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

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Sinbad IR beamline @ DaΦne

INFN-International Masterclass 2015

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

UNESCO definition of “cultural heritage”

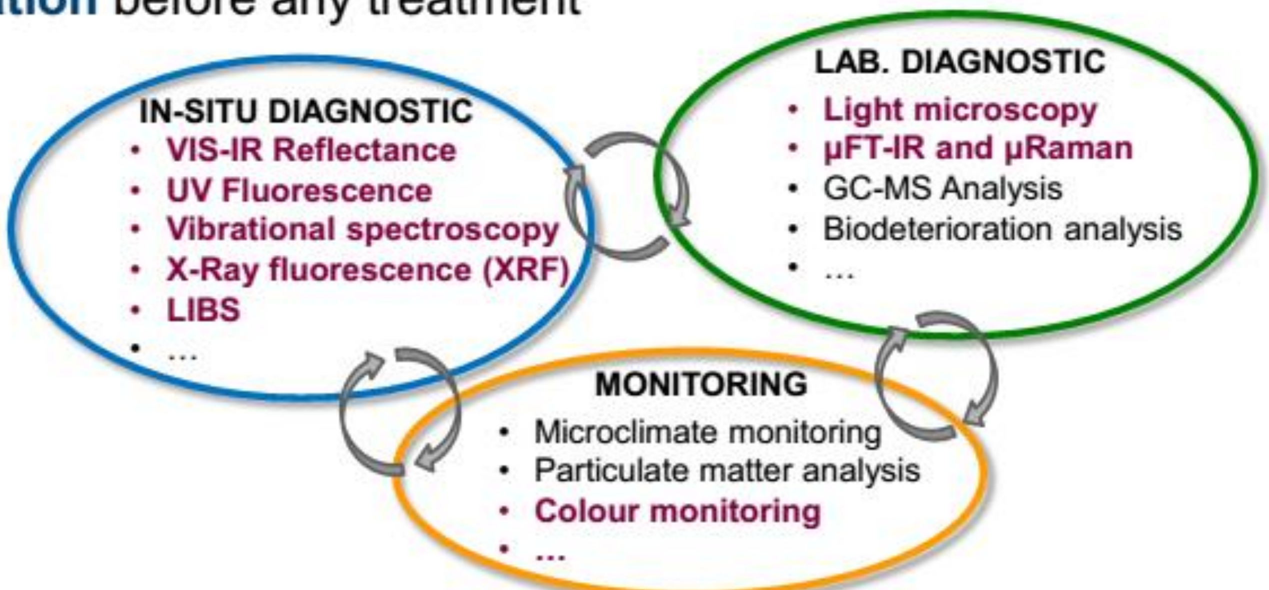
- What is meant by "cultural heritage"?
- The term cultural heritage encompasses several main categories of heritage:
- **Cultural heritage**
  - **Tangible cultural heritage:**
    - movable cultural heritage (paintings, sculptures, coins, manuscripts)
    - immovable cultural heritage (monuments, archaeological sites, and so on)
    - underwater cultural heritage (shipwrecks, underwater ruins and cities)
  - **Intangible cultural heritage**: oral traditions, performing arts, rituals
- **Natural heritage:** natural sites with cultural aspects such as cultural landscapes, physical, biological or geological formations
- **Heritage in the event of armed conflict**

The scientific approach to conservation

- Material aging, climate change, atmospheric pollution, **anthropic pressure** pose serious threats to our cultural heritage

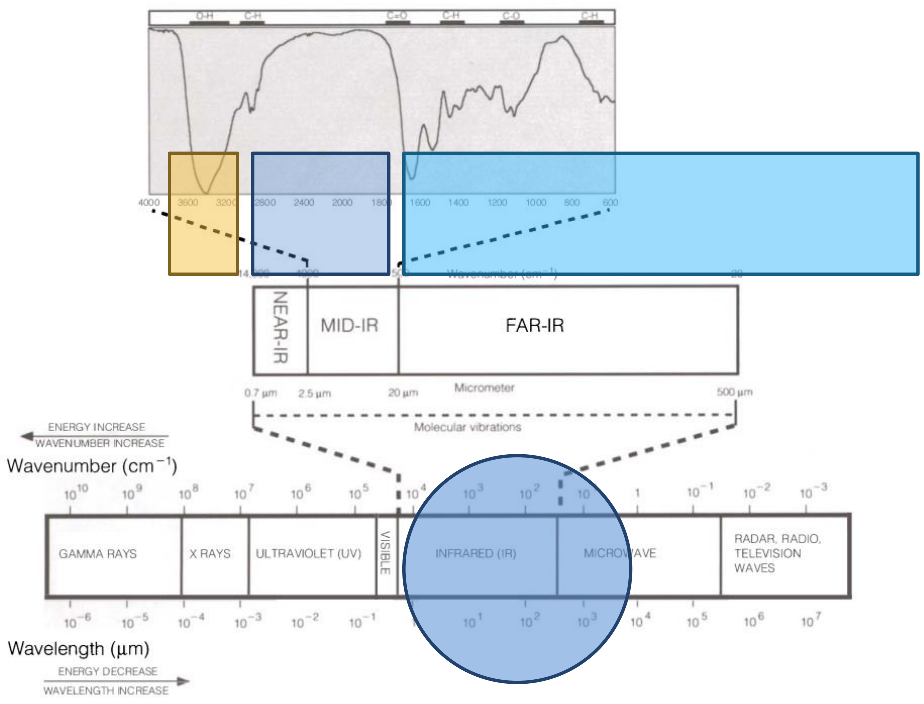
- Inappropriate conservation and restoration procedures have also contributed to degradation of works of art

- The **modern approach** to conservation requires a deep scientific **investigation** before any treatment

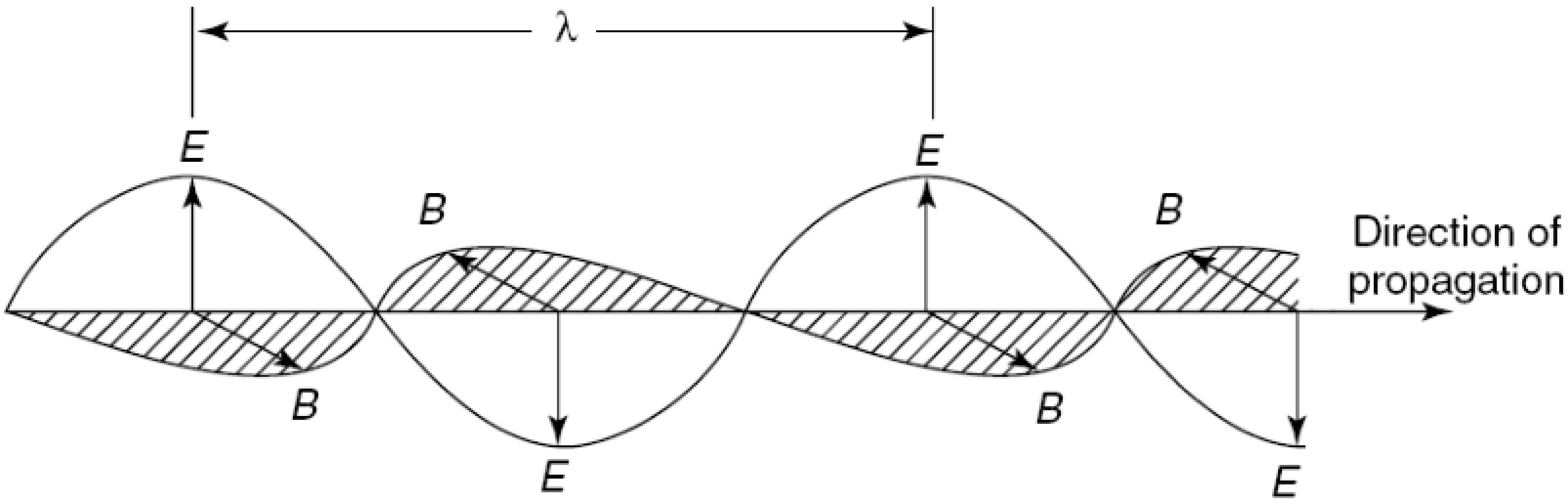


FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR): physical principles

Electromagnetic spectrum and IR



The EM field



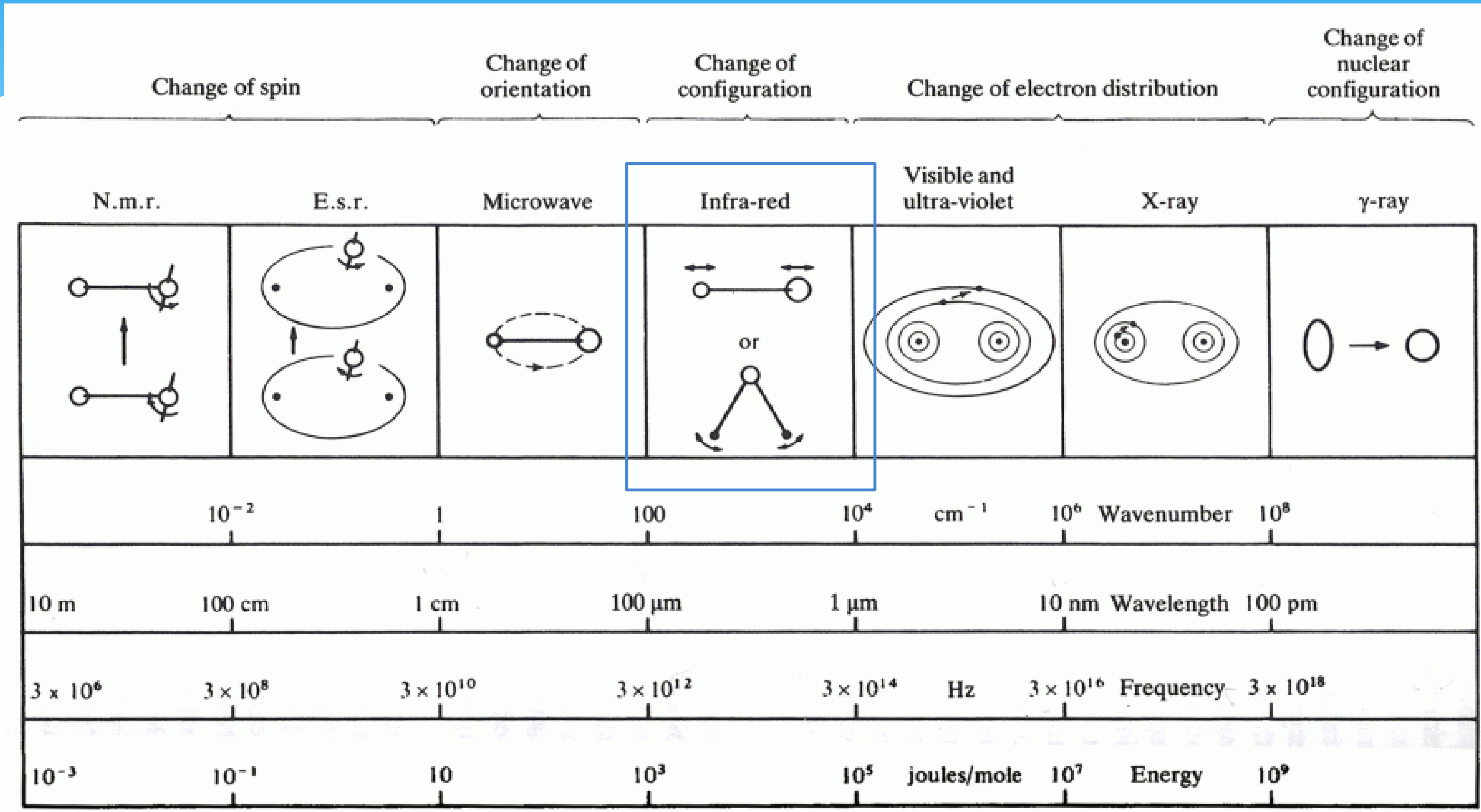
IR Units

- 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}**)

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

What happens when «light» interacts with matter

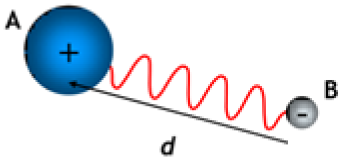


$E_{total} = E_{translational} + E_{rotational} + E_{vibrational}$

Every molecule interacts with the IR EM field?

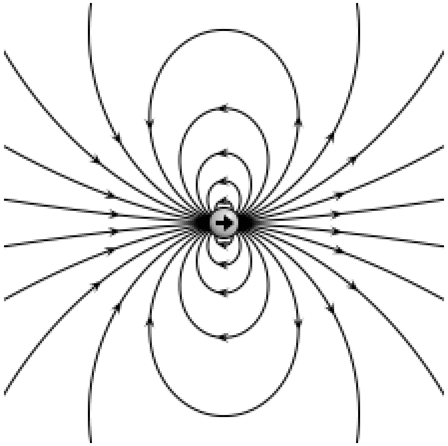
- In the simple case of two point charges, one with charge +*q* and the other one with charge −*q*, the electric dipole moment **p** is:

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

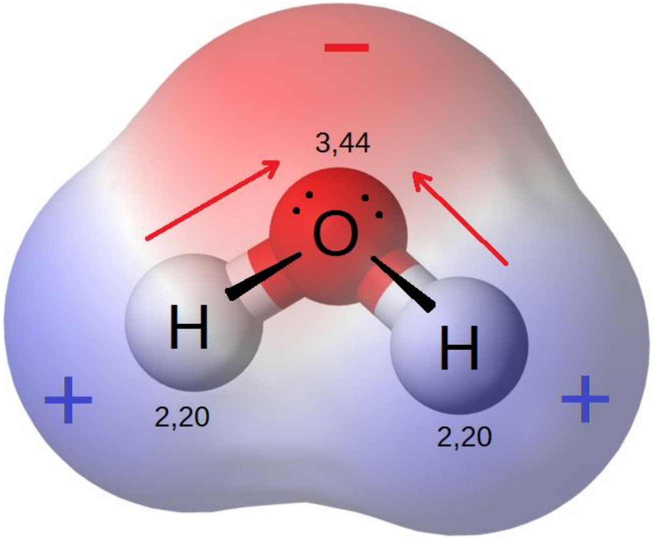


- **d** is the displacement vector pointing from the negative charge to the positive charge. Thus, the electric dipole moment vector **p** points from the negative charge to the positive charge.

