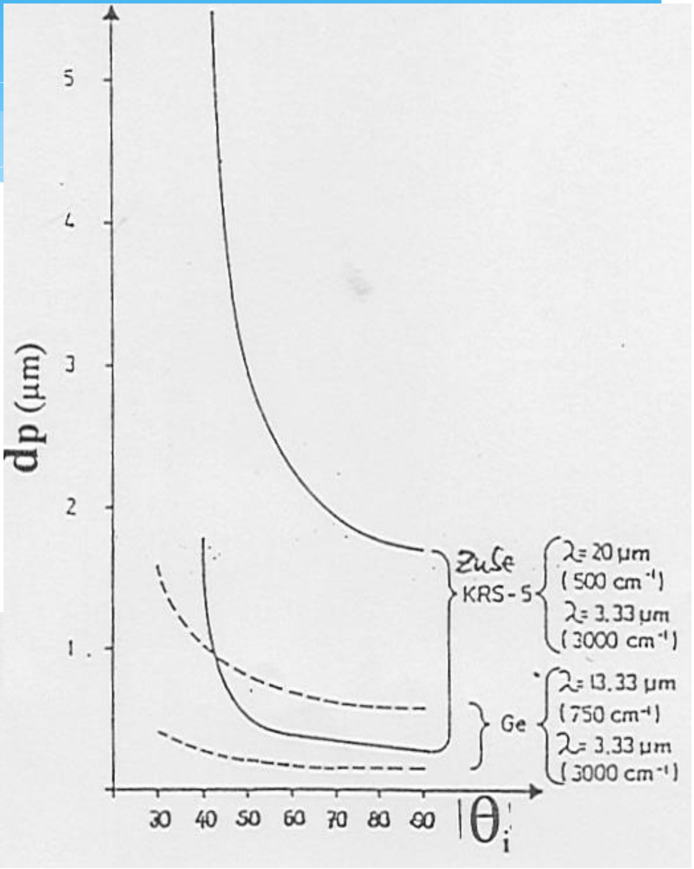
IR beam
ATR crystal
sample
α
n1
n2
= λ
n1 > n2
sample

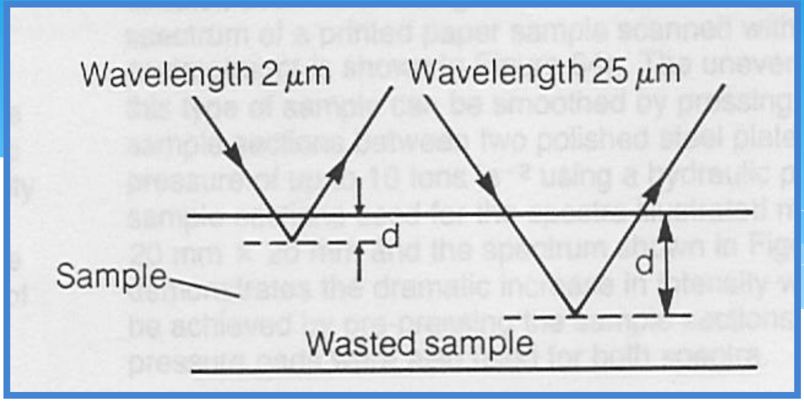
Penetration depth

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

θi	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 * ν [cm^{-1}] / 1000 [cm^{-1}]

- Quick
- Non invasive
- (semi)destructive

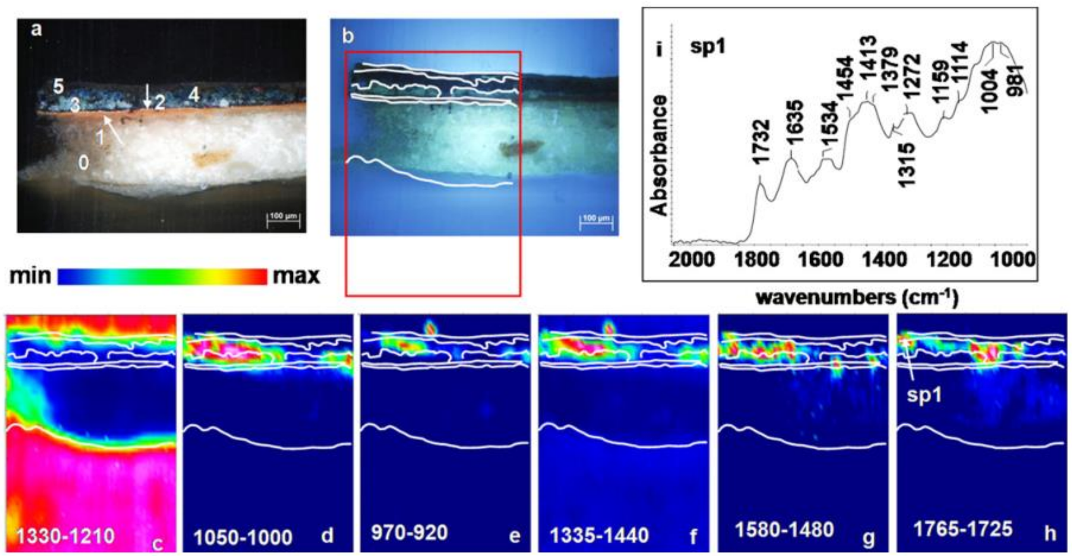
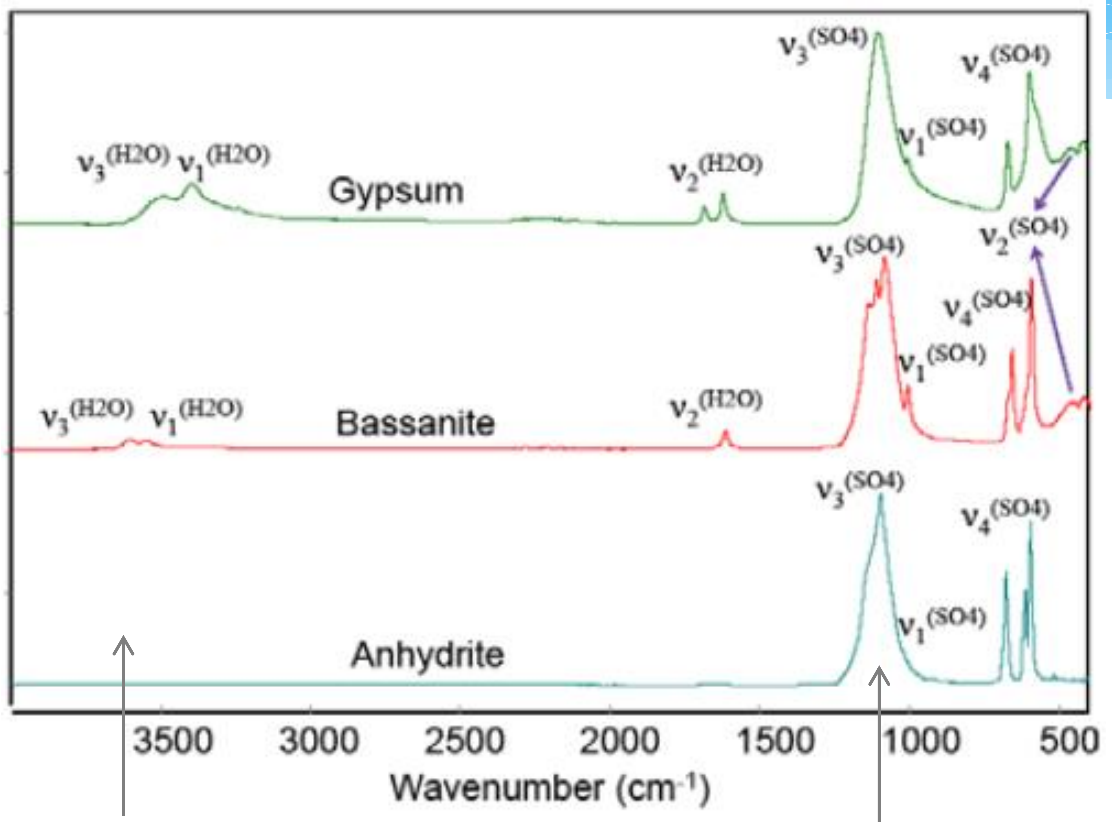


Fig. 2. Detail of a cross-section from the polychrome sculpture (Fe2): (a) visible microscopic image; (b) image of sample under ultraviolet light; (c) FT-IR image created by plotting the integrated absorbance of the embedding resin band between 1330 and 1200 cm^{-1}; (d) FT-IR image showing the distribution 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