Electric field of an electric dipole. The dipole consists of two point electric charges of opposite polarity located close together



Polar molecules



A molecule of water is polar because of the unequal sharing of its electrons in a "bent" structure. A separation of charge is present with negative charge in the middle (red shade), and positive charge at the ends (blue shade).

Examples of polar molecules of materials that are gases under standard conditions are:

Ammonia (**NH_3**)

Sulfur Dioxide (**SO_2**)

Hydrogen Sulfide (**H_2S**).

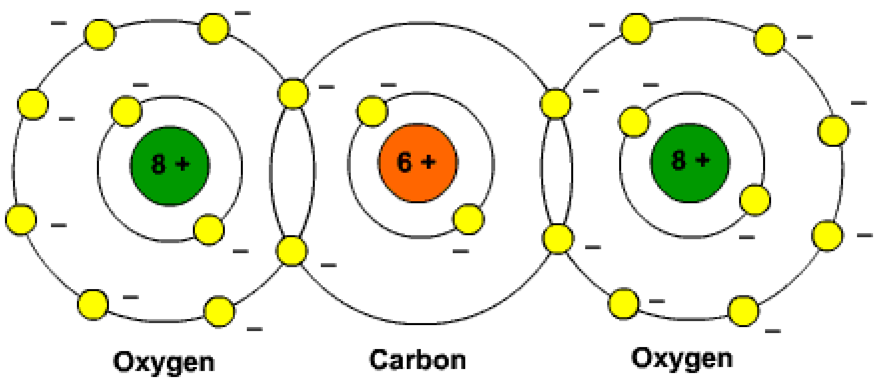
Non polar molecules

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 (**H_2**)
* Nitrogen (**N_2**)
* Oxygen (**O_2**)
* Carbon Dioxide (**CO_2**)
* Methane (**CH_4**)
* Ethylene (**C_2H_4**)
*



IR active modes

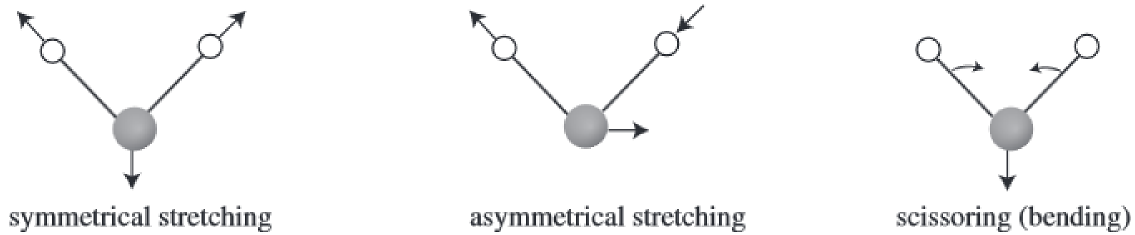


Figure : Stretching and bending vibrational modes for H_2O

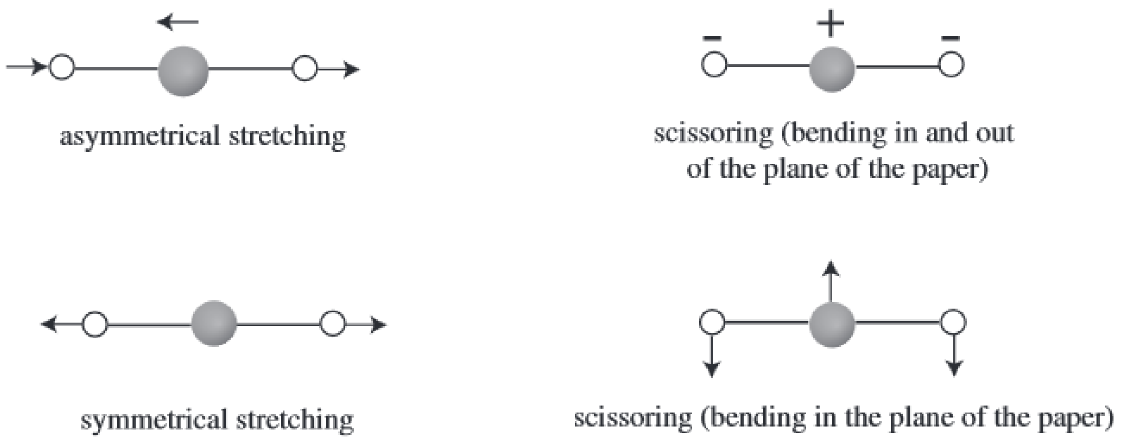
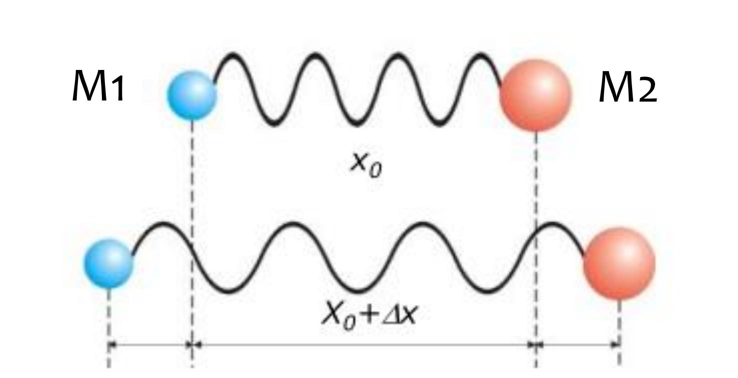


Figure : Stretching and bending vibrational modes for CO_2

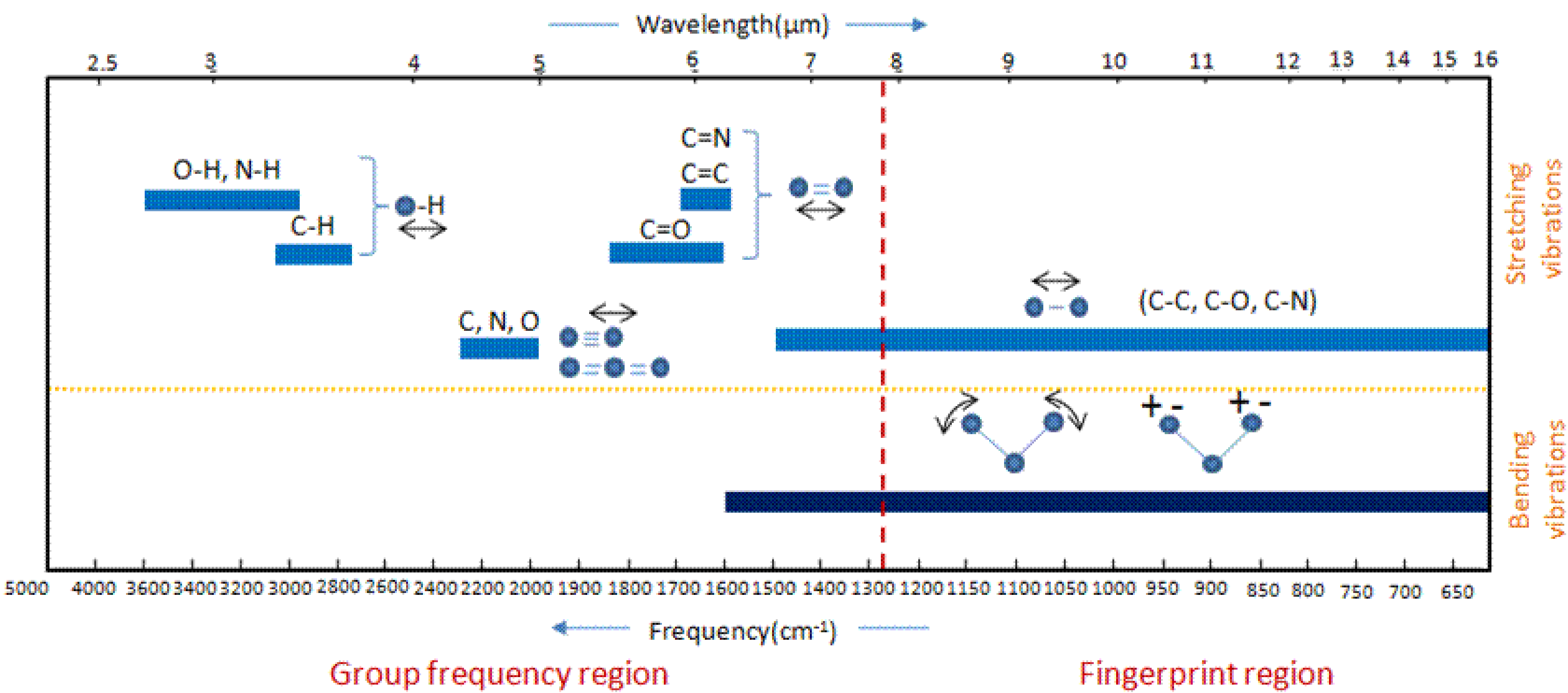
- O_2, H_2, Cl_2, N_2 are not IR active!



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

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

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



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 ≡O, C ≡N → 2000-2300 cm^{-1}

C-H, N-H, O-H → 2700-3800 cm^{-1}

Normal modes of vibration

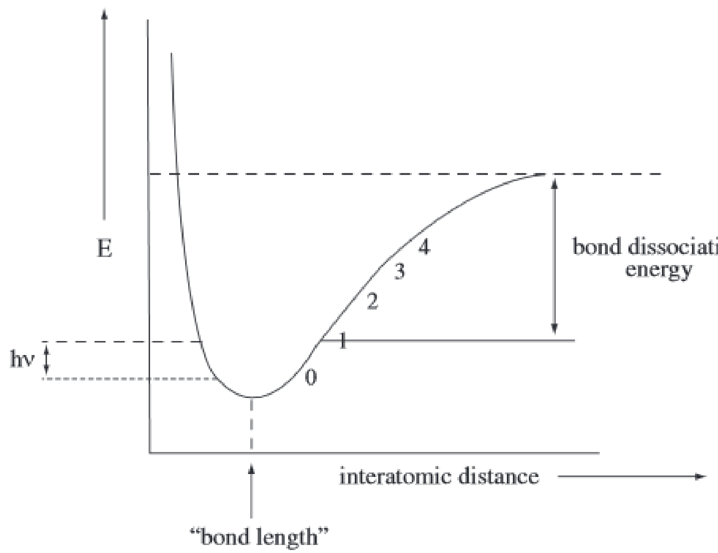


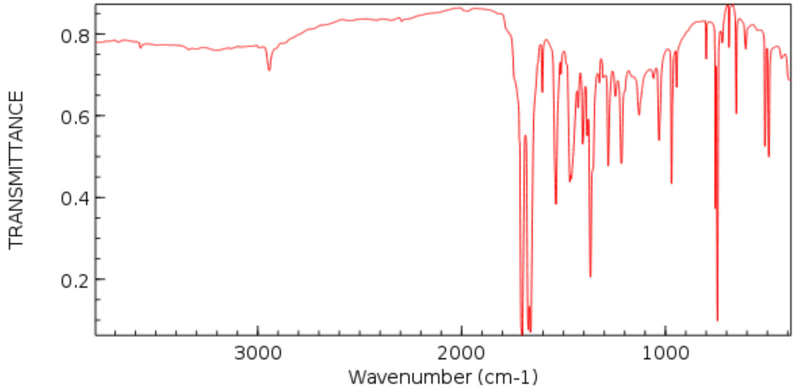
Figure 15.8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

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

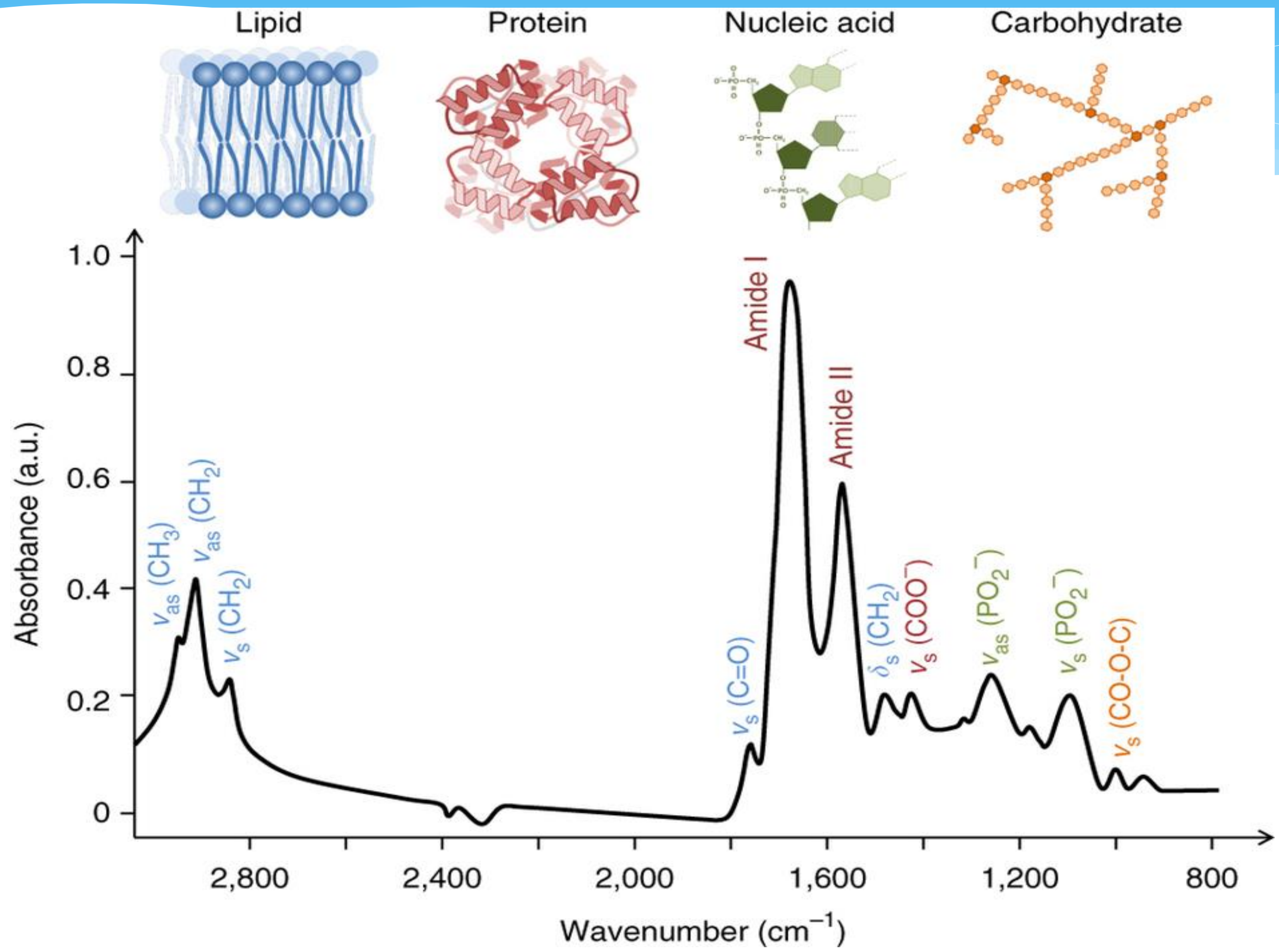
(quantized energy levels)