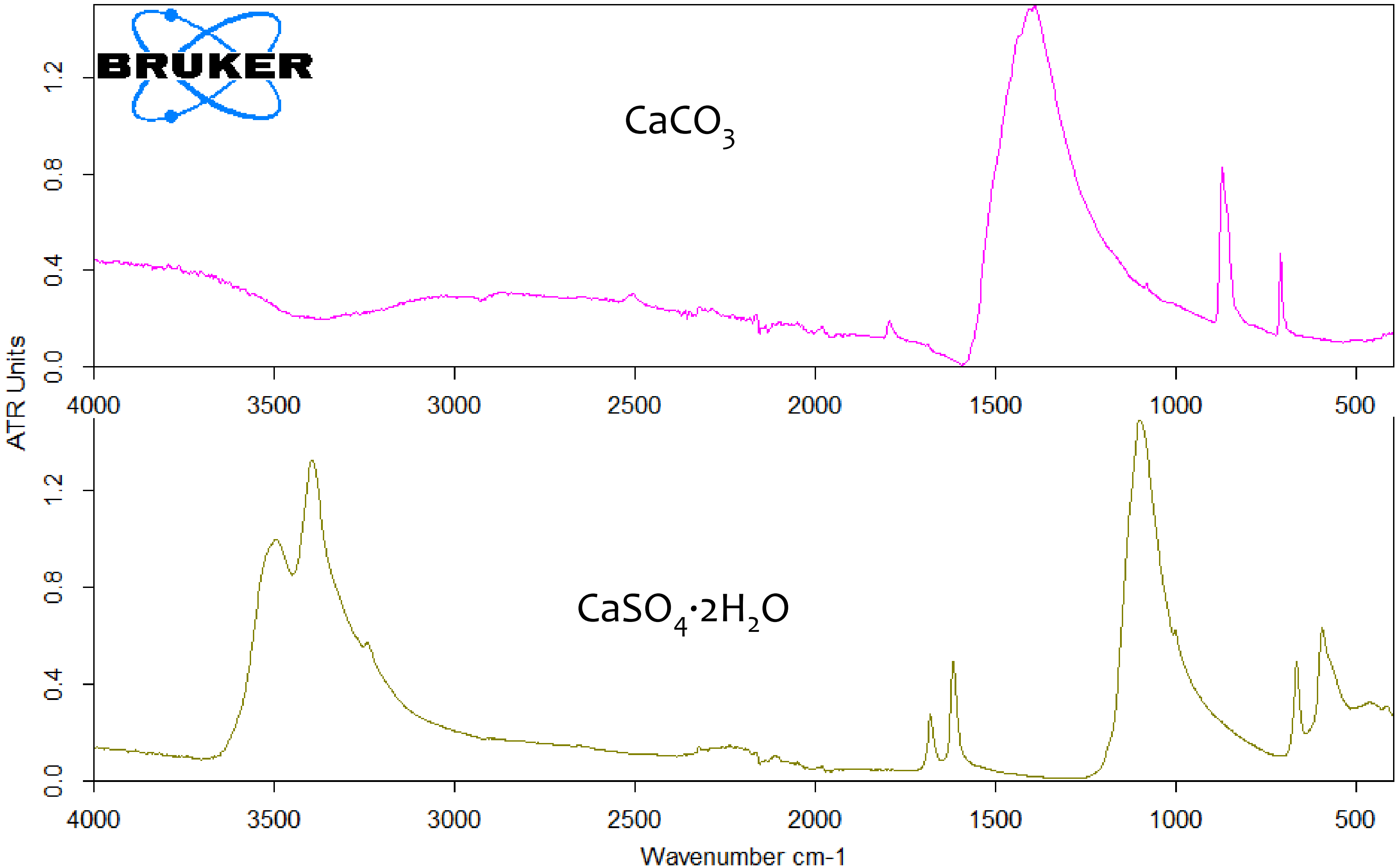
$CaSO_4{\cdot}2H_2O$

$CaSO_4.0.5H_2O$

$CaSO_4$

Water molecule:
Stretching symmetric
and antisymmetric of H_2O

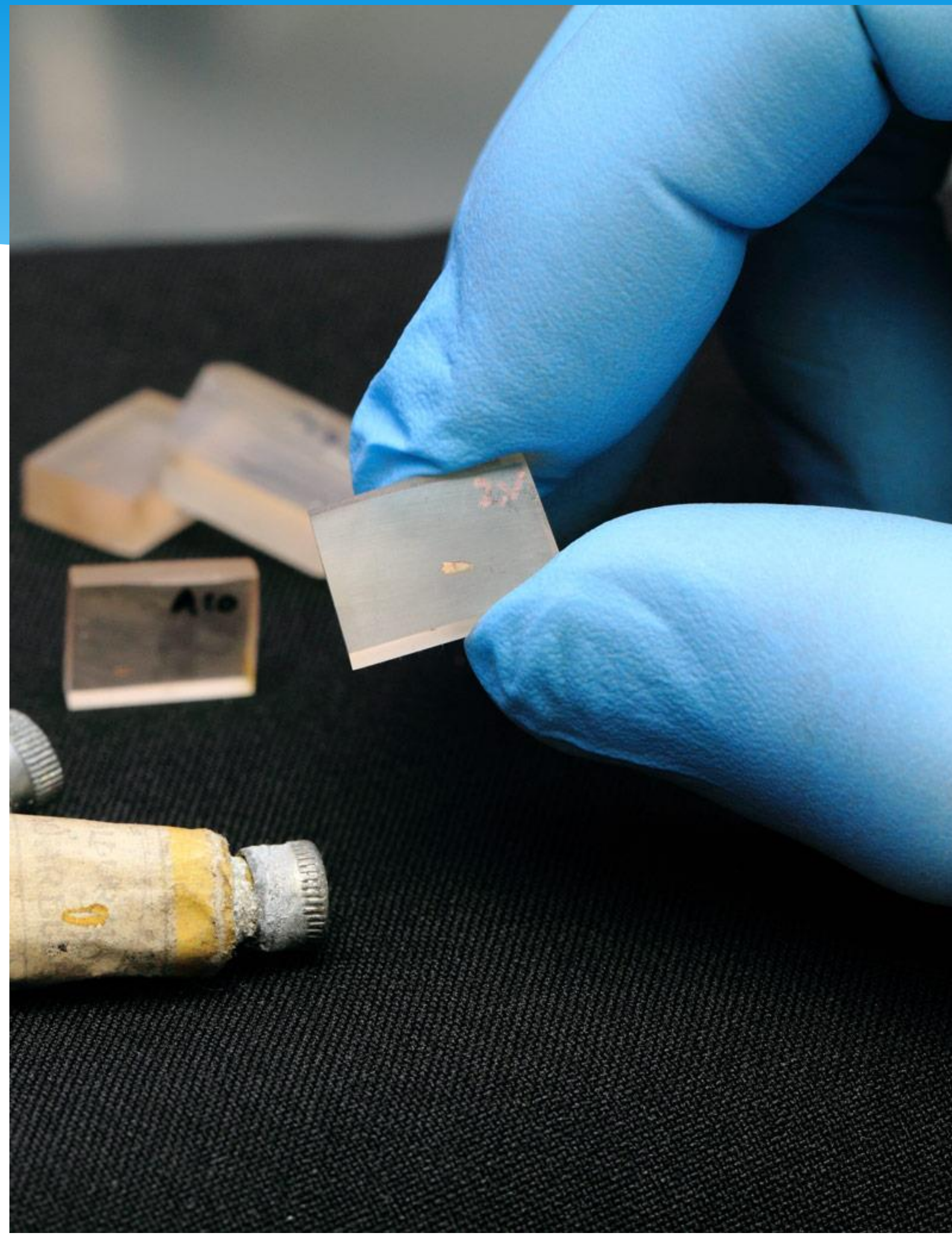
ν_3 Stretching antisymmetric of SO_4 tetrahedra
ν_1 Stretching symmetric of SO_4 tetrahedra



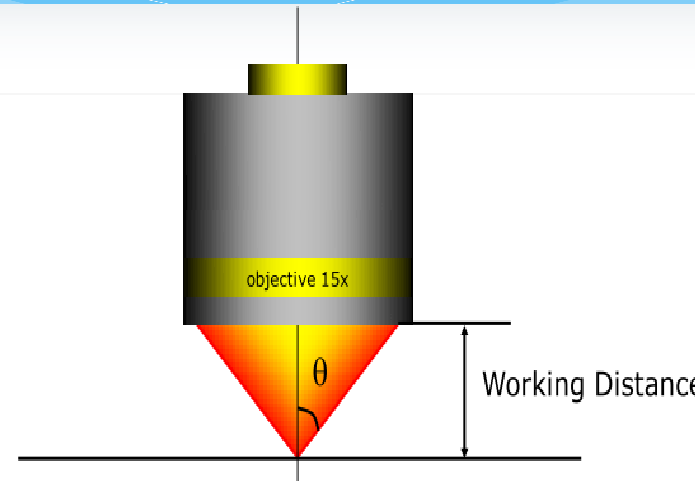
C:\Users\Mariangela\Documents\AAA-Misure, Analisi dati\mb	\Libreria BOPT Beni Culturali\Calcium Carbonate CaCO3 P-ATR.0	28/04/2010
C:\Users\Mariangela\Documents\AAA-Misure, Analisi dati\mb	\Libreria BOPT Beni Culturali\Calcium Sulfate CaSO4 P-ATR.0	28/04/2010

Page 1/1

What if the sample is VERY small?



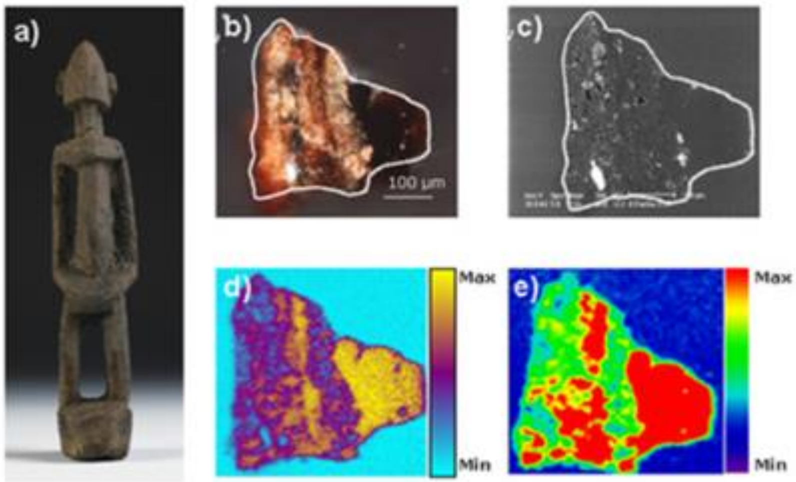
Microscopy and Imaging



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

The IR microscope is essentially a beam condenser

FTIR imaging



Study of the patina sample from a Dogon statuette:

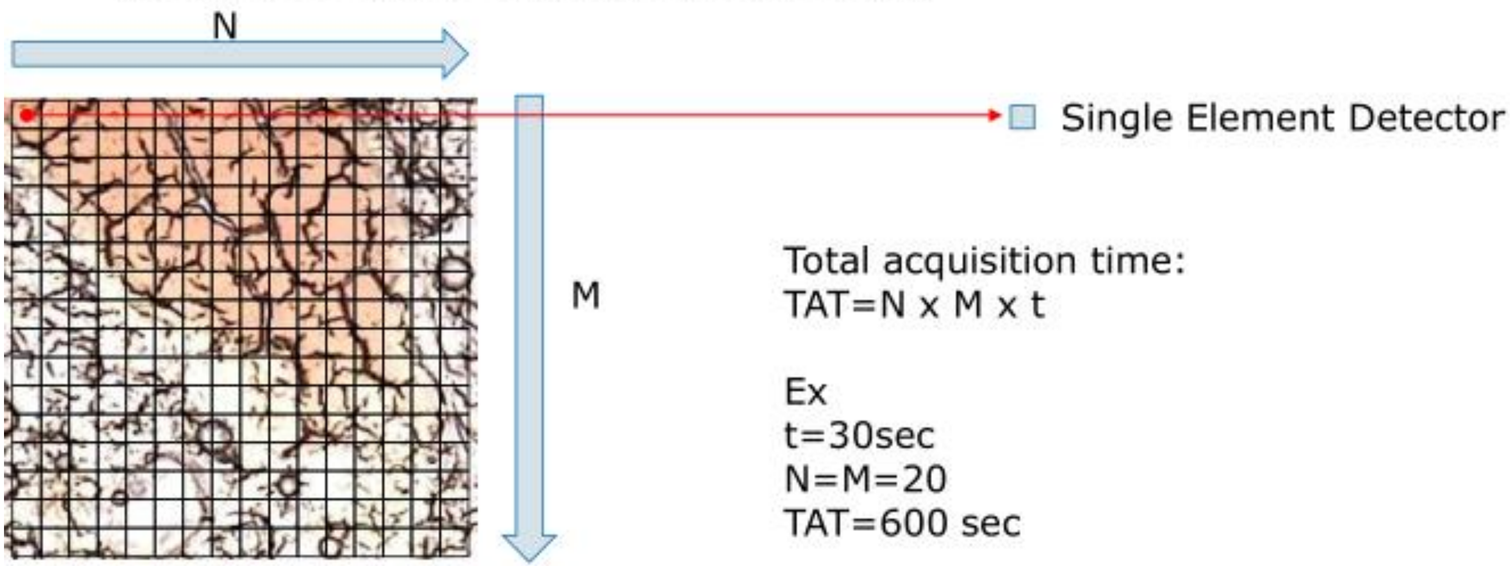
a) Photograph of the object, Quai Branly Museum, inventory no 71.1935.105.169, (copyright C2RMF, D. Vigears);
b) Dark field microscopic view of the cross-section of the sample;
c) Backscattered electron micrograph;
d) ToF-SIMS image of protein fragment ions;
e) SR-µFTIR image of proteins.

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

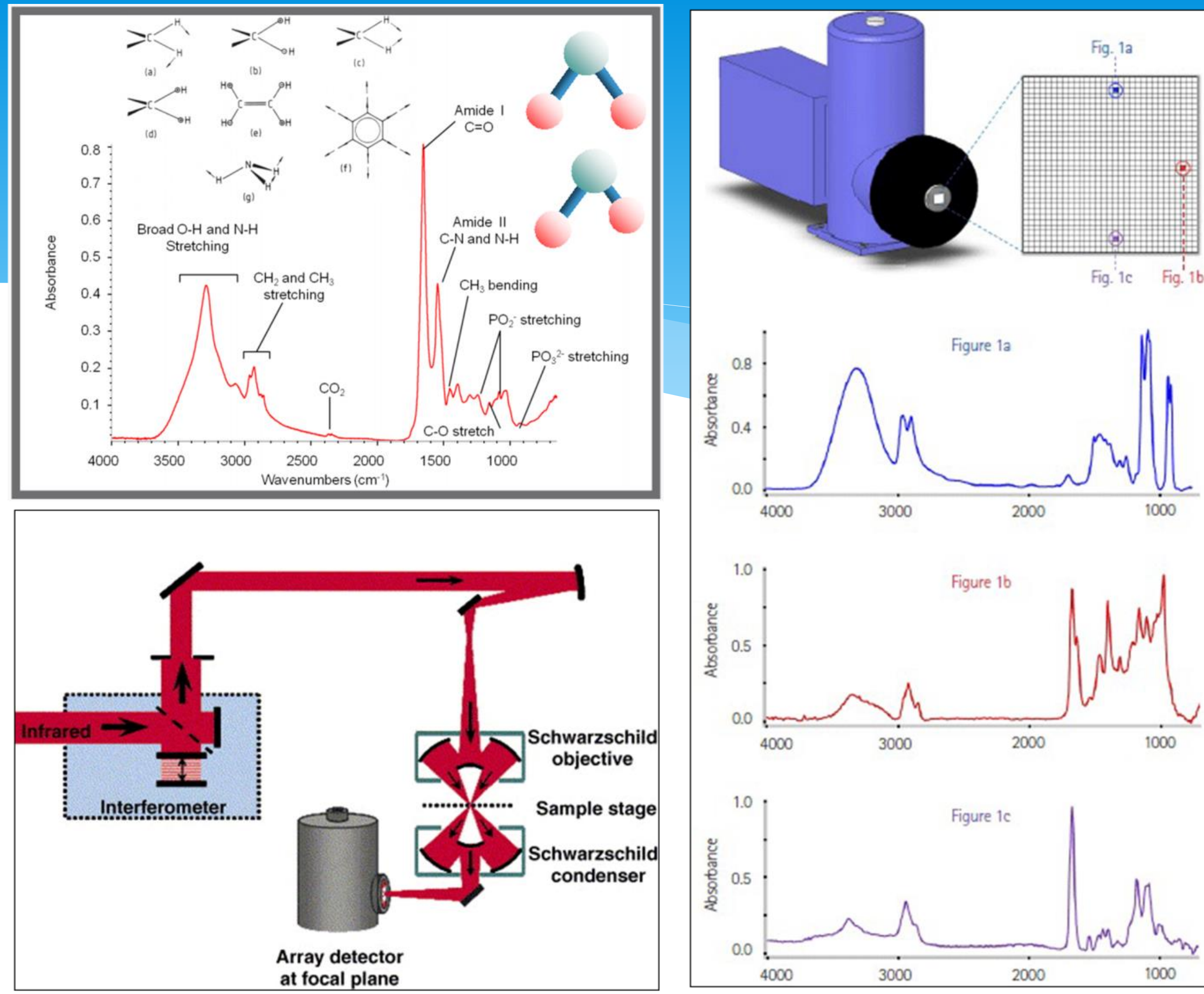
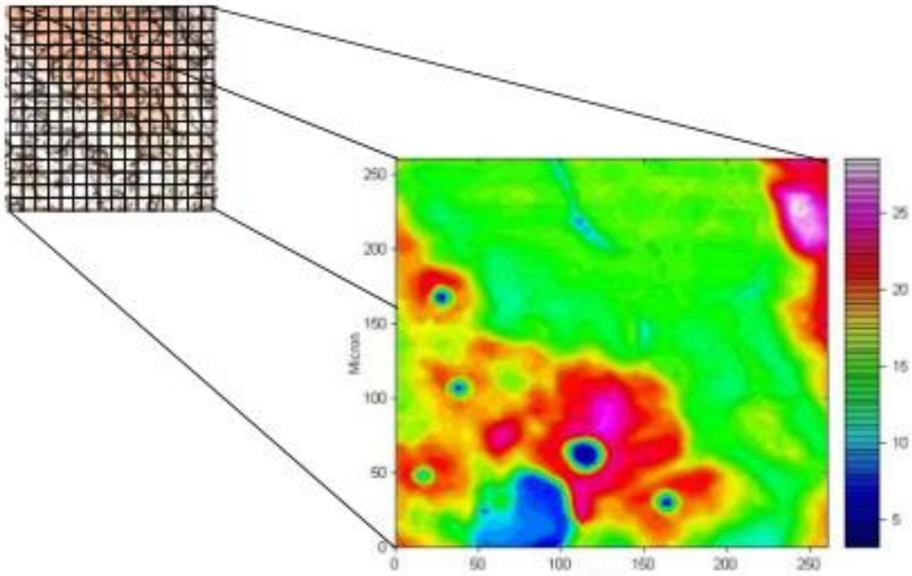


Figura 2: (a) Lo spettro IR di un composto organico mostra gli assorbimenti dovuti alle vibrazioni molecolari. (b) Schema ottico del microscopio IR accoppiato allo spettrometro ed al detector FPA. (c) Schema di funzionamento di un detector FPA.