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

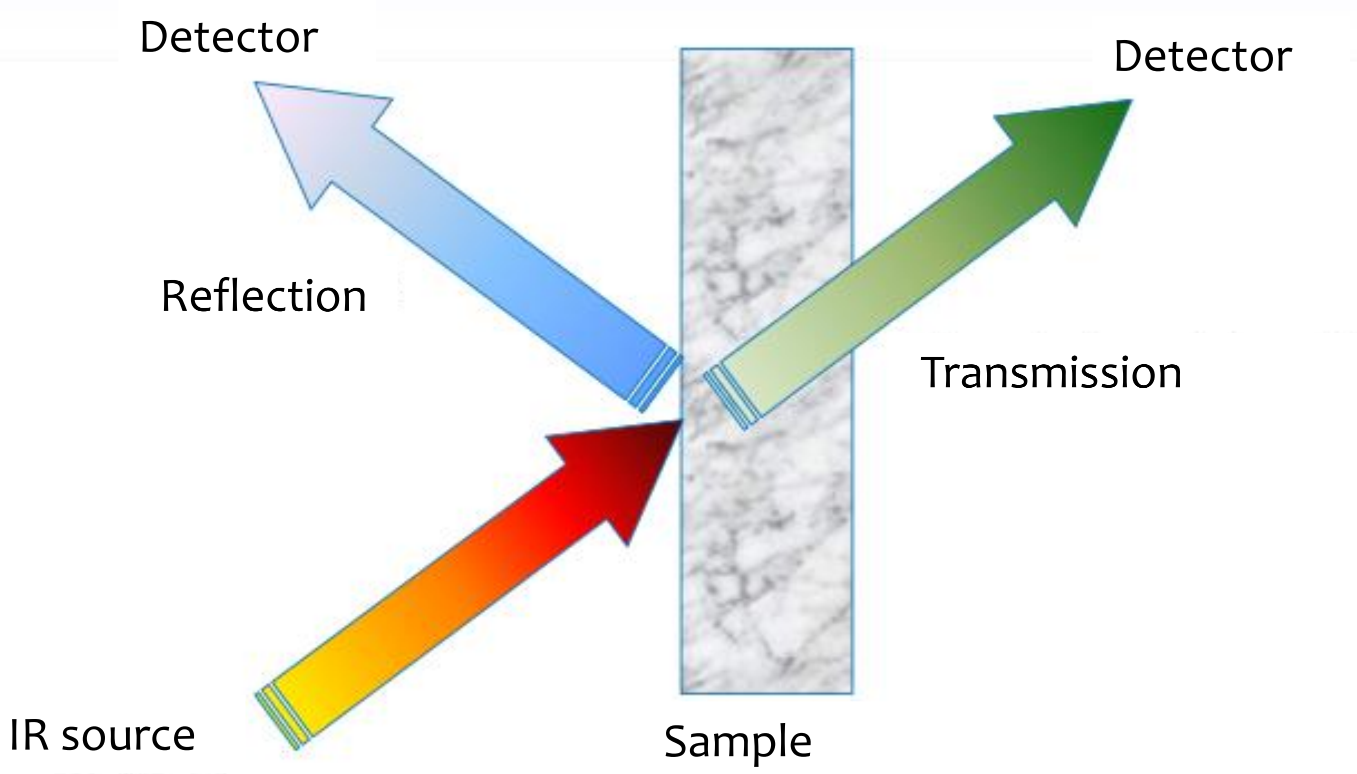
Every molecule has its unique IR spectrum



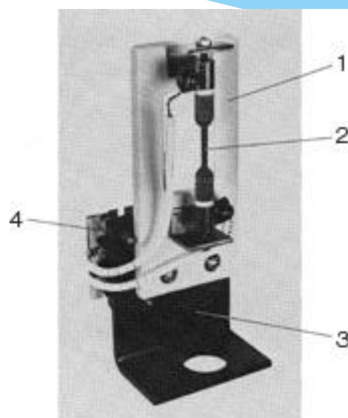
Also very complex molecules…

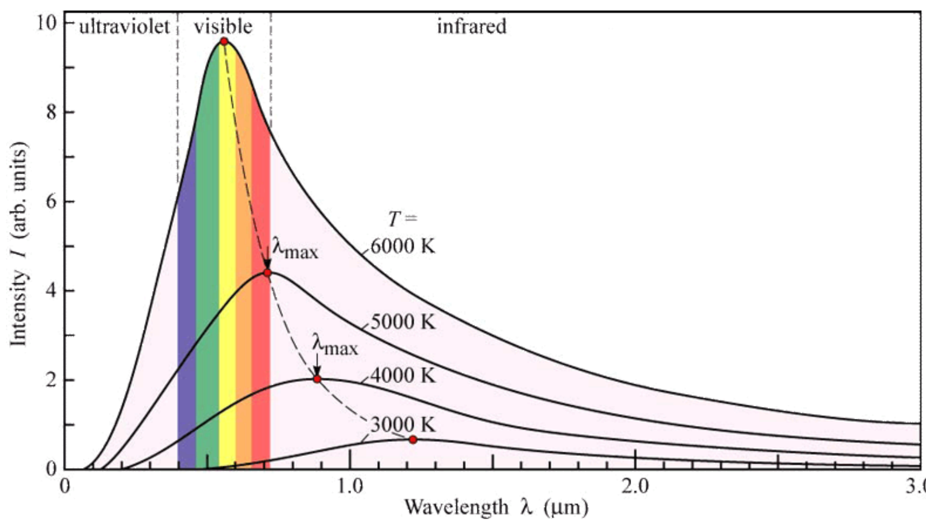


Fourier Transform Infrared Spectroscopy (FT-IR)

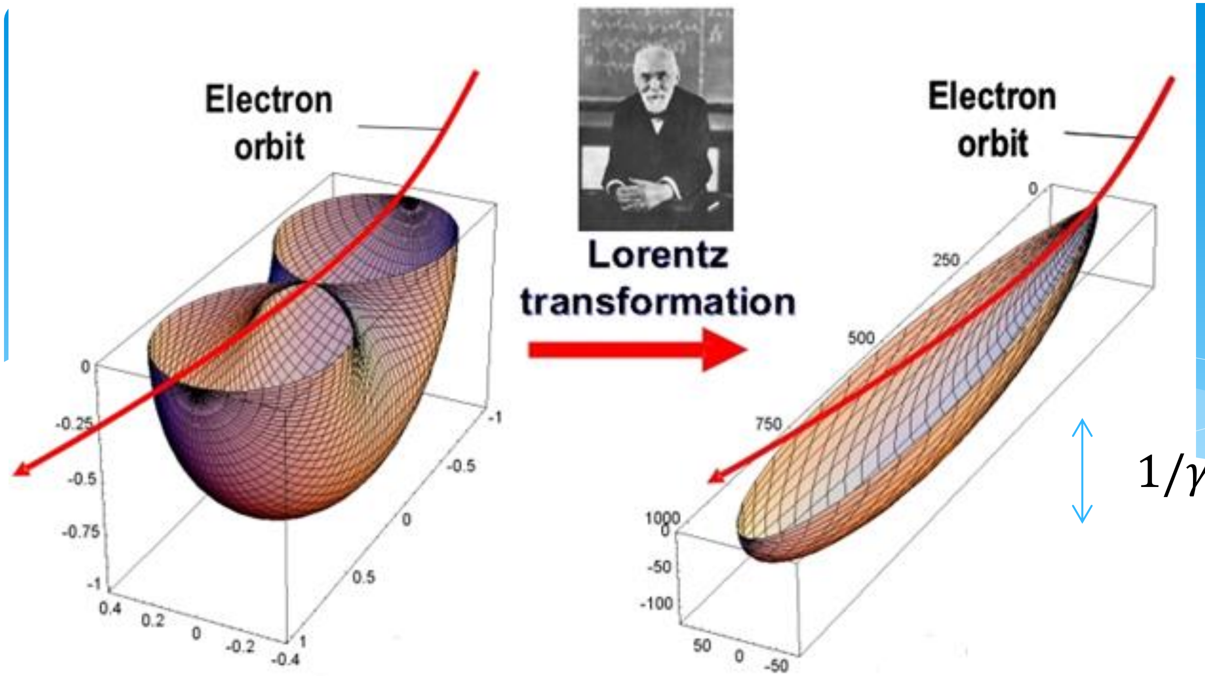

Detector
Detector
Reflection
Transmission
IR source
Sample

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
1.0
2.0
3.0

Synchrotron radiation



Classic (v<<c)

Relativistic ($v \approx c$)

Every moving electric charge emits EM radiation.

$$\beta = v/c$$

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

Per β=0.99 $1/\gamma$= 10 mrad

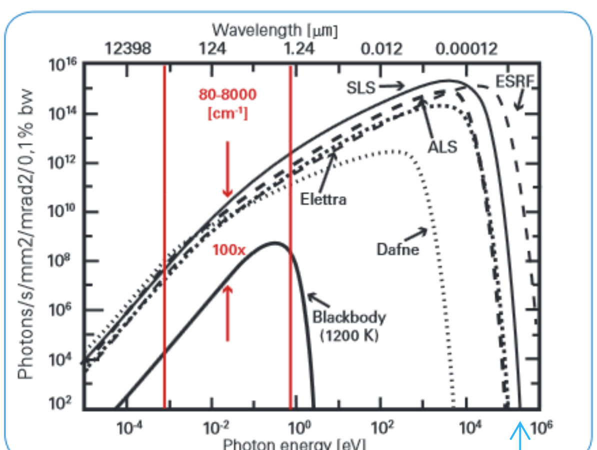
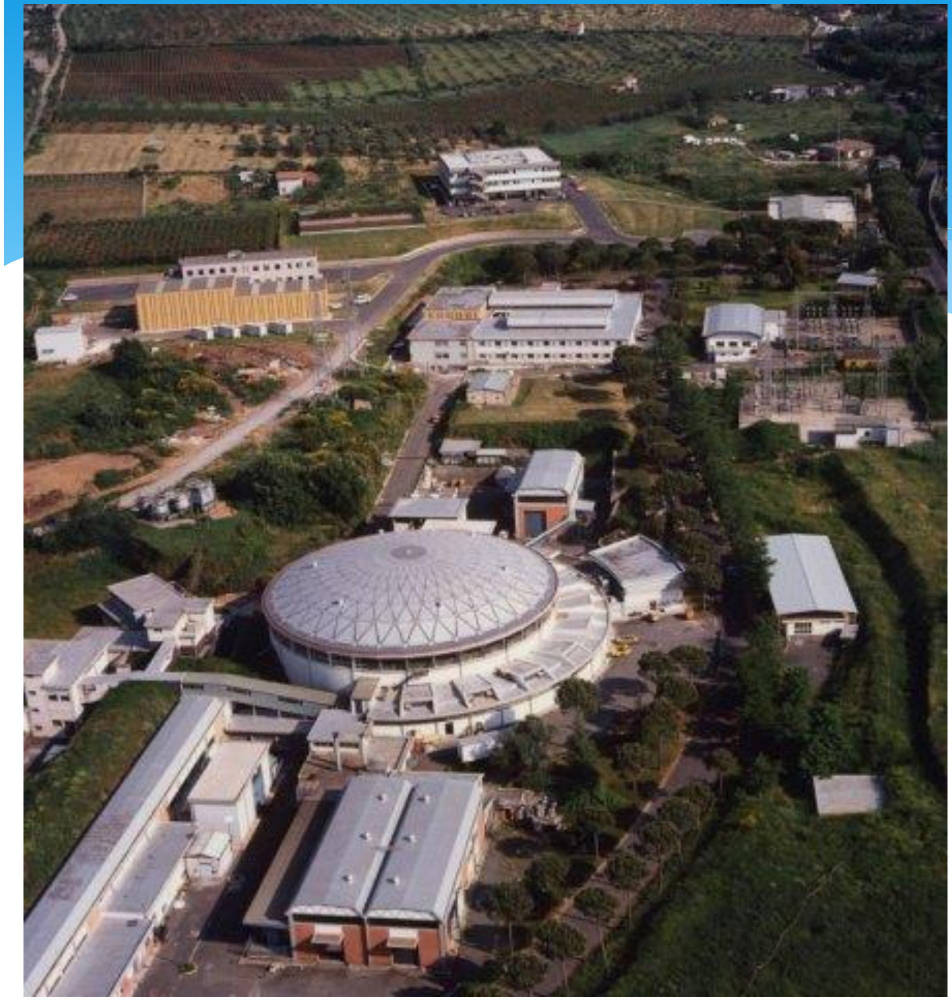
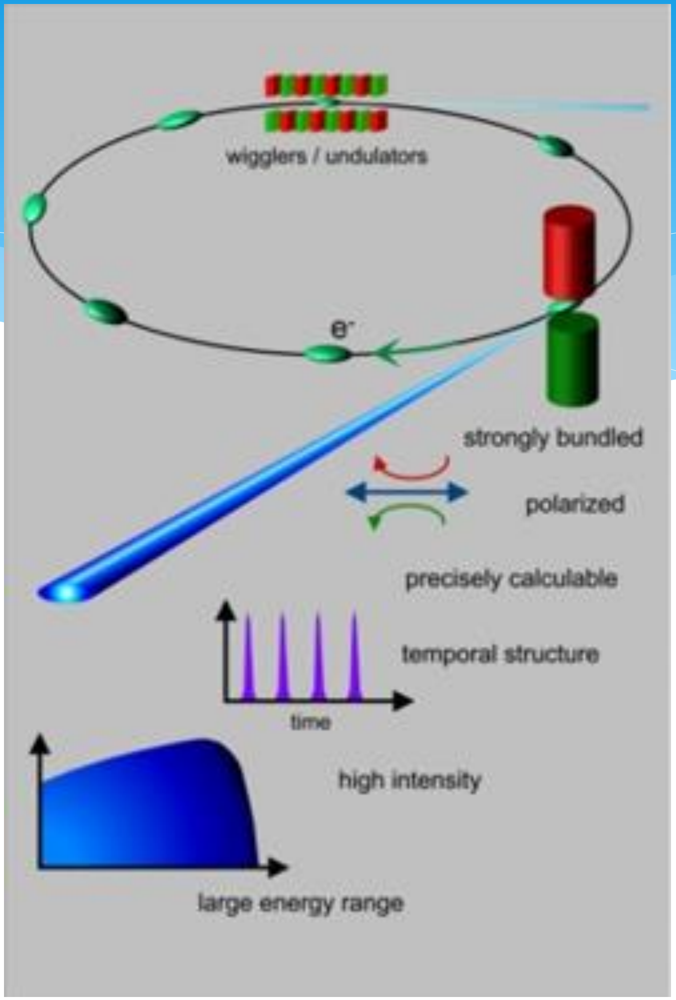