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

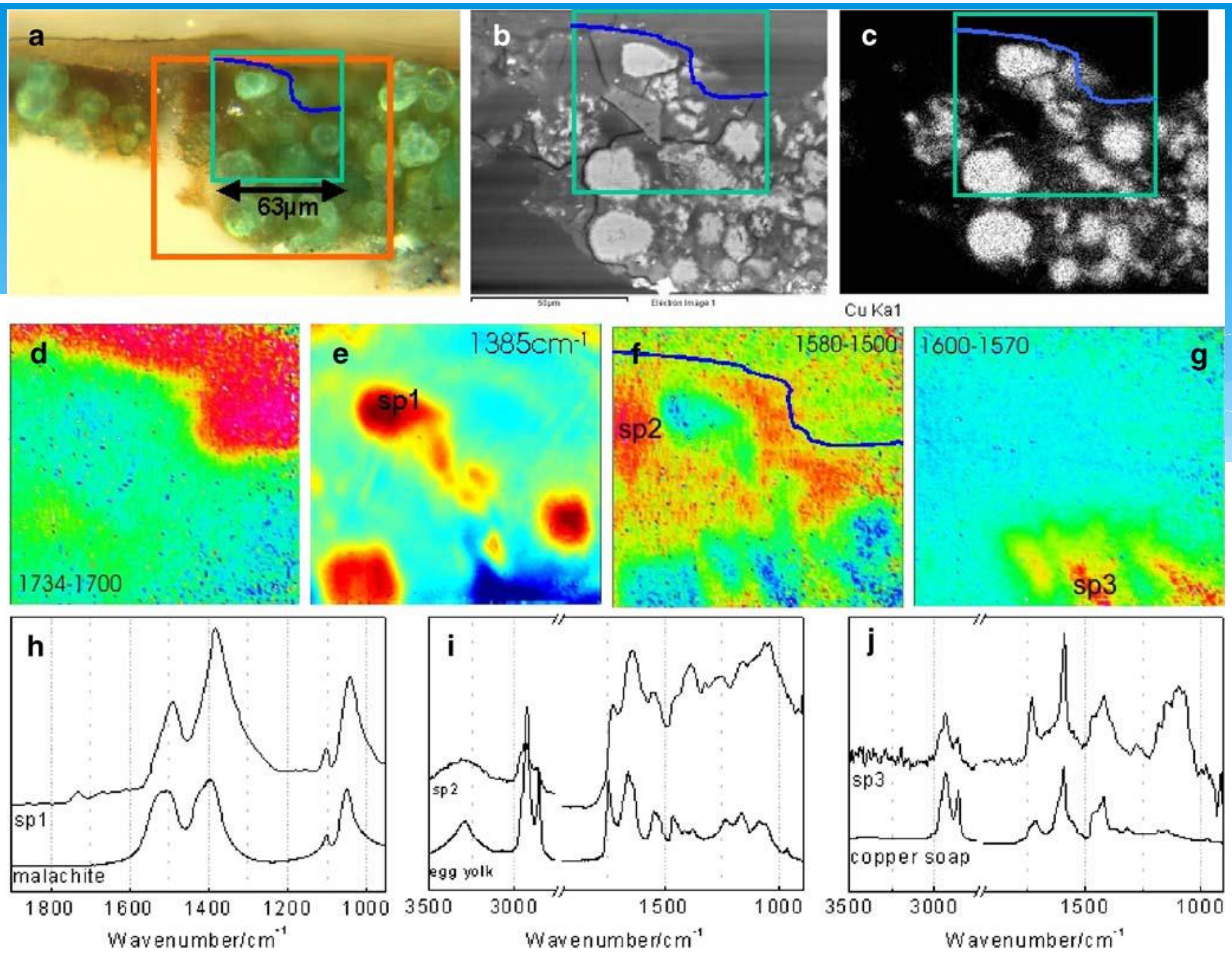


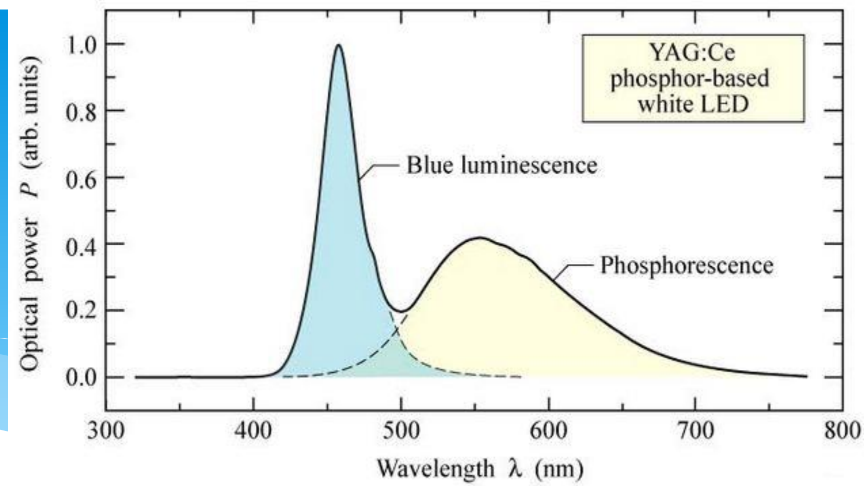
Figura 1. Sezione stratigrafica di un frammento prelevato dalla veste verde di un dipinto raffigurante la Madonna col Bambino: a) sezione stratigrafia al microscopio ottico in luce visibile; b) immagine ottenuta al microscopio elettronico (SEM); c) mappatura dell'elemento rame (Cu) eseguita mediante 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

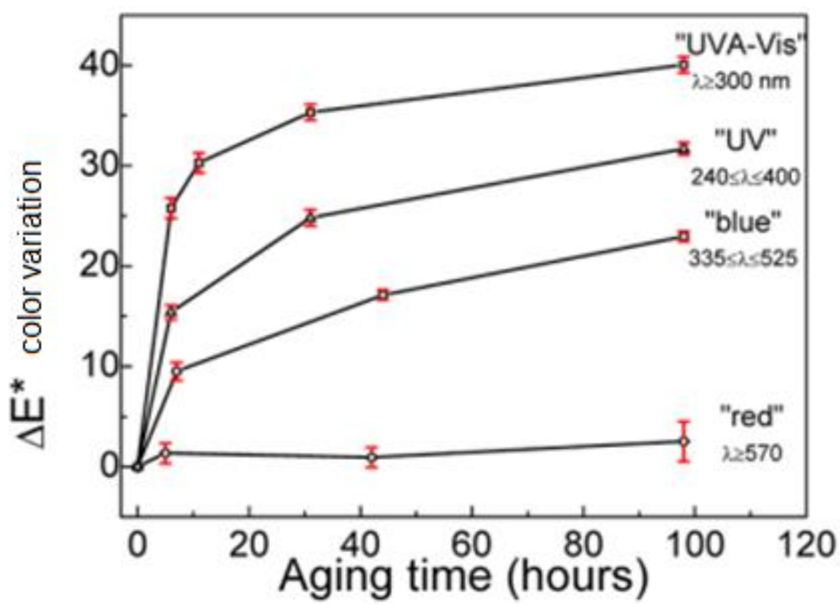
LED lights may be bad for *Van Gogh* Paintings

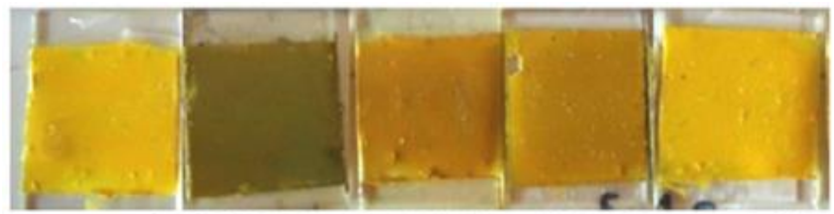
http://www.vangogh.ua.ac.be/

The darkening of chrome yellow is a phenomenon widely observed on several paintings by Vincent van Gogh such as the famous versions of the Sunflowers. Analysis of artificially aged model samples of lead chromate using the combined use of various synchrotron radiation based analytical techniques (μ-XRD, μ-XANES and μ-FTIR), established that darkening of chrome yellow is caused by reduction of $PbCrO_4$ to $Cr_2O_3.2H_2O$ (viridian green). This is likely accompanied by the presence of another Cr(III) compound, such as either $Cr_2(SO_4)_3.H_2O$ or $(CH_3CO_2)_7Cr_3(OH)_2$ [chromium(III) acetate hydroxide].

Phosphor-based white LED light







unaged “UVA-Vis” “UV” “blue” “red”

To avoid photo induced darkening of the susceptible variants of the lead chromate-based pigments, it is advisable to minimize their exposure to light with wavelengths shorter than about **525 nm**

PbCrO4 → $PbCr_{1-x}S_xO_4$

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

Combined use of Synchrotron Radiation Based Techniques for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh

Micro-X-ray Diffraction

Micro-Fourier Transform Infrared Spectroscopy

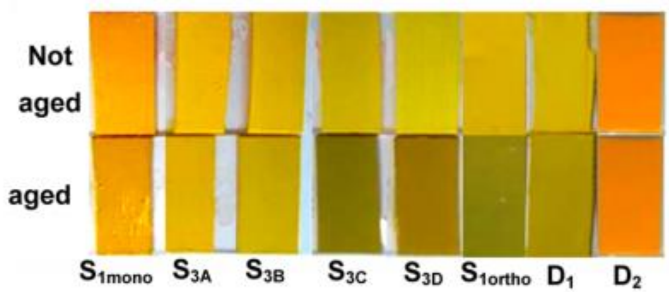
Micro-X-ray Fluorescence

Micro-X-ray Absorption Near-Edge

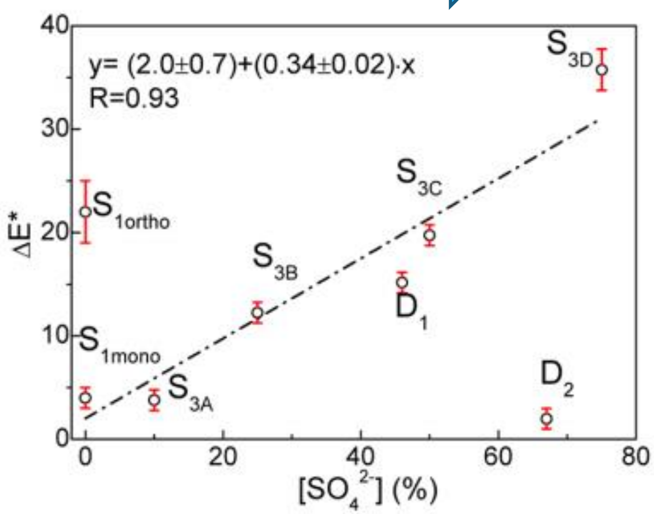
What is the alteration mechanism of the chrome yellow pigments?