Fig. 1: Advantages of the e-Synchrotron radiation source

Critical energy

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





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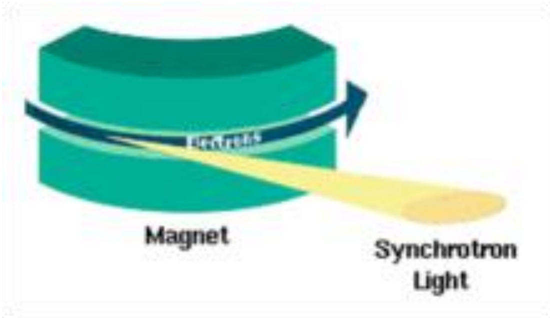
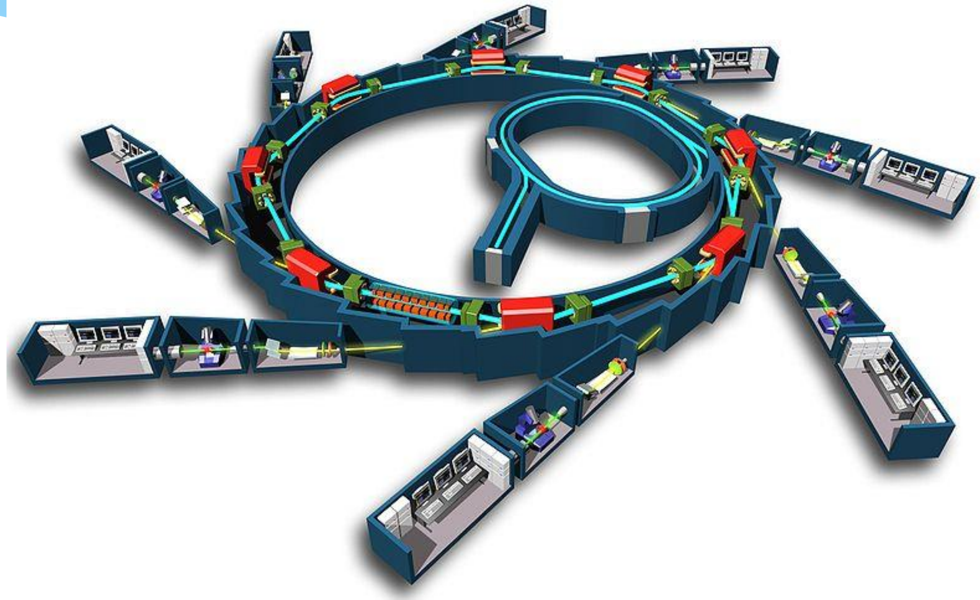
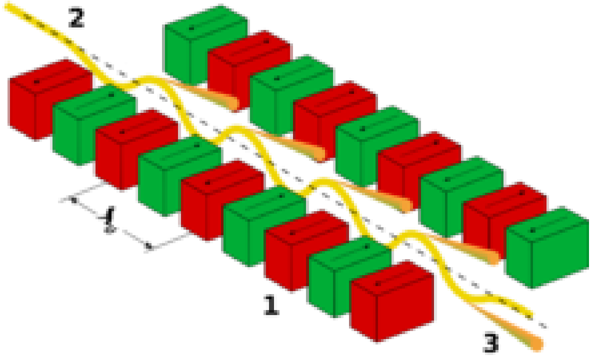
The beamlines





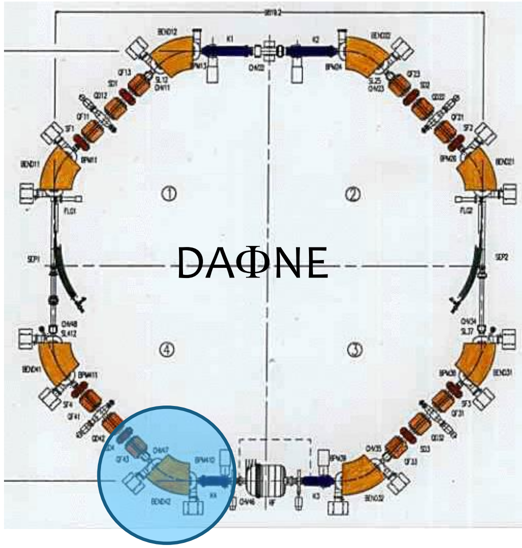


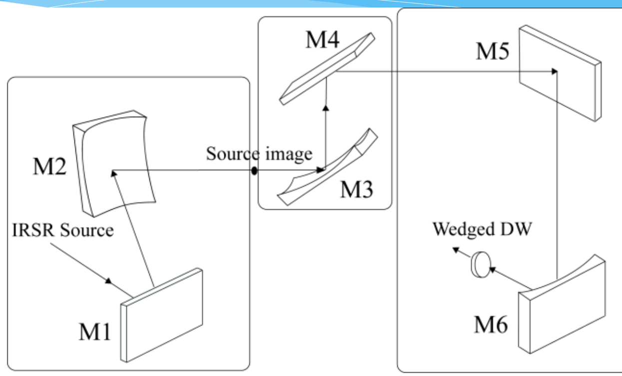
The IR SINBAD beamline

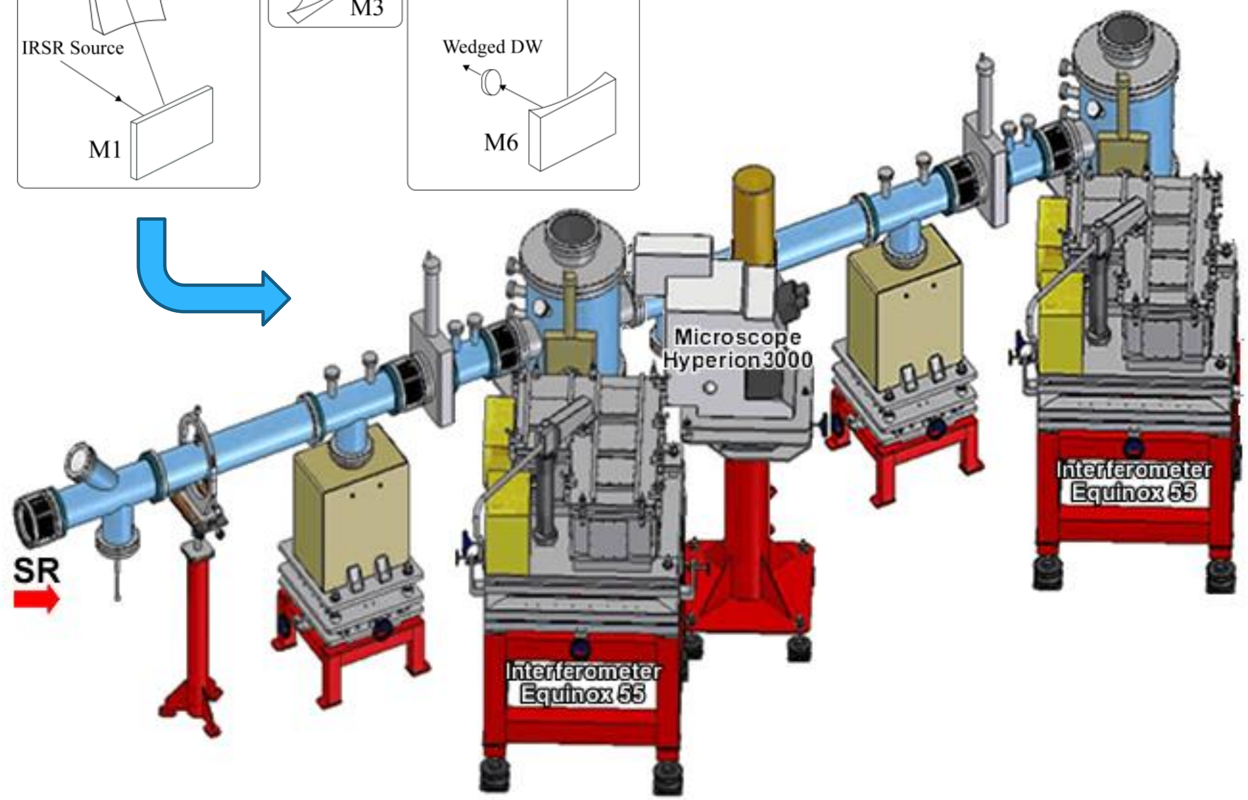
Infrared domain

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

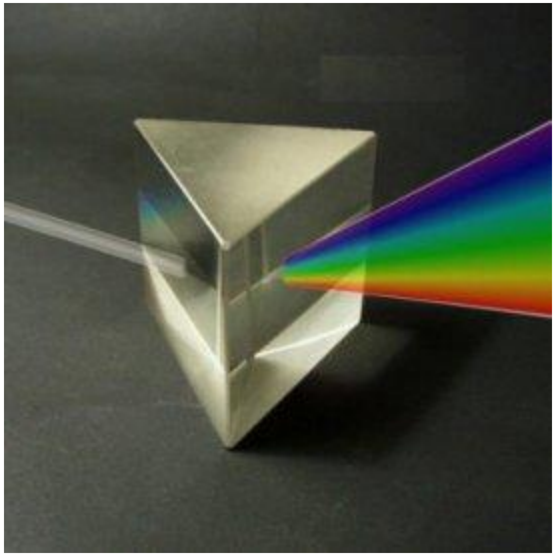
1.24meV to 1.24 eV

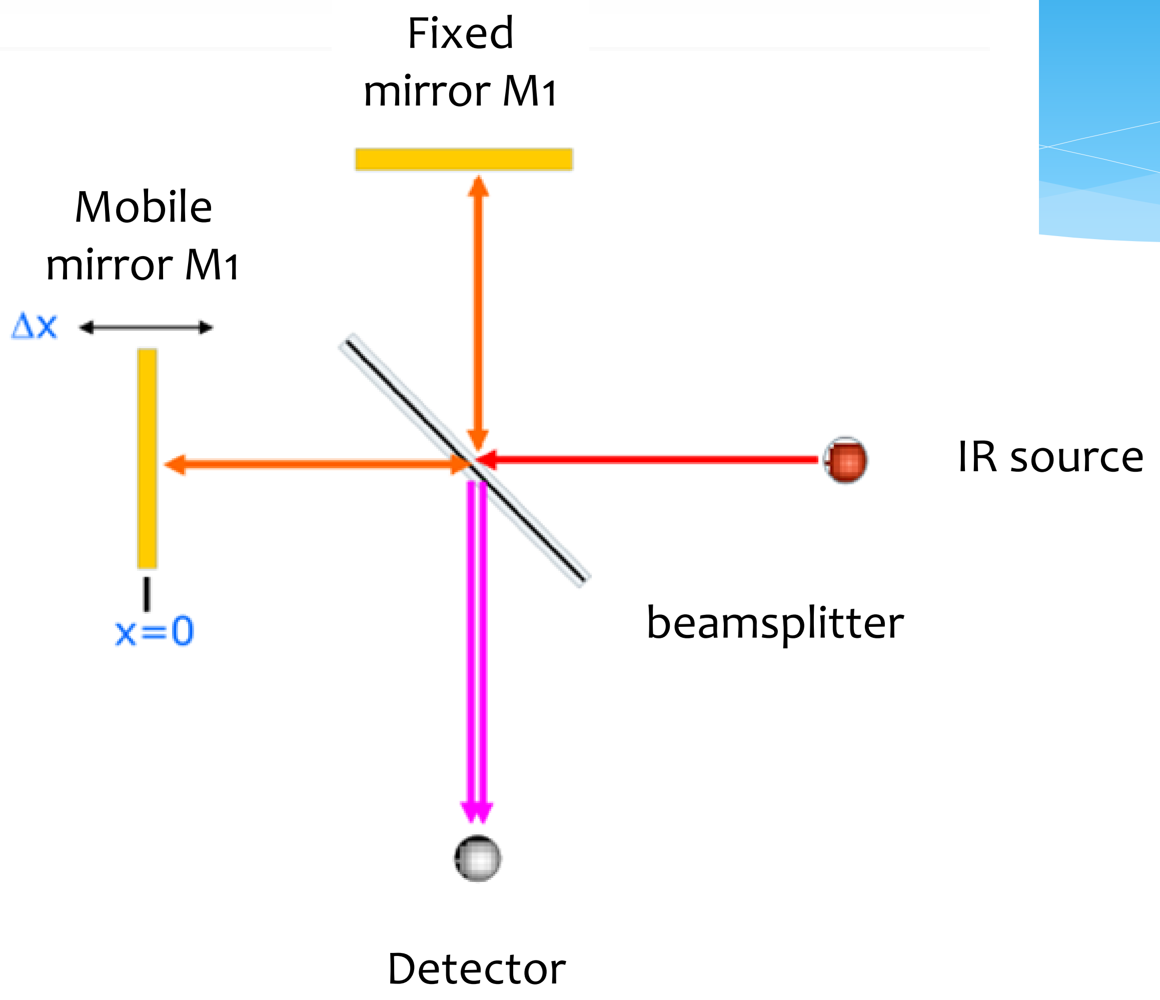






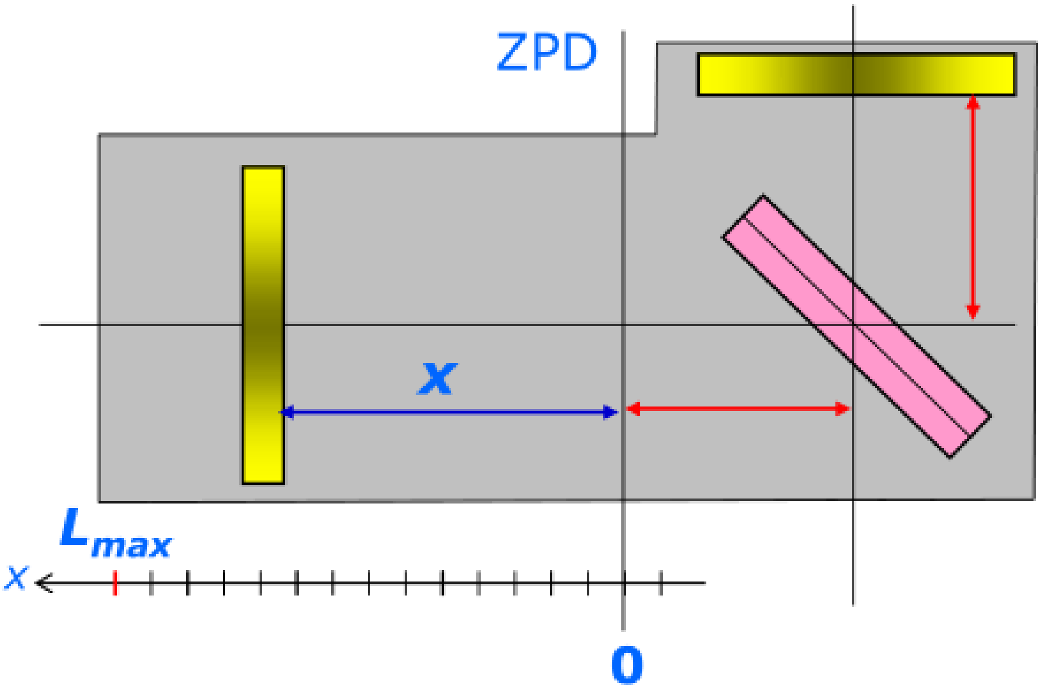
Michelson interferometer





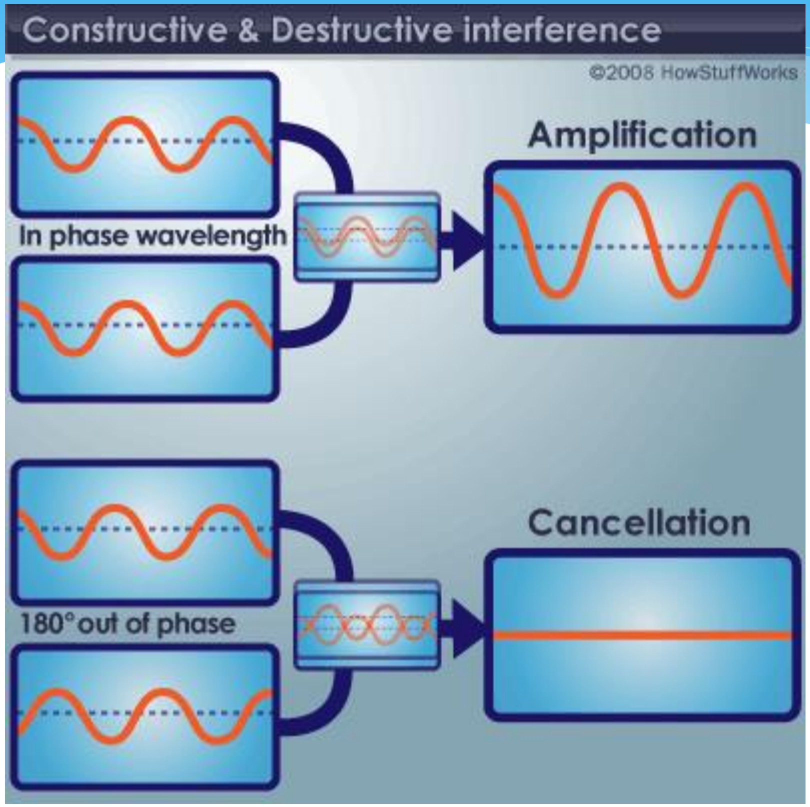
Fixed
mirror M1
Mobile
mirror M1
Δx
x=0
IR source
beamsplitter
Detector

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:

$$2x = 2vt$$

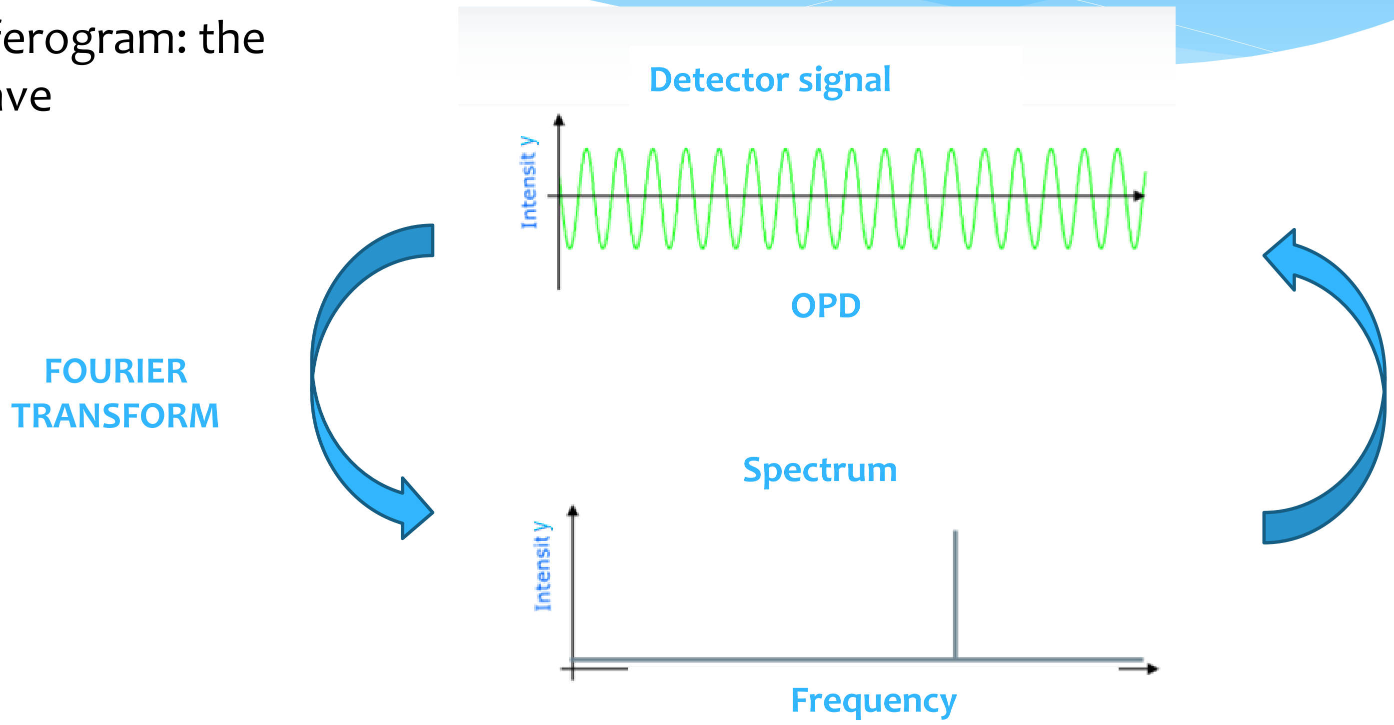


OPD= $2n\frac{\lambda}{2}$ $(n = 0, \pm 1, \pm 2, \ldots)$

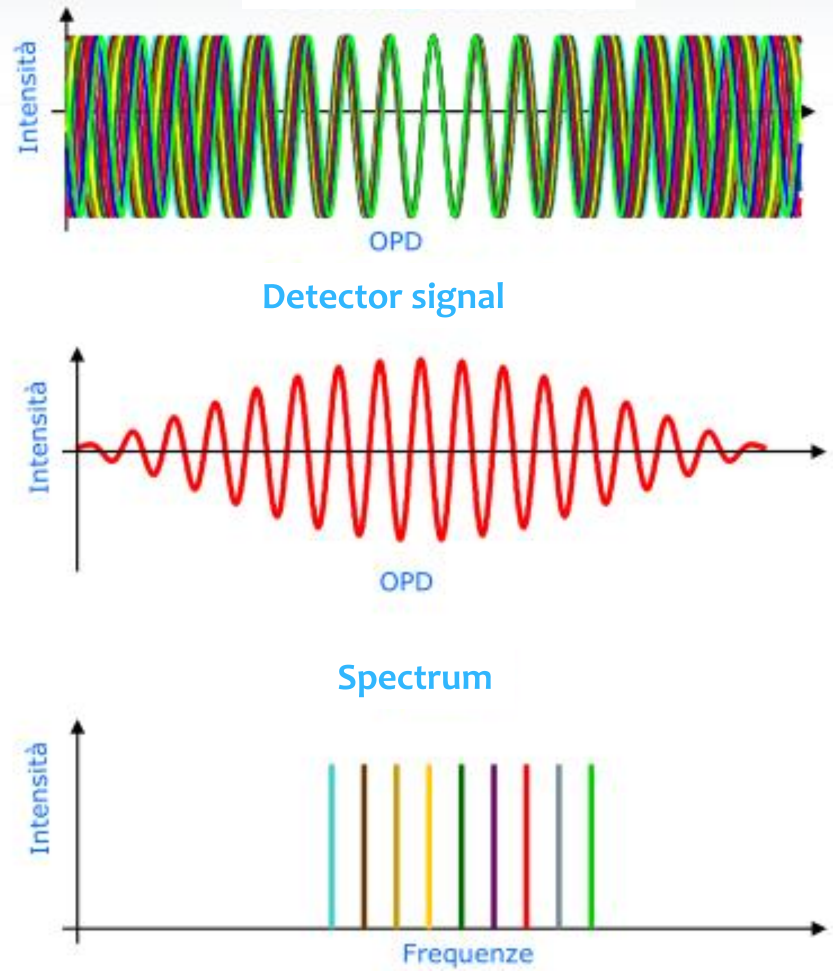
OPD= $(2n+1)\frac{\lambda}{2}$ $(n = 0, \pm 1, \pm 2, \ldots)$

The Fourier transform

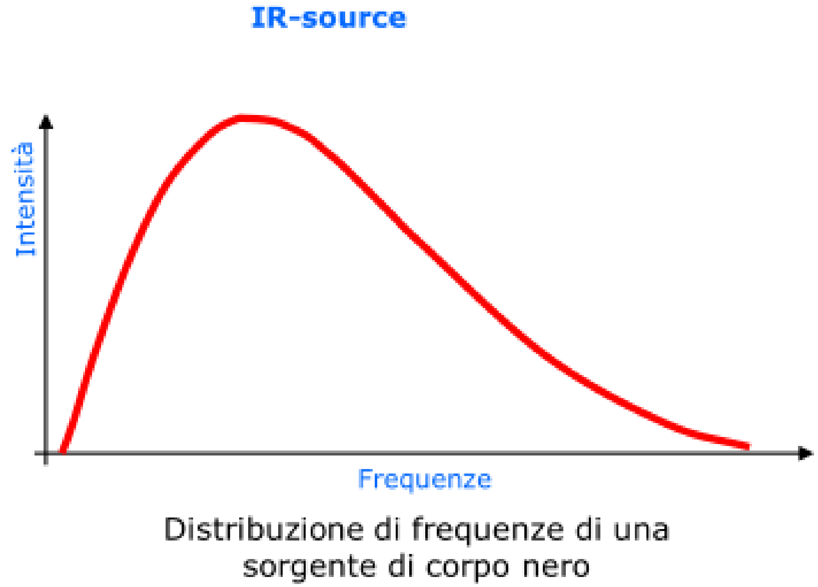
Origin of the interferogram: the momocromatic wave

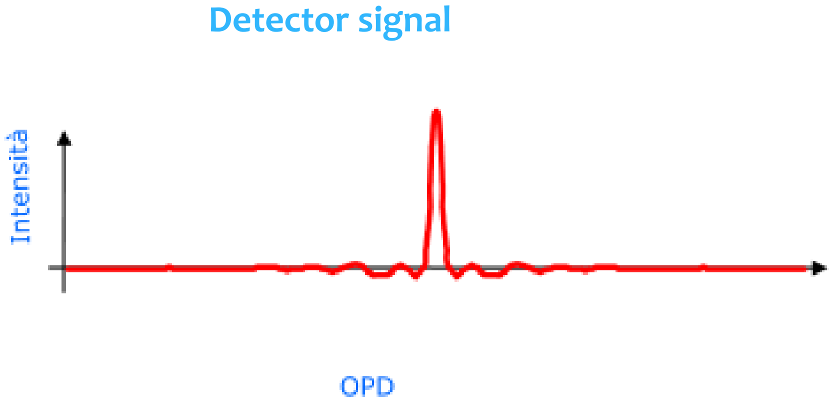


Origin of the interferogram: the policromatic wave (disccrete frequencies)