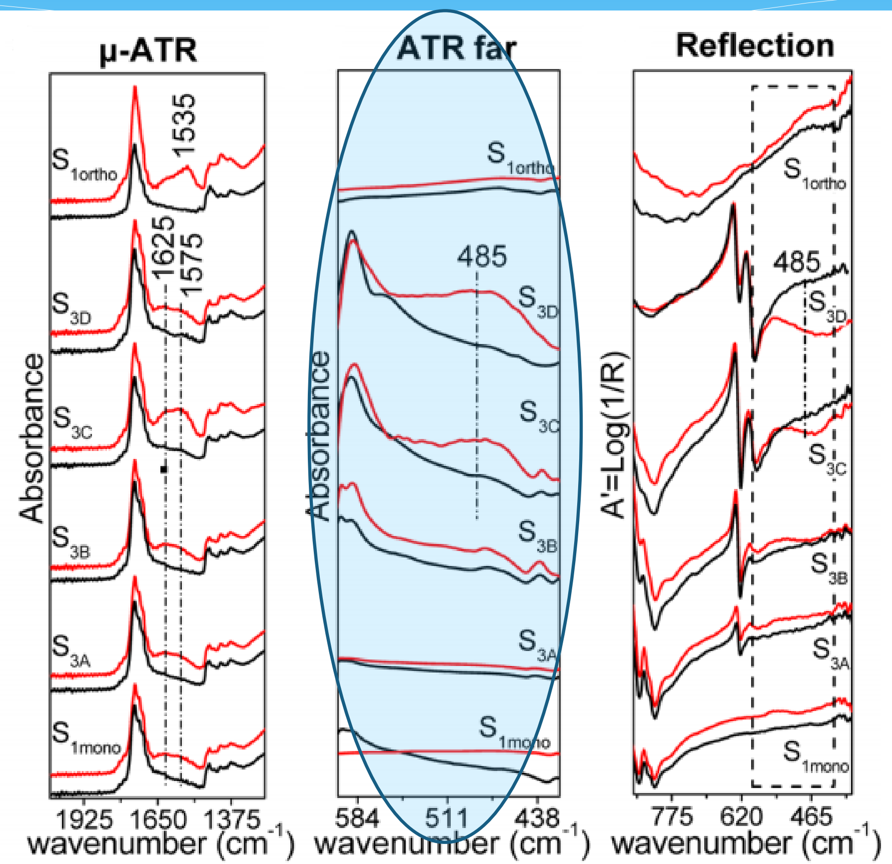
INFN Istituto Nazionale di Fisica Nucleare

Fourier Transform Infrared Spectroscopy (FT-IR) @ LNF



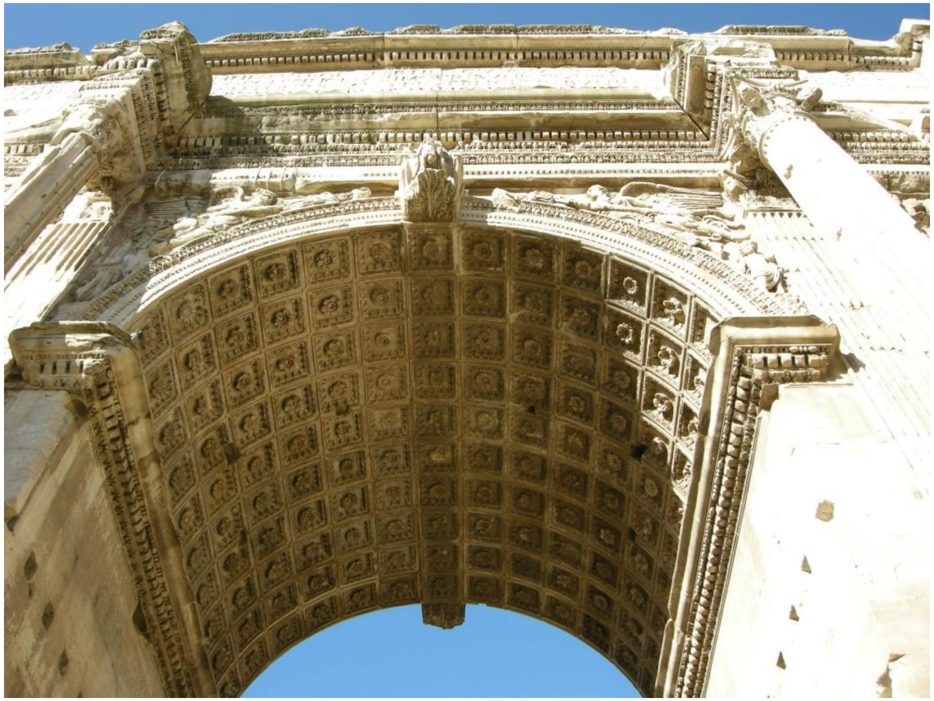
monoclinic → orthorombic

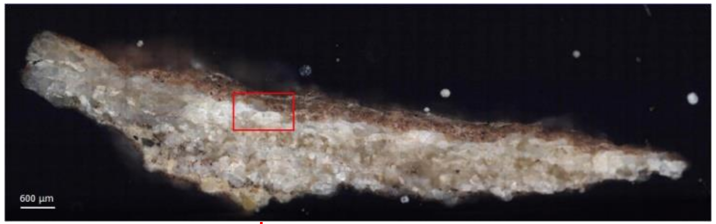


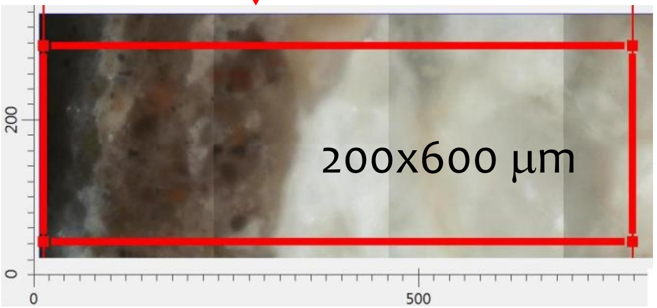


Sulphate [SO_4^{2-}] content

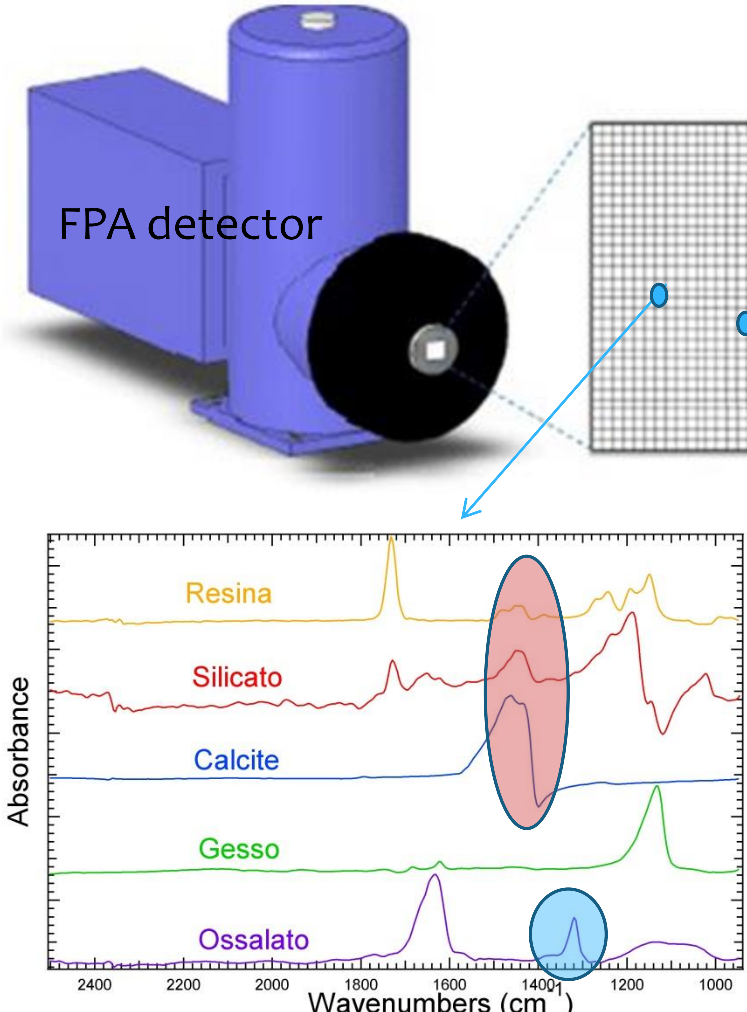
Septimius Severus's Arch degradation products

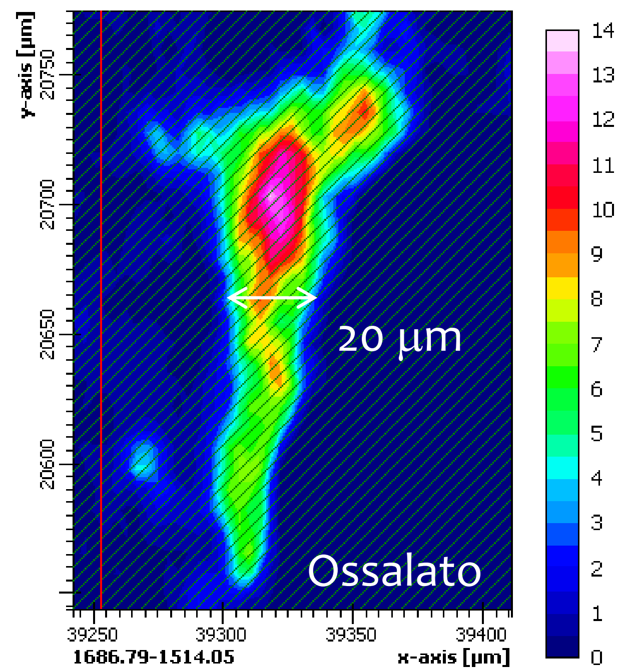




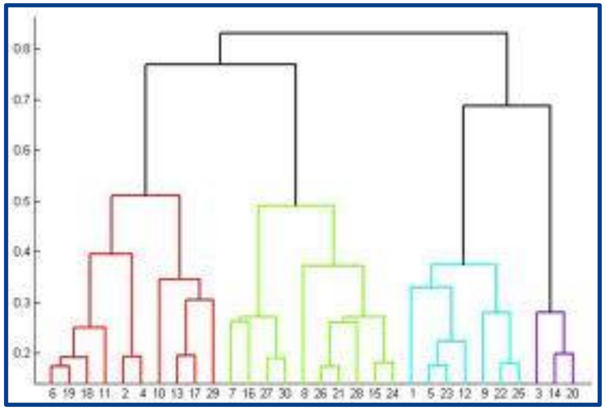


MICRO FT-IR chemical imaging

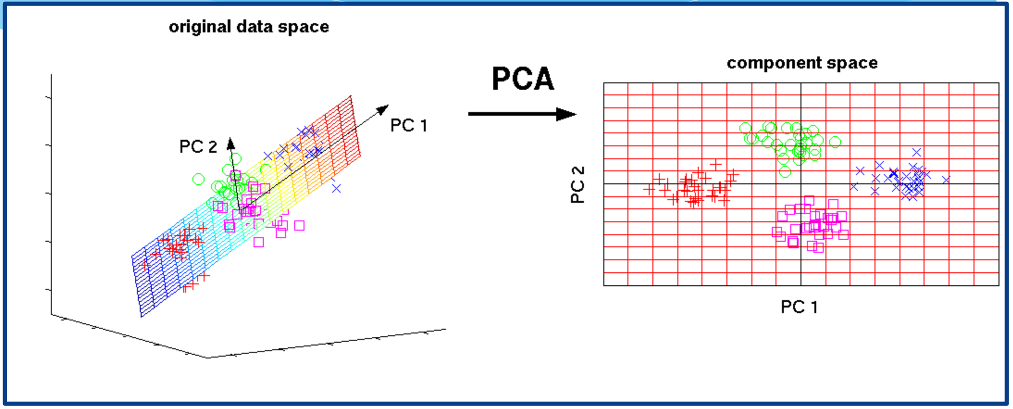




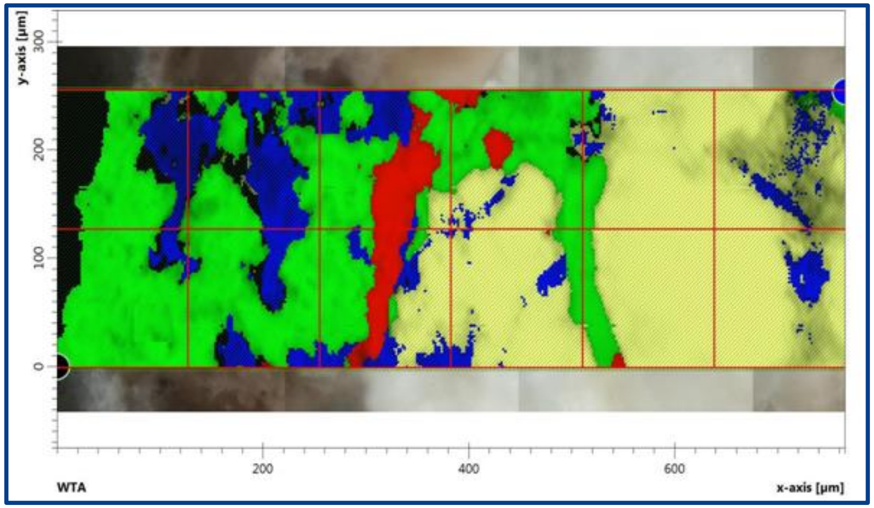
Multivariate analysis combined with FT-IR