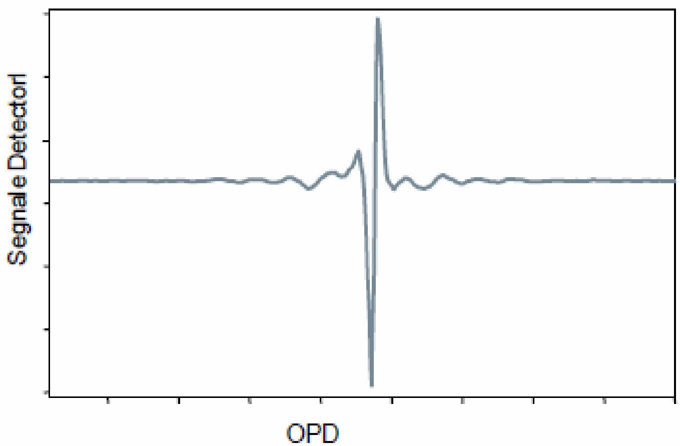
Origin of the interferogram: the policromatic wave (continuous frequencies)

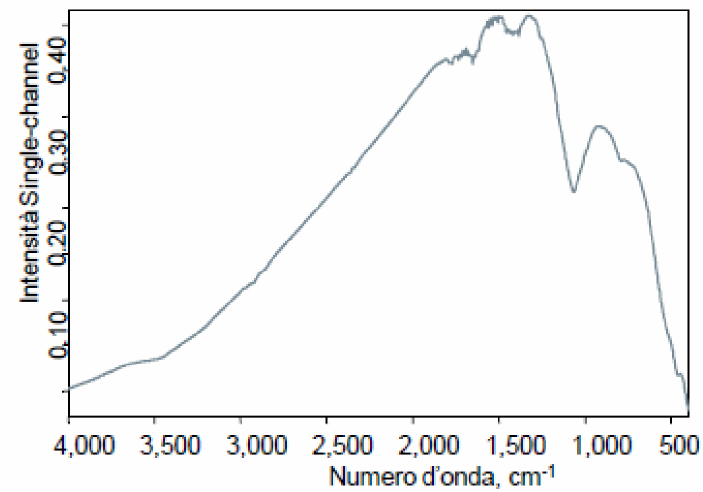




Interferogram → FT → Spectrum

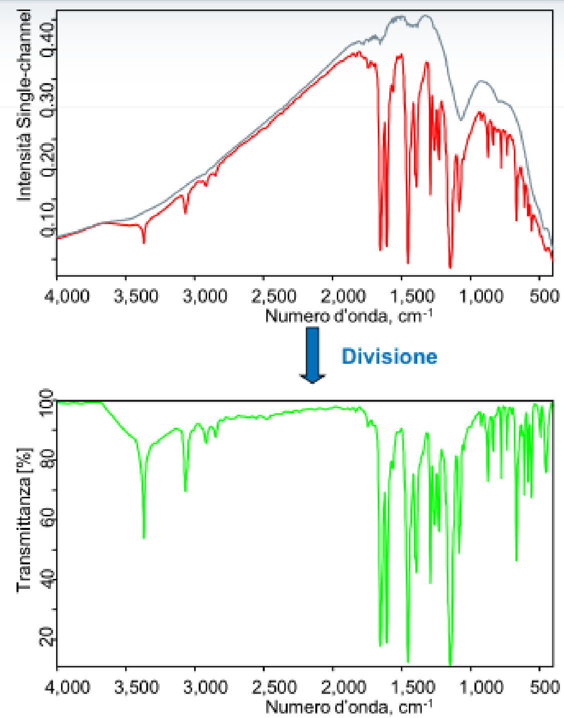
Spectrum → IFT → Interferogram





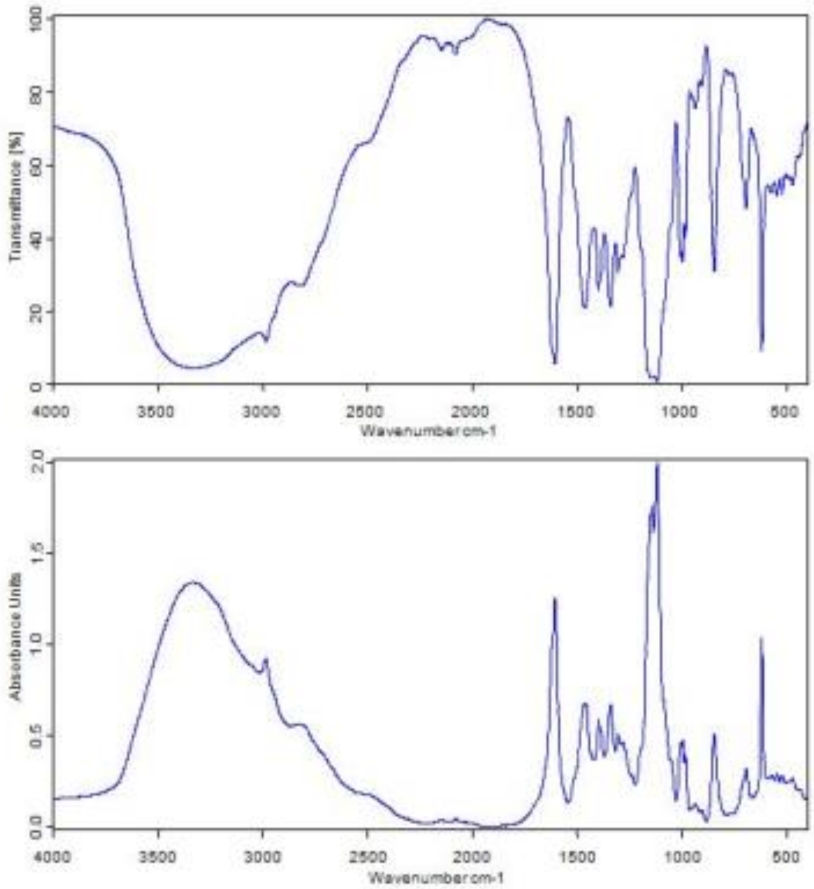
$$S(\nu) = \int_{-\infty}^{\infty} I(x) e^{i2\pi\nu x} dx$$

Measuring an IR spectrum



TRANSMITTANCE

T(ν) = SSC/RSC



ABSORBANCE

A = -Log T

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:

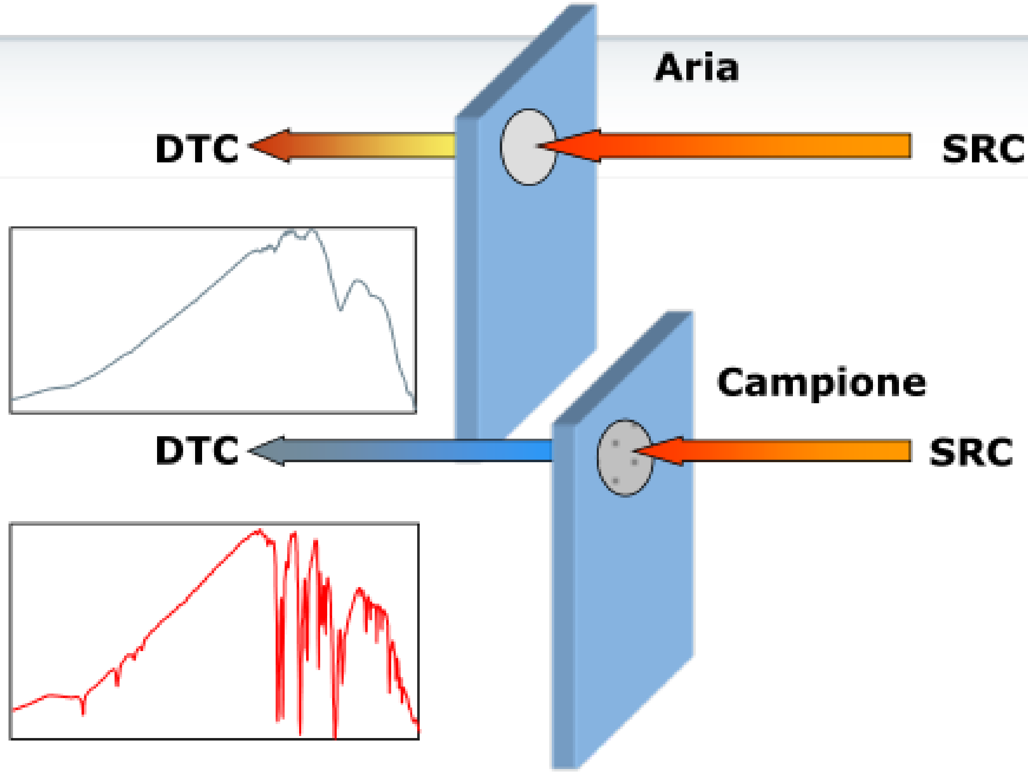
* Transmission (liquids, powders, thin sections)
* Specular reflection (crystals, polished sections)
* Diffuse reflectance (powders)
* Attenuated Total Reflection (ATR) (thick samples, non reflecting surfaces)

Transmission
KBr powder pellets

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

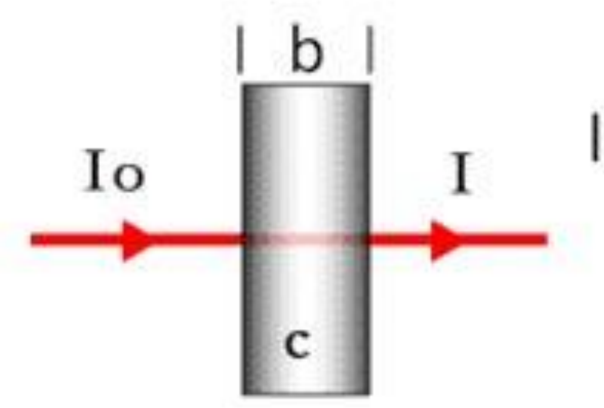
- Background (I_0)

- Sample (I)



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

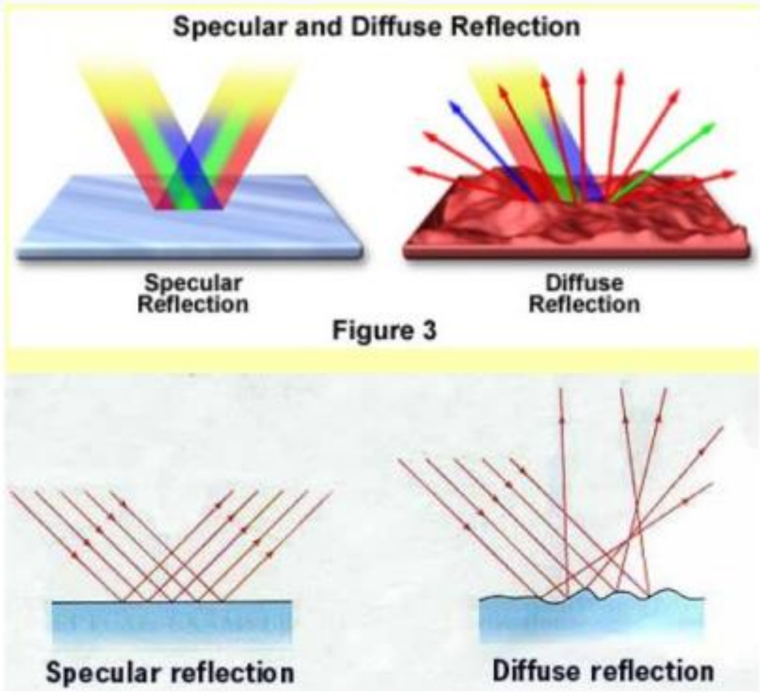
Beer-Lambert law
$A = \log I_0/I = \varepsilon\, C\, b$



$$\log I_0 / I = \varepsilon \cdot C \cdot b$$

Absorbance is proportional to the concentration

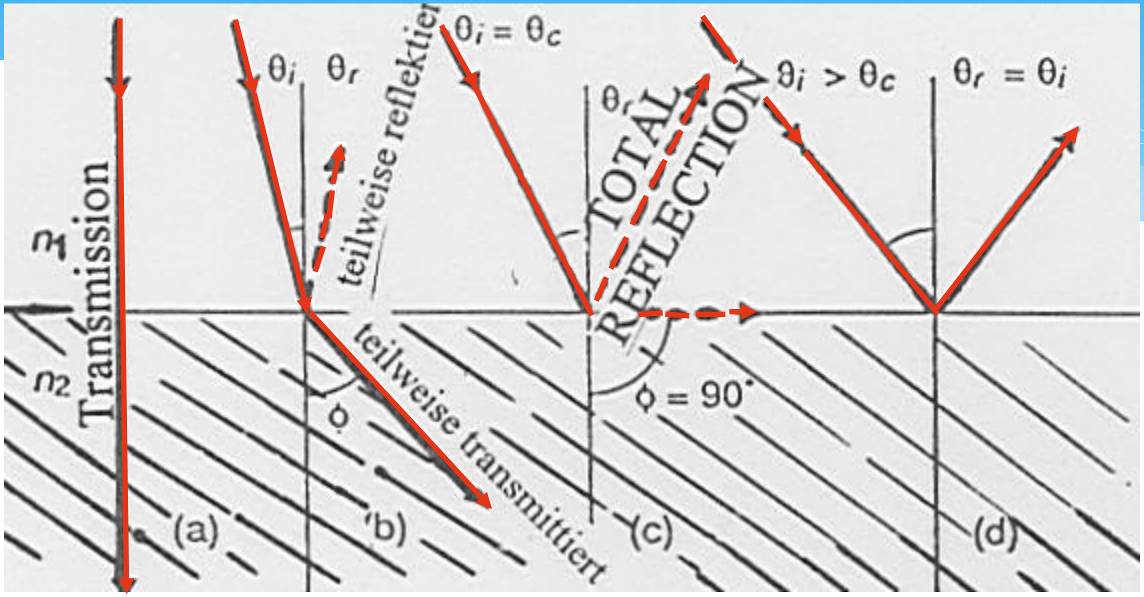
Reflection spectroscopy



Preparation of the surface – polishing ☹
Thick samples ☺

Attenuated Total Reflection (ATR)