Cluster Analysis

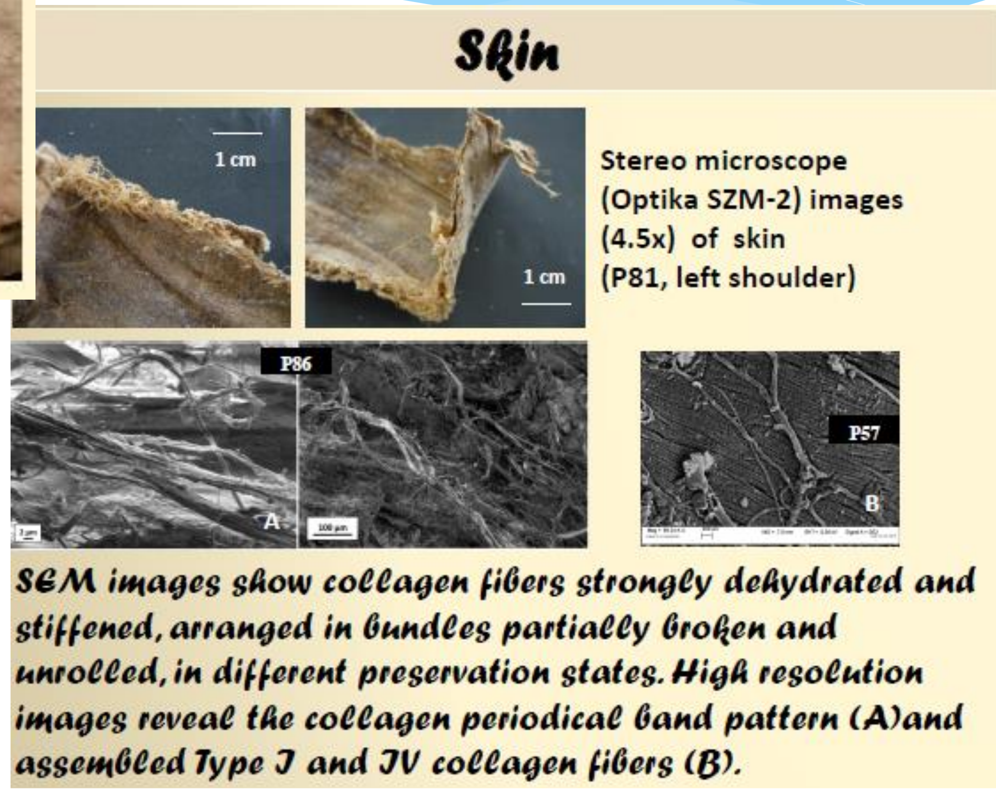


Principal Component Analysis

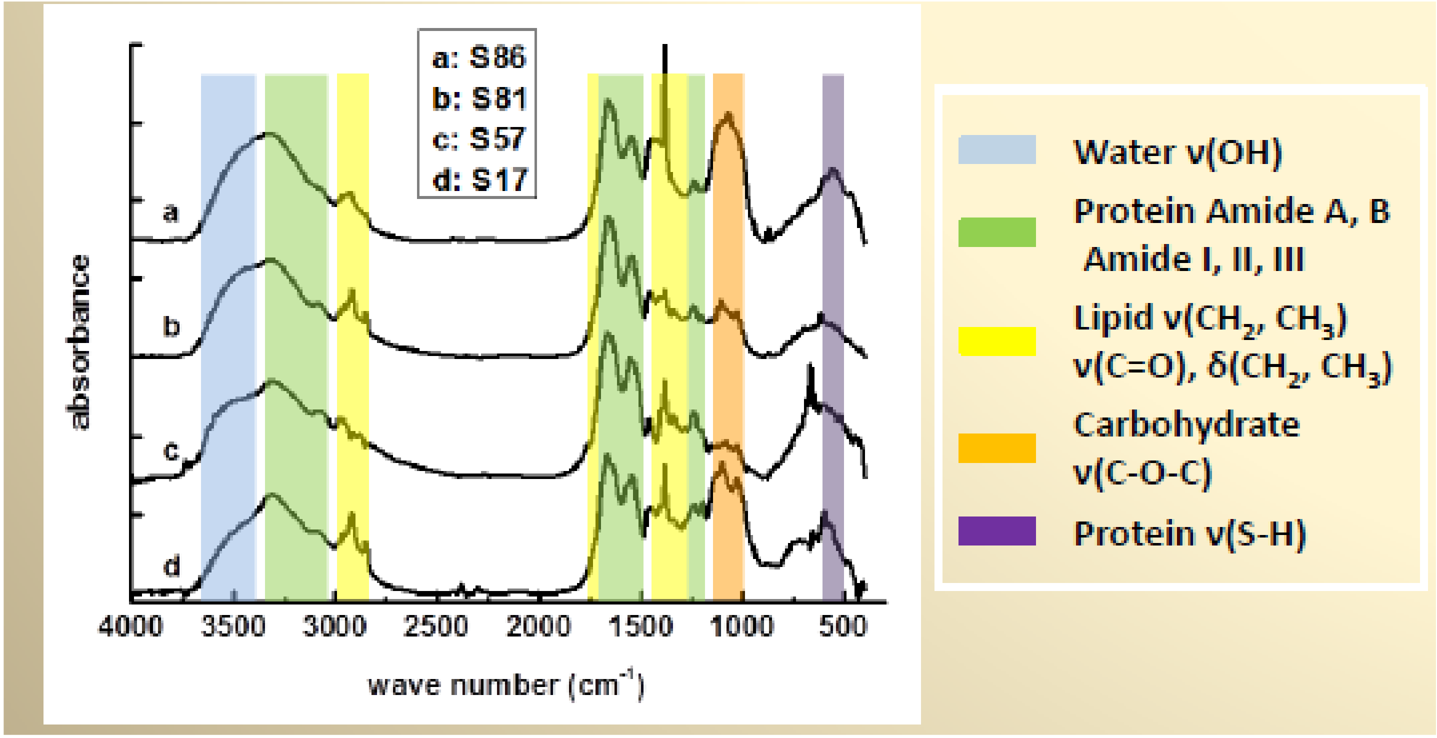


RGB map of the sample composition

Tuissues preservation of 16-18th century mummies

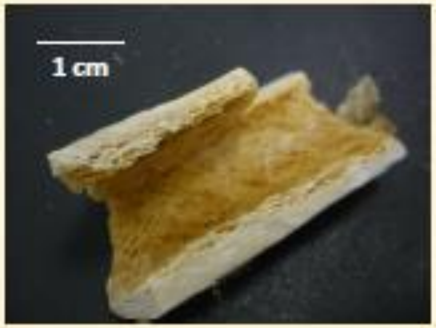


(M.G. Bridelli et al, Università degli studi di Parma)

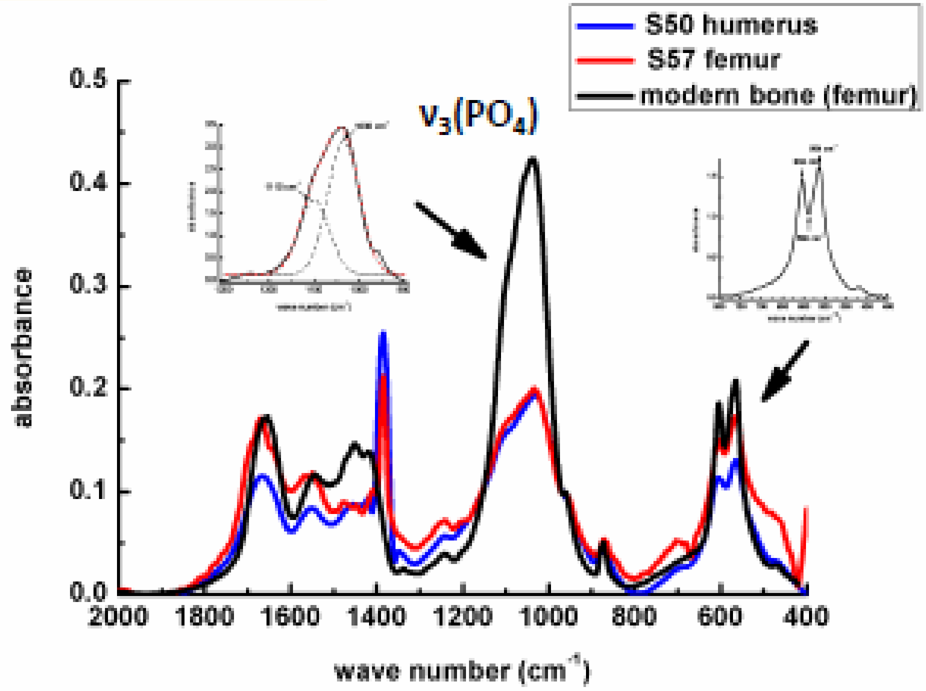


a: S86
b: S81
c: S57
d: S17
a
b
c
d
absorbance
4000
3500
3000
2500
2000
1500
1000
500
wave number (cm^{-1})
Water v(OH)
Protein Amide A, B
Amide I, II, III
Lipid v(CH_2, CH_3)
v(C=O), δ(CH_2, CH_3)
Carbohydrate
v(C-O-C)
Protein v(S-H)

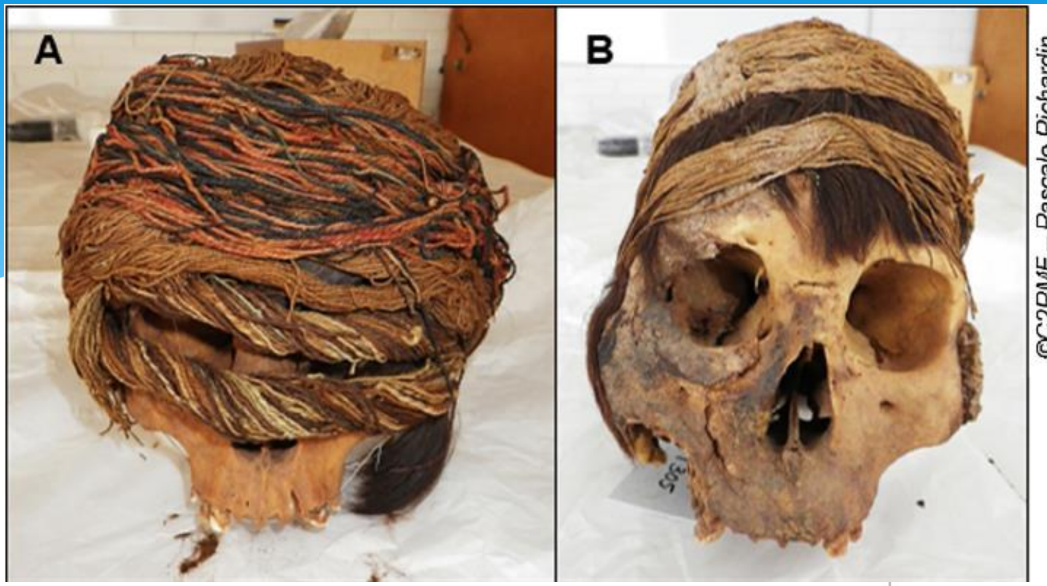
Bones

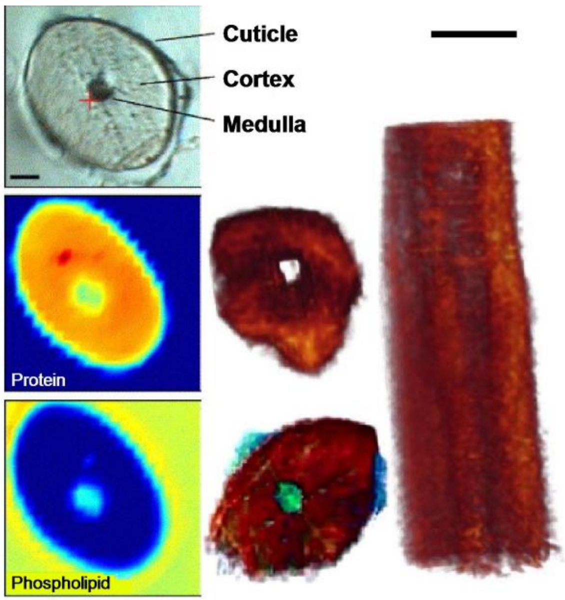


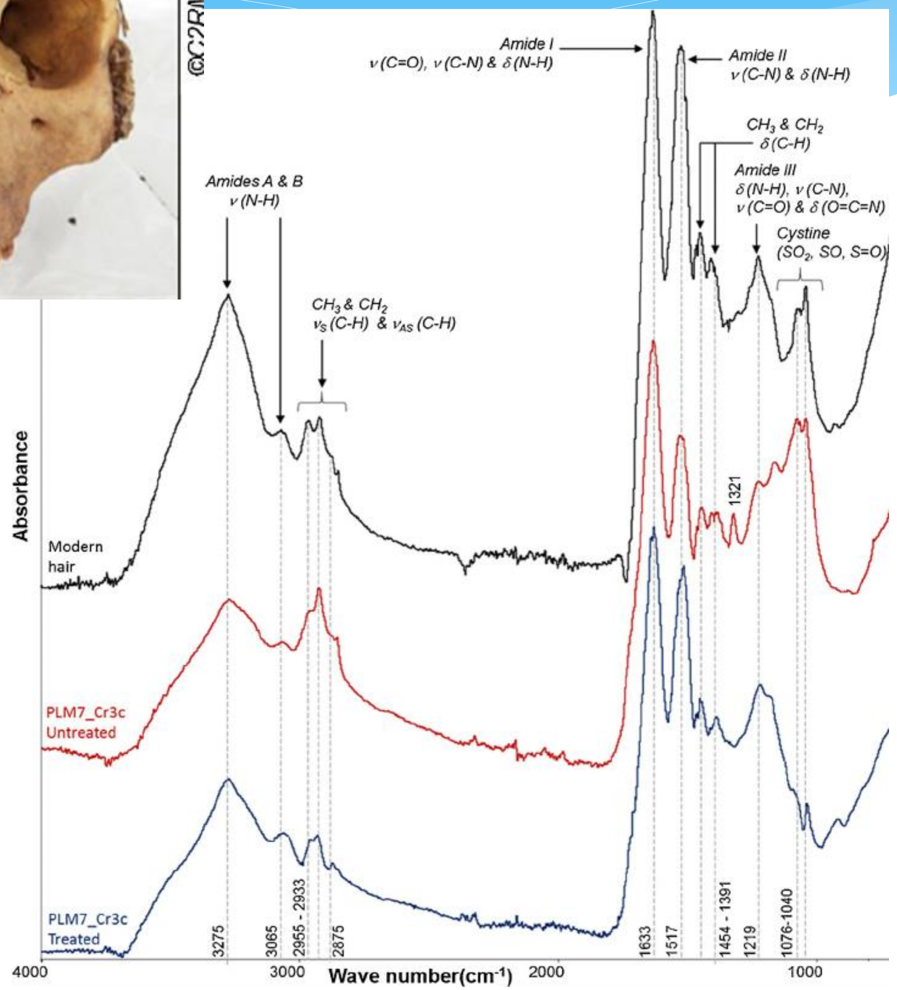
Stereo microscope (Optika SZM-2) image (4.5x) of compact bone, transverse section (S81, right femur)