Principles of Attenuated Total Reflection spectroscopy (ATR)



Crystal n_1

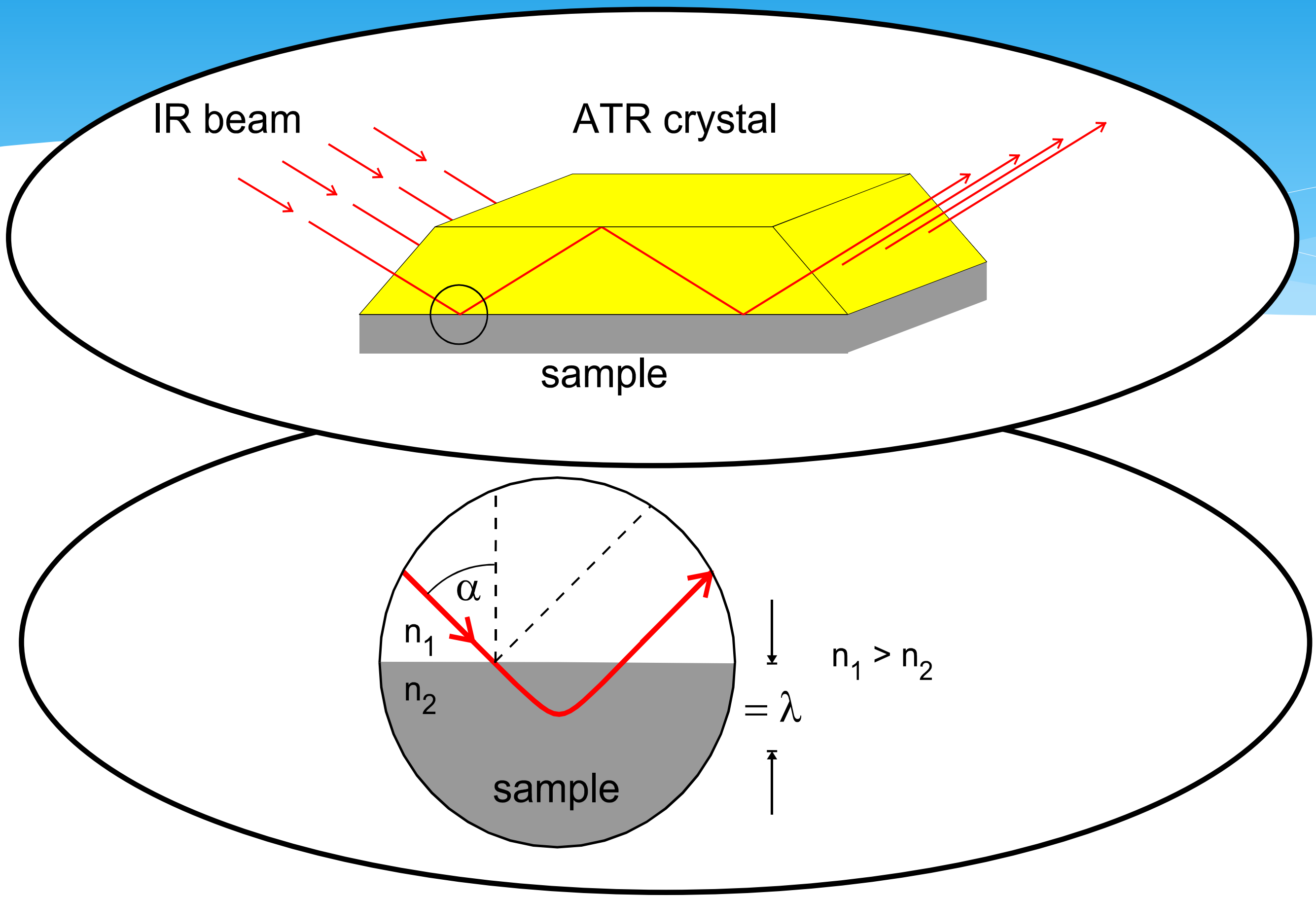
Sample n_2

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)

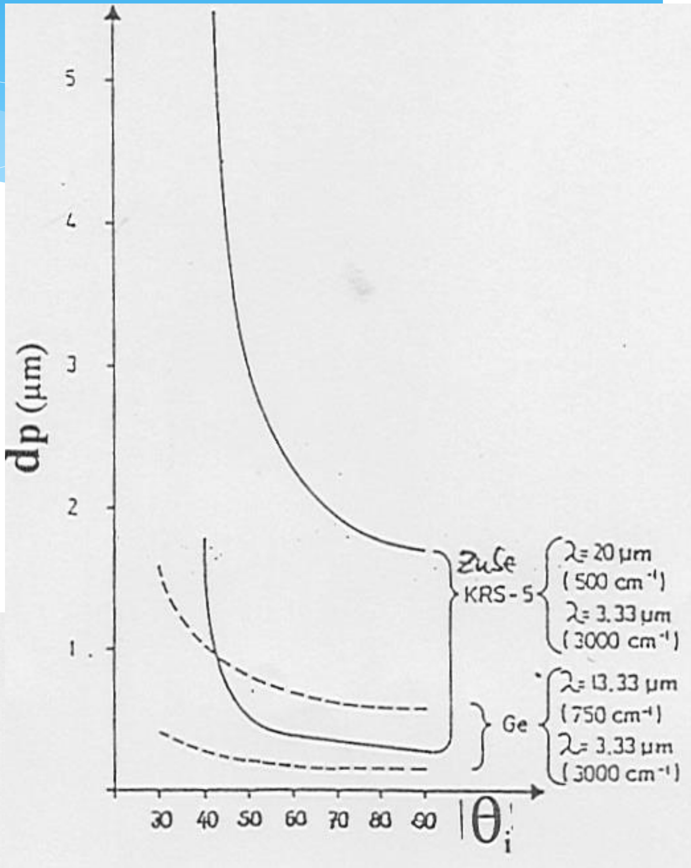

IR beam
ATR crystal
sample
α
n_1
n_2
sample
$= \lambda$
$n_1 > n_2$

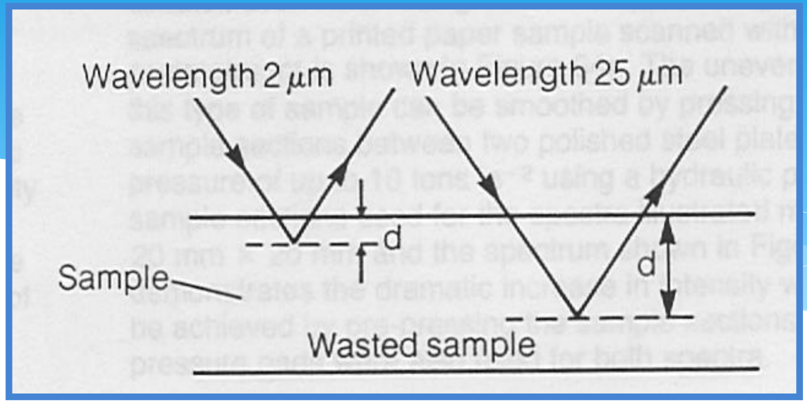
Penetration depth

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

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

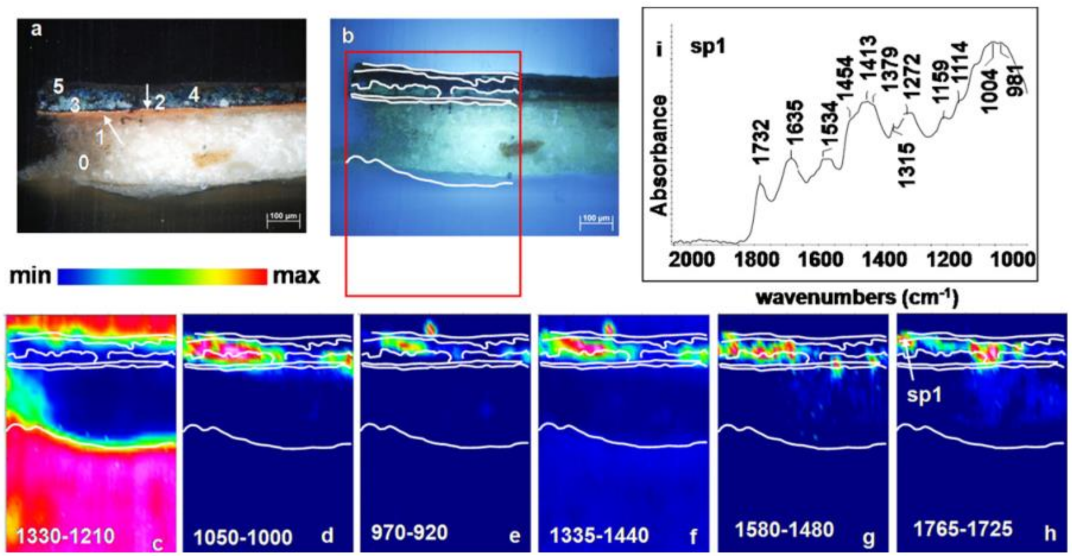
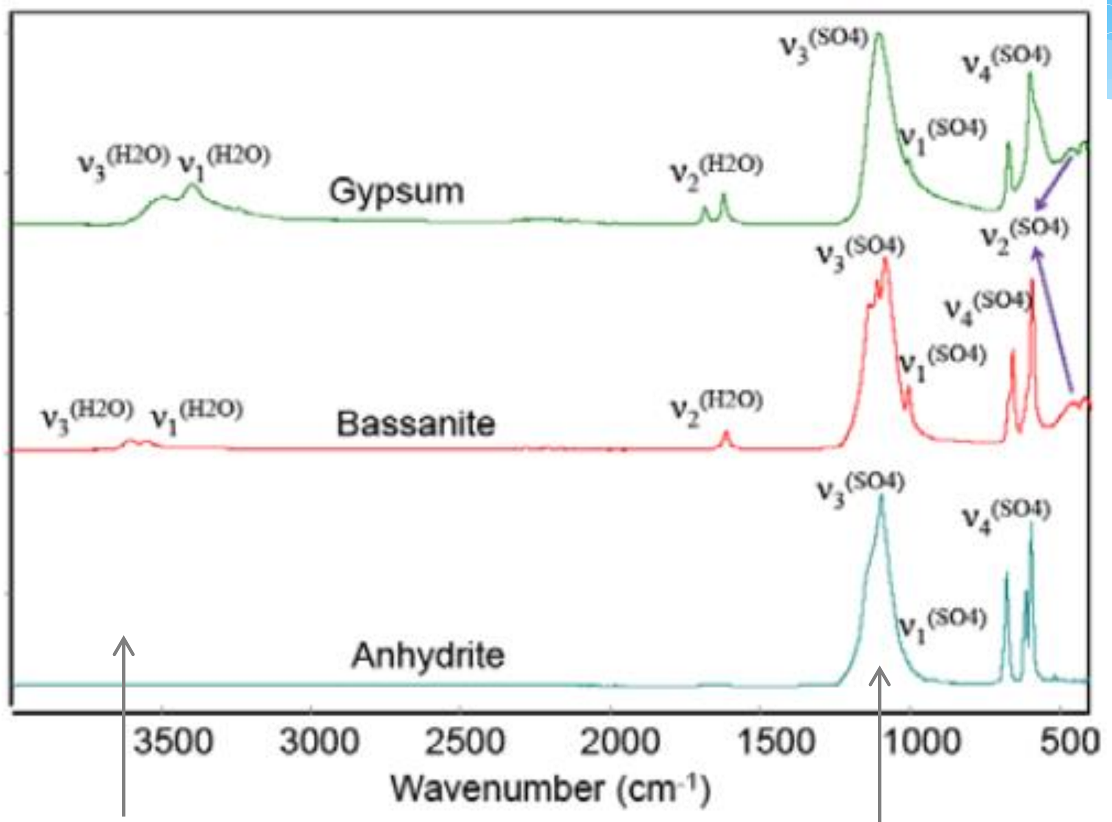


Fig. 2. Detail of a cross-section from the polychrome sculpture (Fe2): (a) visible microscopic image; (b) image of sample under ultraviolet light; (c) FT-IR image created by plotting the integrated absorbance of the embedding resin band between 1330 and 1200 cm^{-1}; (d) FT-IR image showing the distribution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