Hair


A
B
©C2RMF – Pascale Richardin


Cuticle
Cortex
Medulla
Protein
Phospholipid


Amide I
ν (C=O), ν (C-N) & δ (N-H)
Amide II
ν (C-N) & δ (N-H)
CH_3 & CH_2
δ (C-H)
Amide III
δ (N-H), ν (C-N),
ν (C=O) & δ (O=C=N)
Cystine
(SO_2, SO, S=O)
Amides A & B
ν (N-H)
CH_3 & CH_2
ν_S (C-H) & ν_{AS} (C-H)
1321
Absorbance
Modern hair
PLM7_Cr3c Untreated
PLM7_Cr3c Treated
3275
3065
2955 - 2933
2875
1633
1517
1454 - 1391
1219
1076-1040
4000
3000
Wave number(cm^{-1})
2000
1000

Centro Conservazione e Restauro
La Venaria Reale

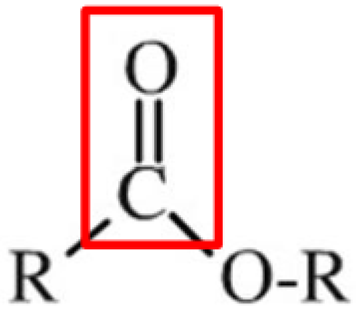
Il carbonile

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

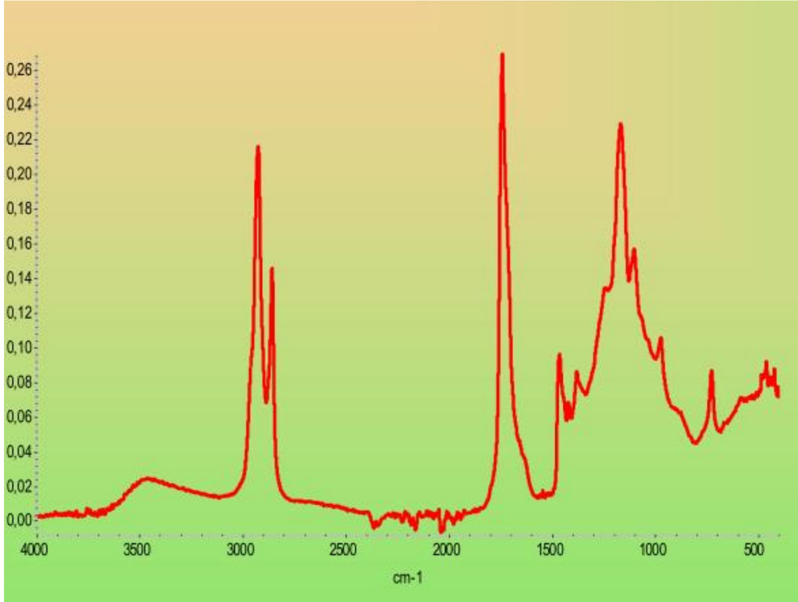
Solventi
Leganti
Vernici
Fibre

Ma anche in alcuni pigmenti inorganici

Gli esteri

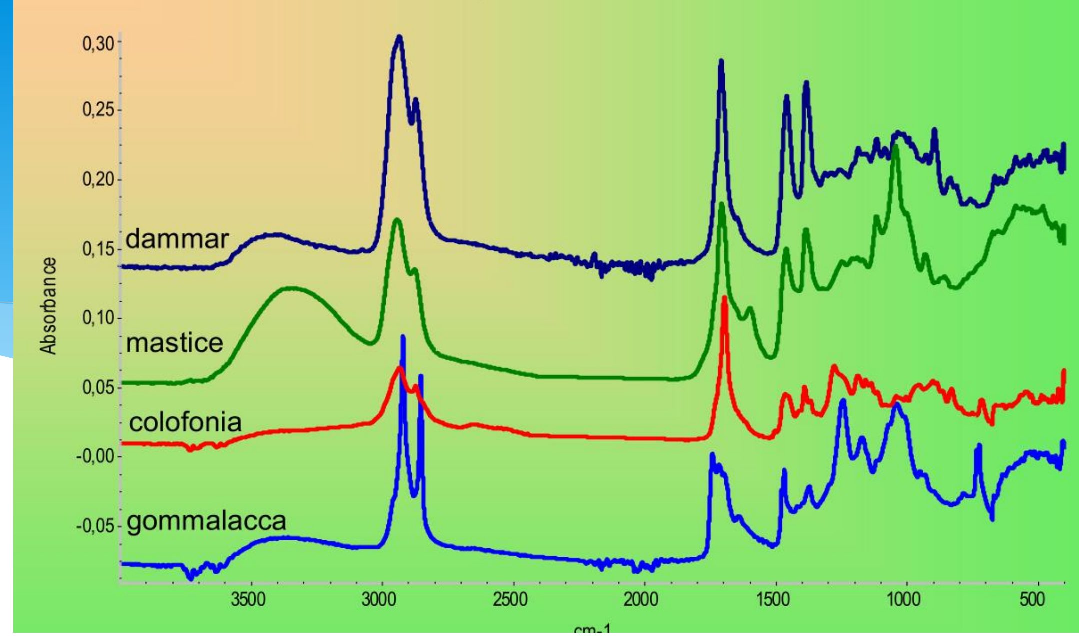


Olii siccativi
Resine naturali
Cere
Resine sintetiche
Additivi
Plastiche

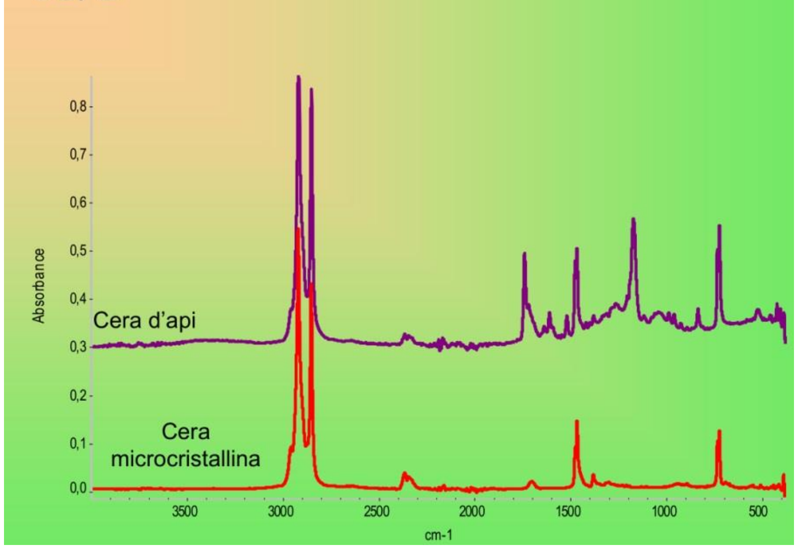


Olio di lino cotto

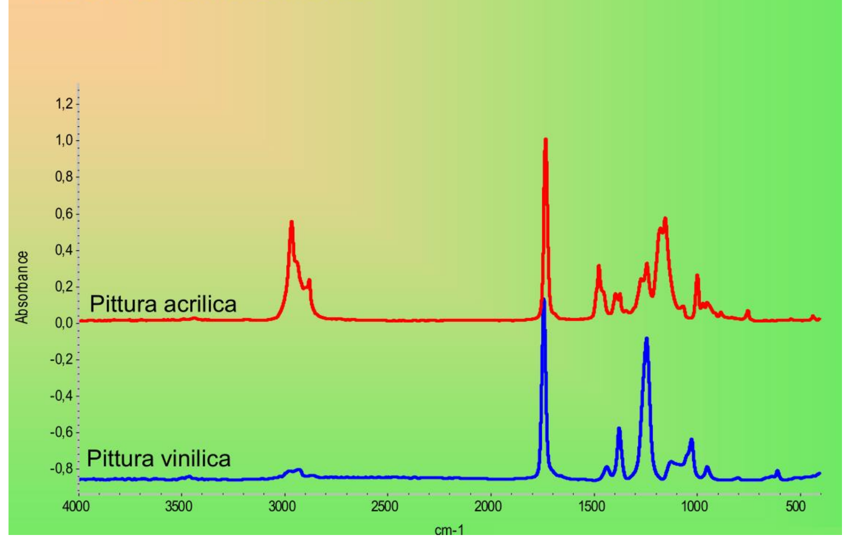
Resine naturali



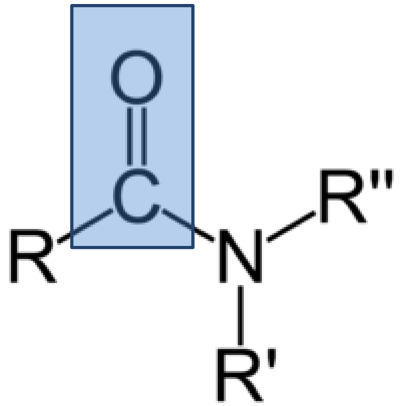
Cere



Resine sintetiche

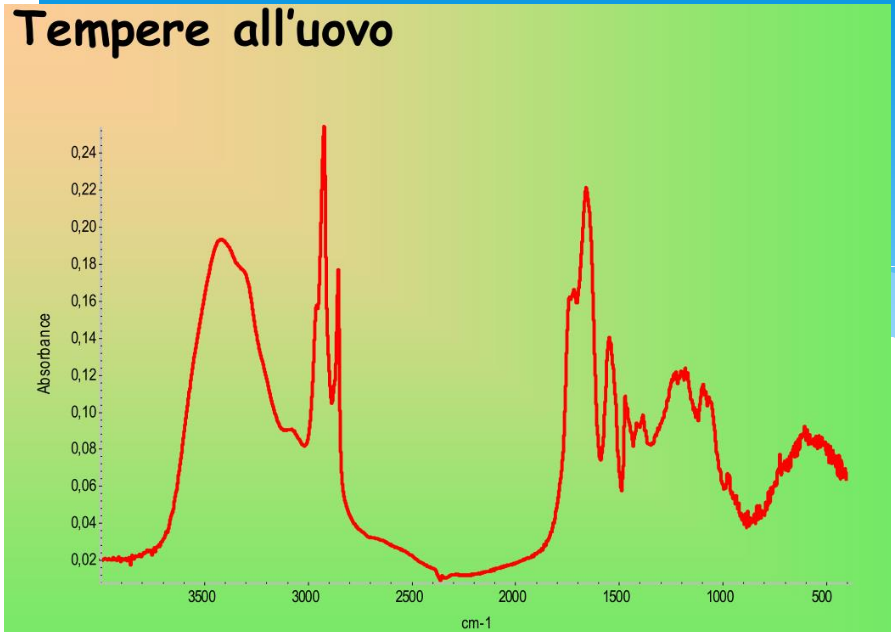


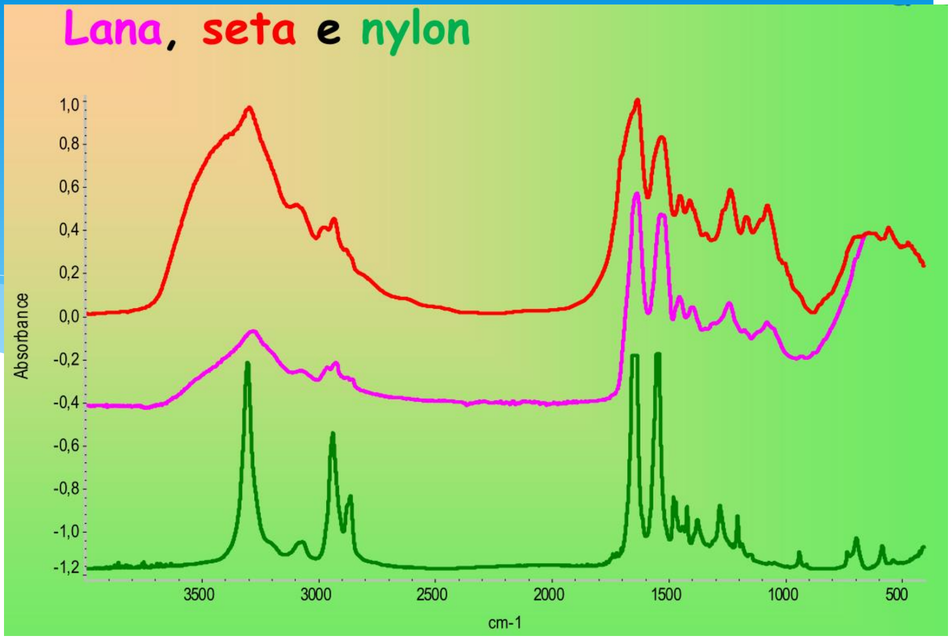
Le ammidi

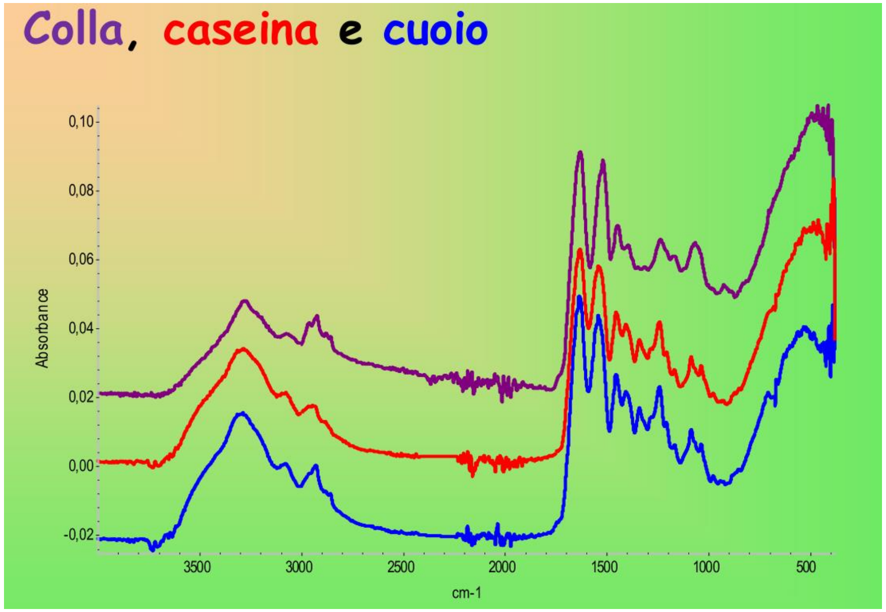


Struttura generale di un'ammide. Se R' e R'' sono idrogeni l'ammide si dice primaria, se solo uno fra R' ed R'' è un H, si dice secondaria, se R' ed R'' non sono idrogeni, l'ammide si dice terziaria

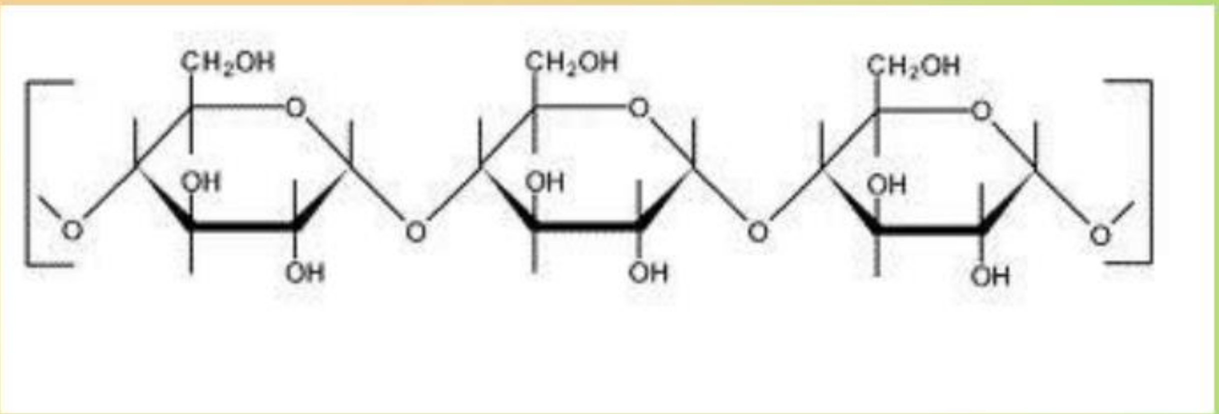
Tempere all'uovo
Tempera grassa
Lana e seta
Colle animali
Cuoio e pelle
Caseina
Plastica


Tempere all'uovo
Absorbance
cm-1


Lana, seta e nylon
Absorbance
cm-1


Colla, caseina e cuoio
Absorbance
cm-1

I polisaccaridi



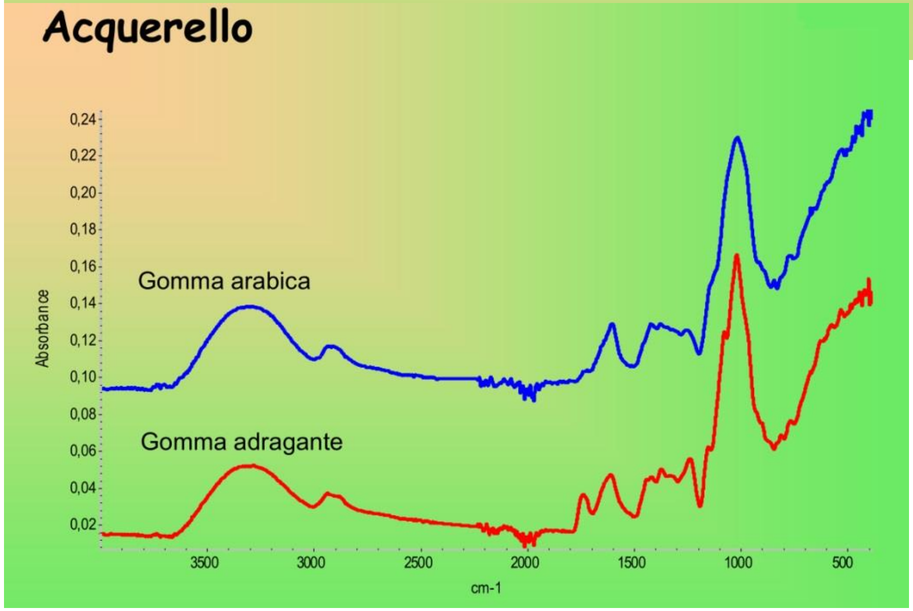
Acquerello

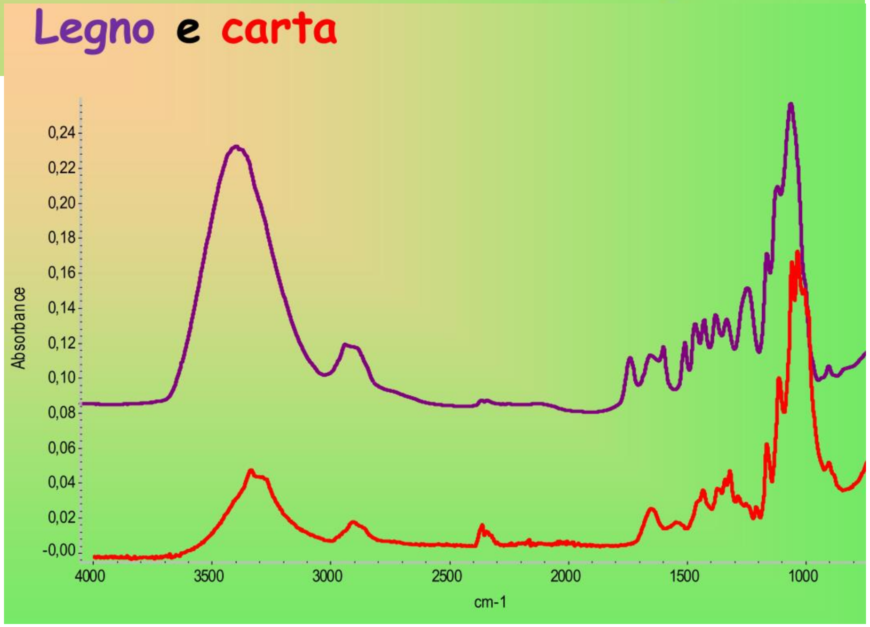
Gomme naturali

Legno

Carta

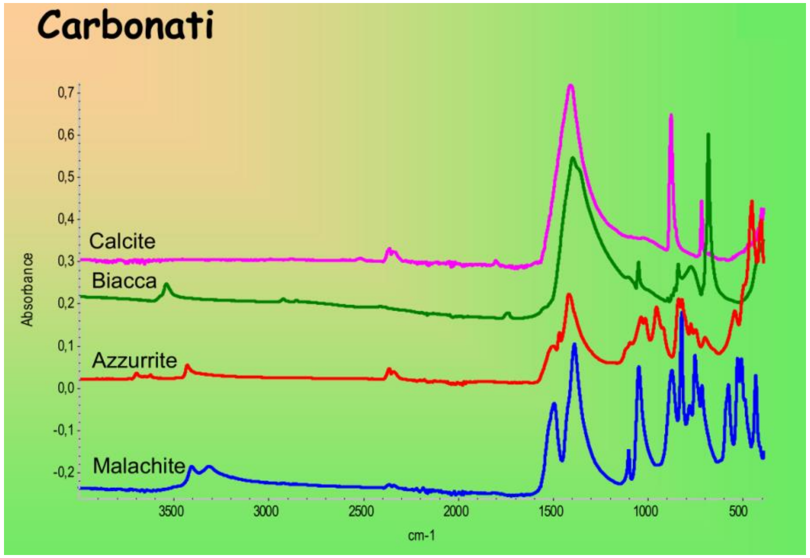
Fibre vegetali

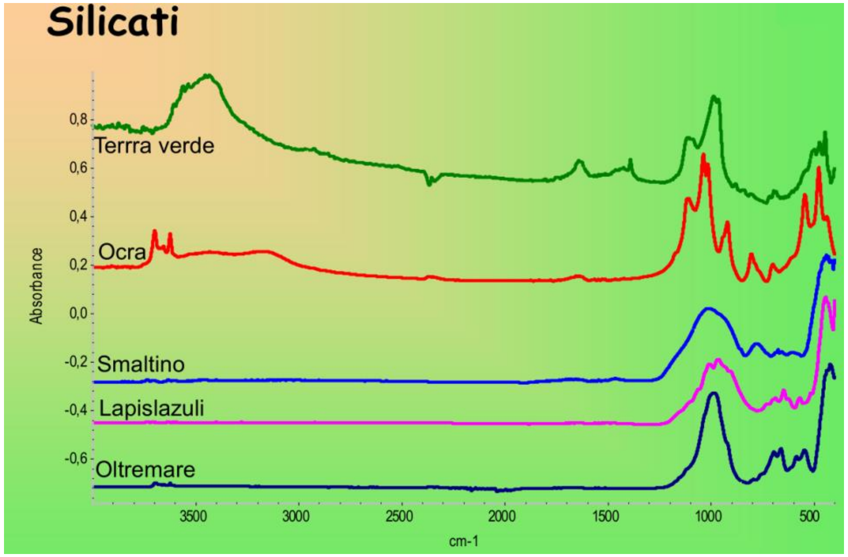




I pigmenti

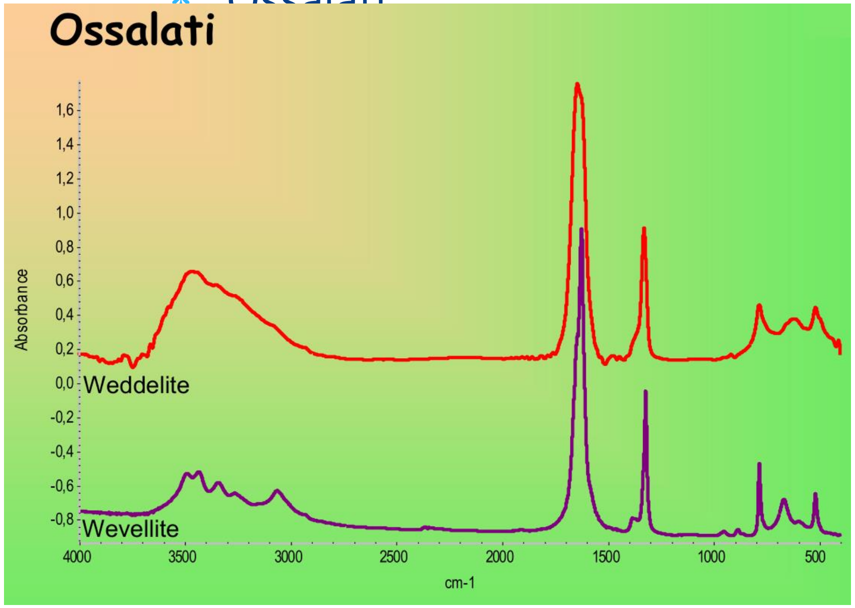
- Carbonati
- Silicati
- Solfati
- Pigmenti organici

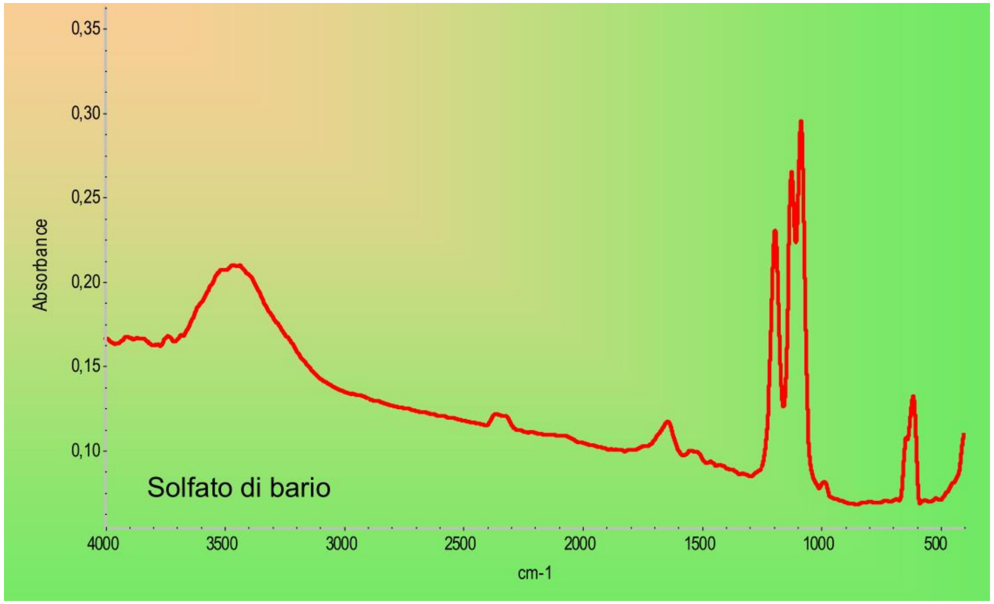


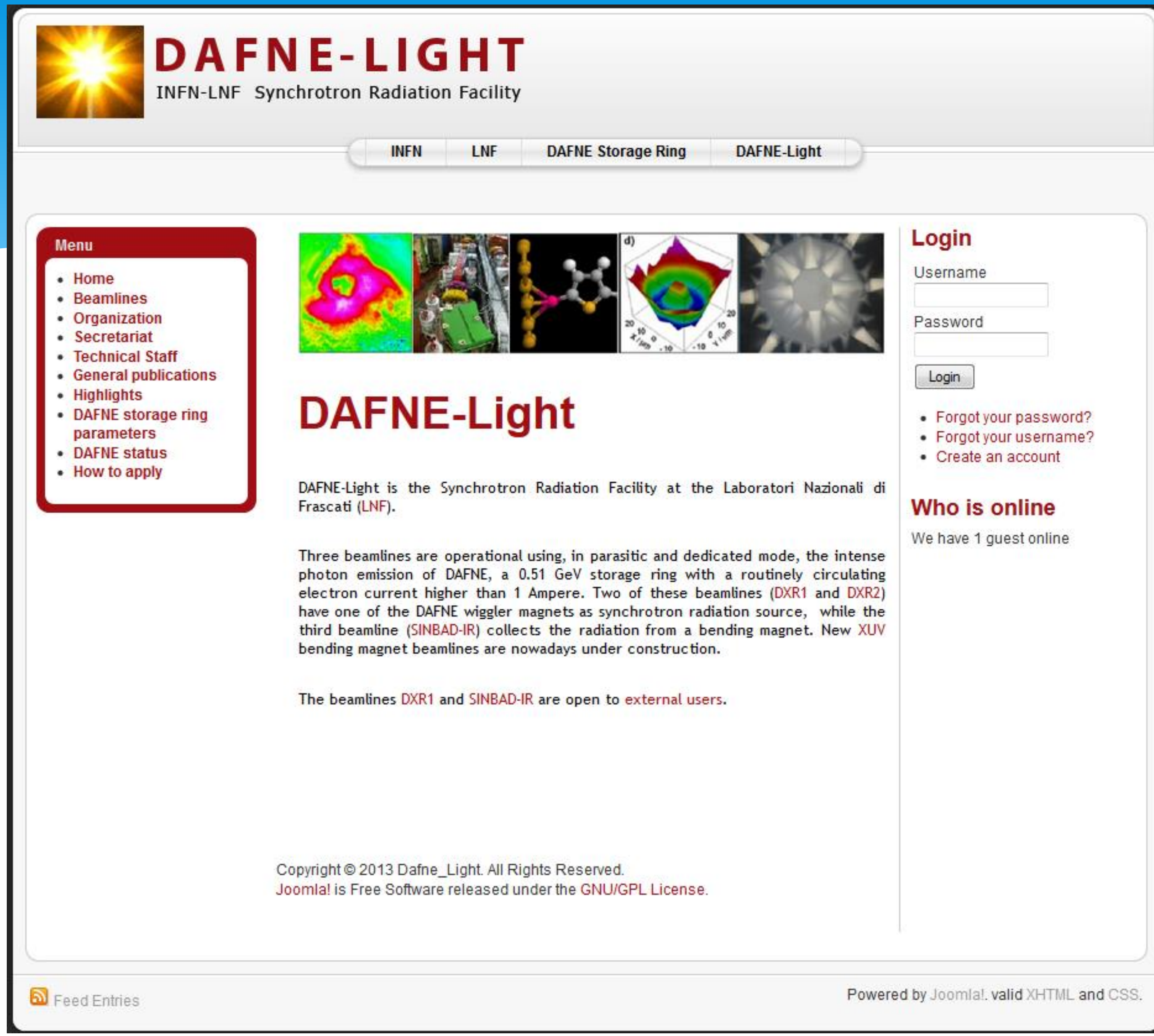


Prodotti di degrado comuni

* Solfati
* Ossalati



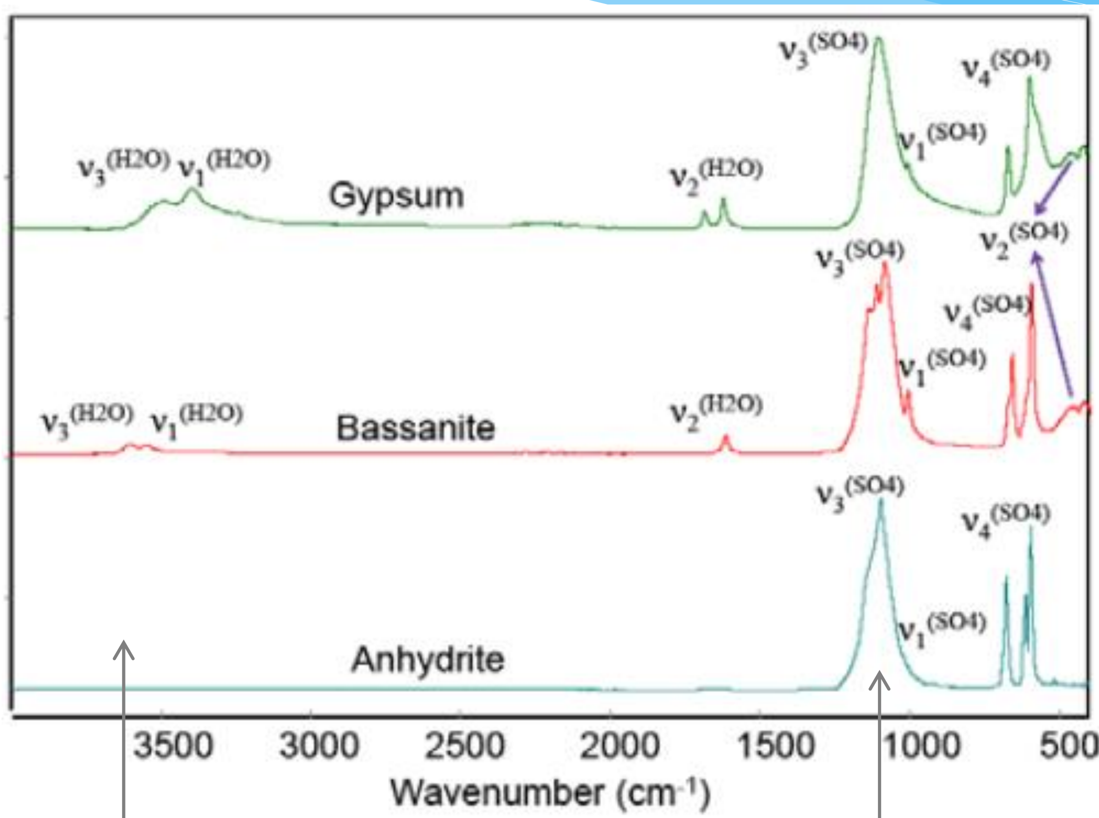




https://web2.infn.it/Dafne_Light/

cestelli@lnf.infn.it

ATR spectrum of gypsum



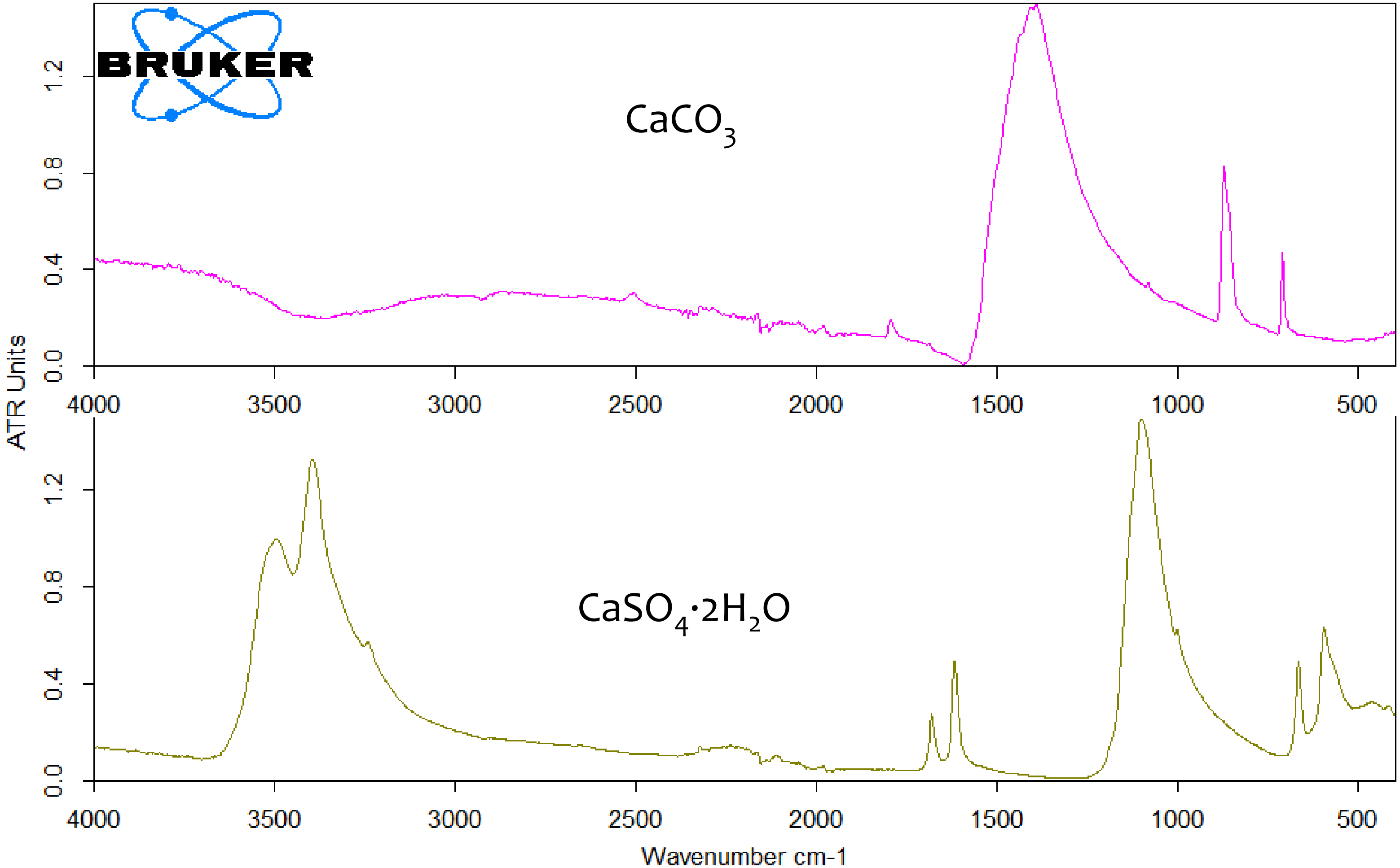
$CaSO_4 \cdot 2H_2O$

$CaSO_4.0.5H_2O$

$CaSO_4$

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