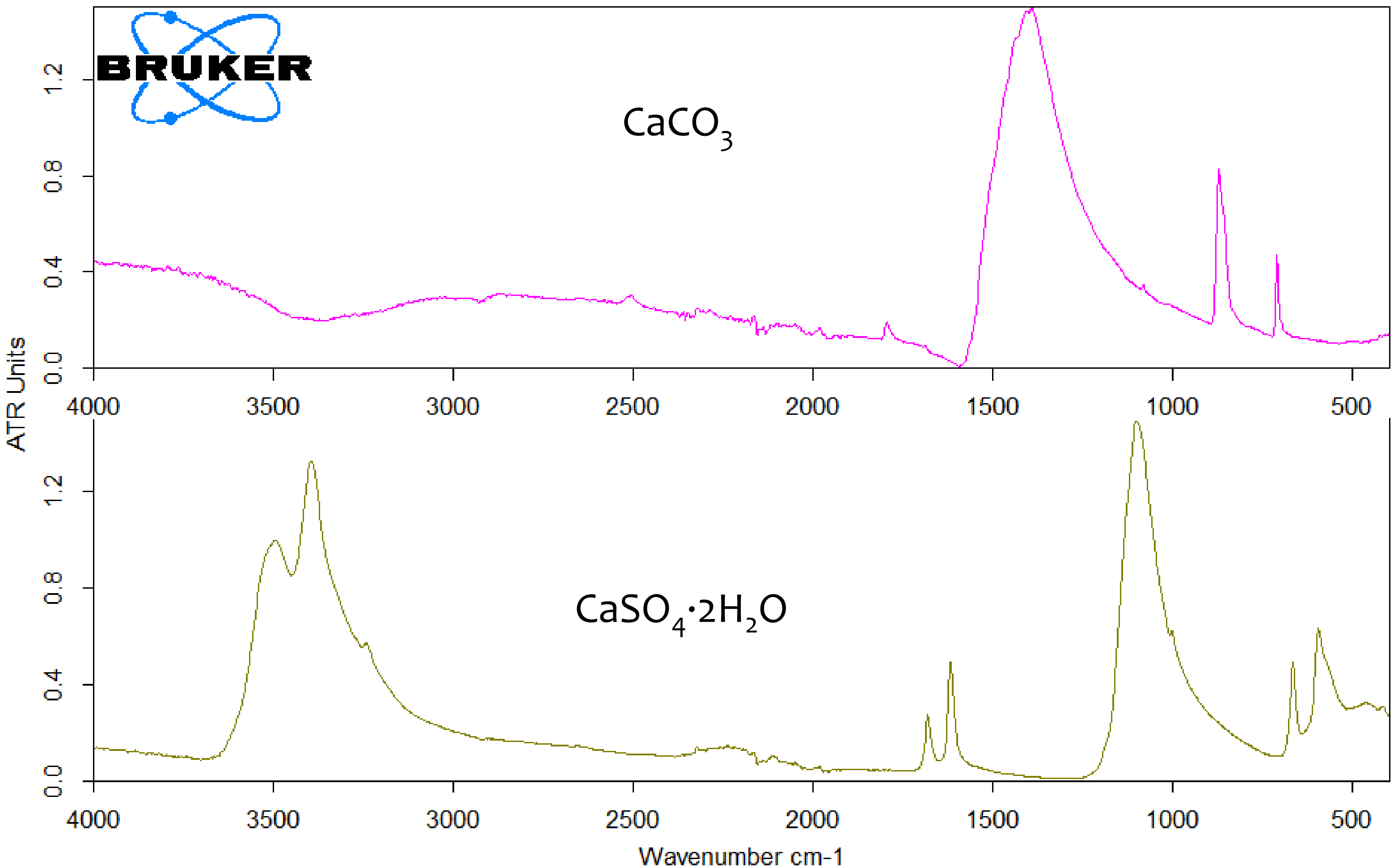
$CaSO_4{\cdot}2H_2O$

$CaSO_4.0.5H_2O$

$CaSO_4$

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



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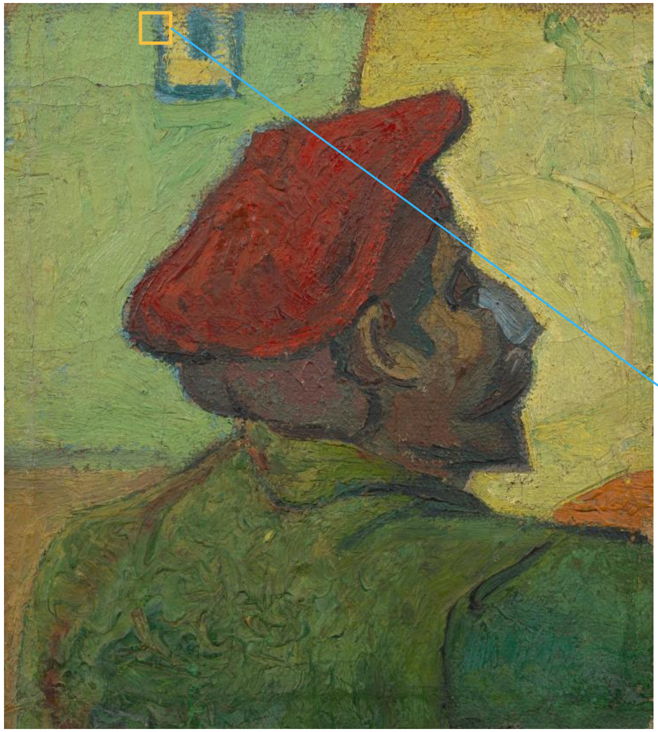
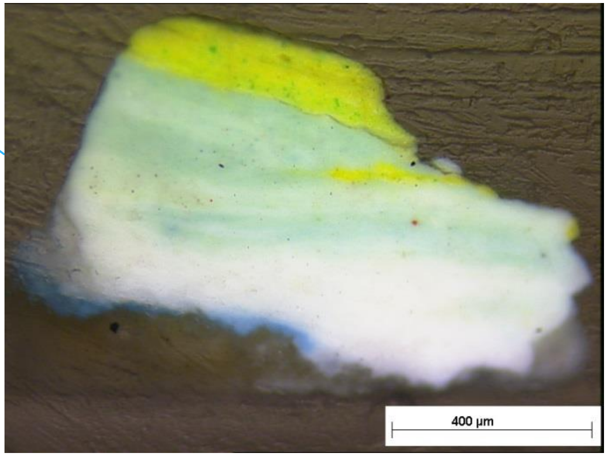
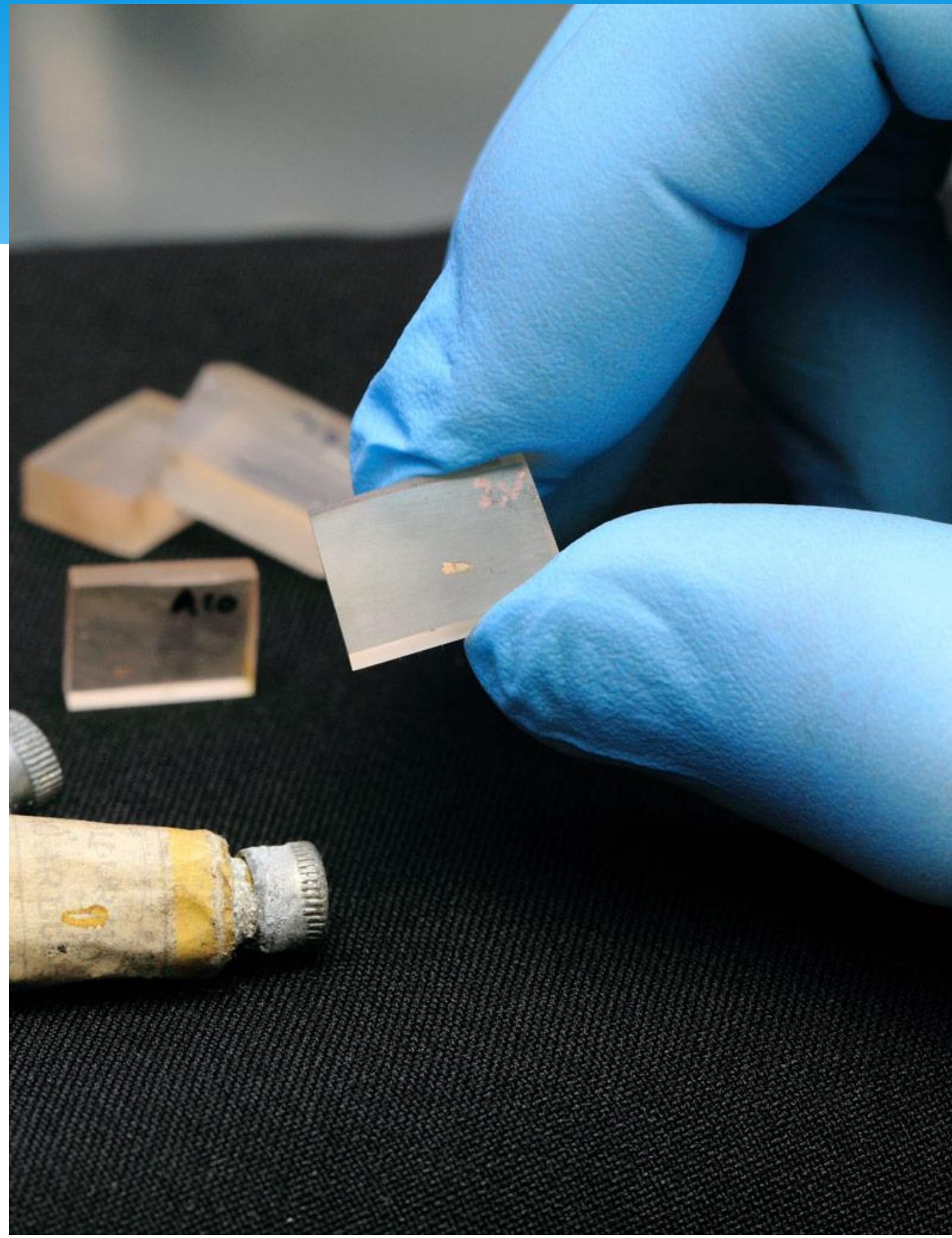
Page 1/1

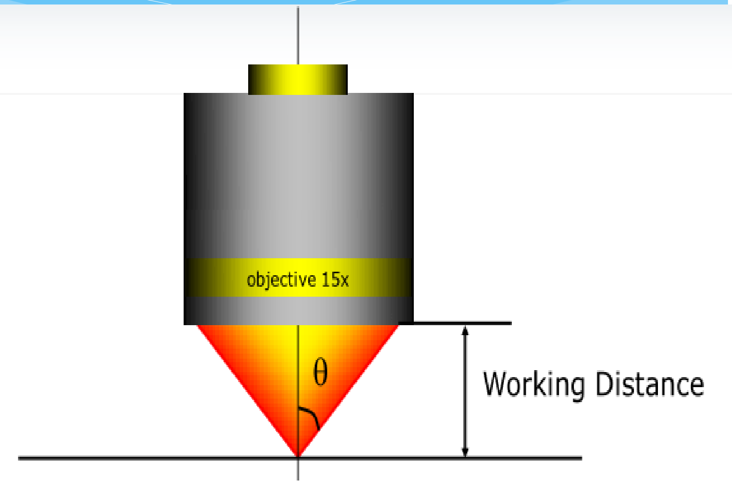
What if the sample is VERY small?







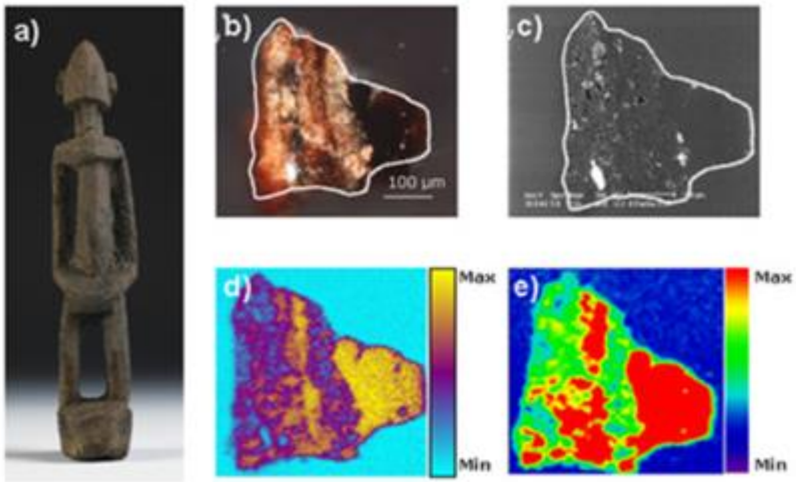
Microscopy and Imaging



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

The IR microscope is essentially a beam condenser

FTIR imaging



Study of the patina sample from a Dogon statuette:

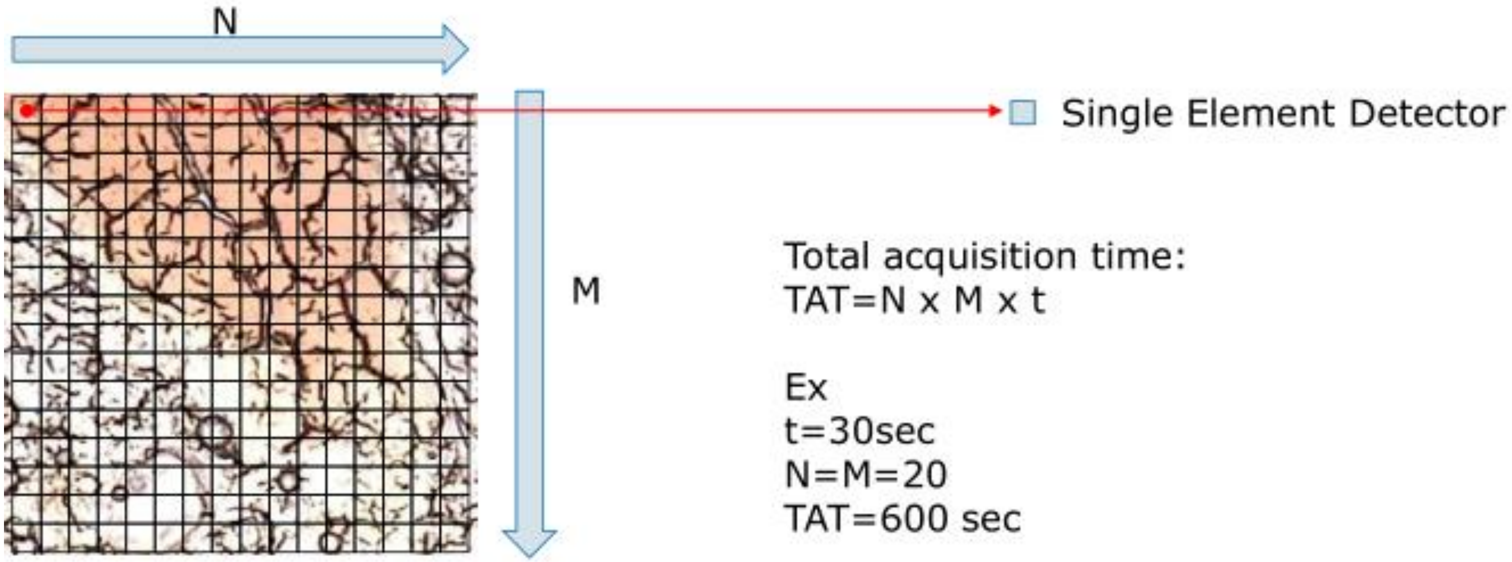
a) Photograph of the object, Quai Branly Museum, inventory no 71.1935.105.169, (copyright C2RMF, D. Vigears);
b) Dark field microscopic view of the cross-section of the sample;
c) Backscattered electron micrograph;
d) ToF-SIMS image of protein fragment ions;
e) SR-µFTIR image of proteins.

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

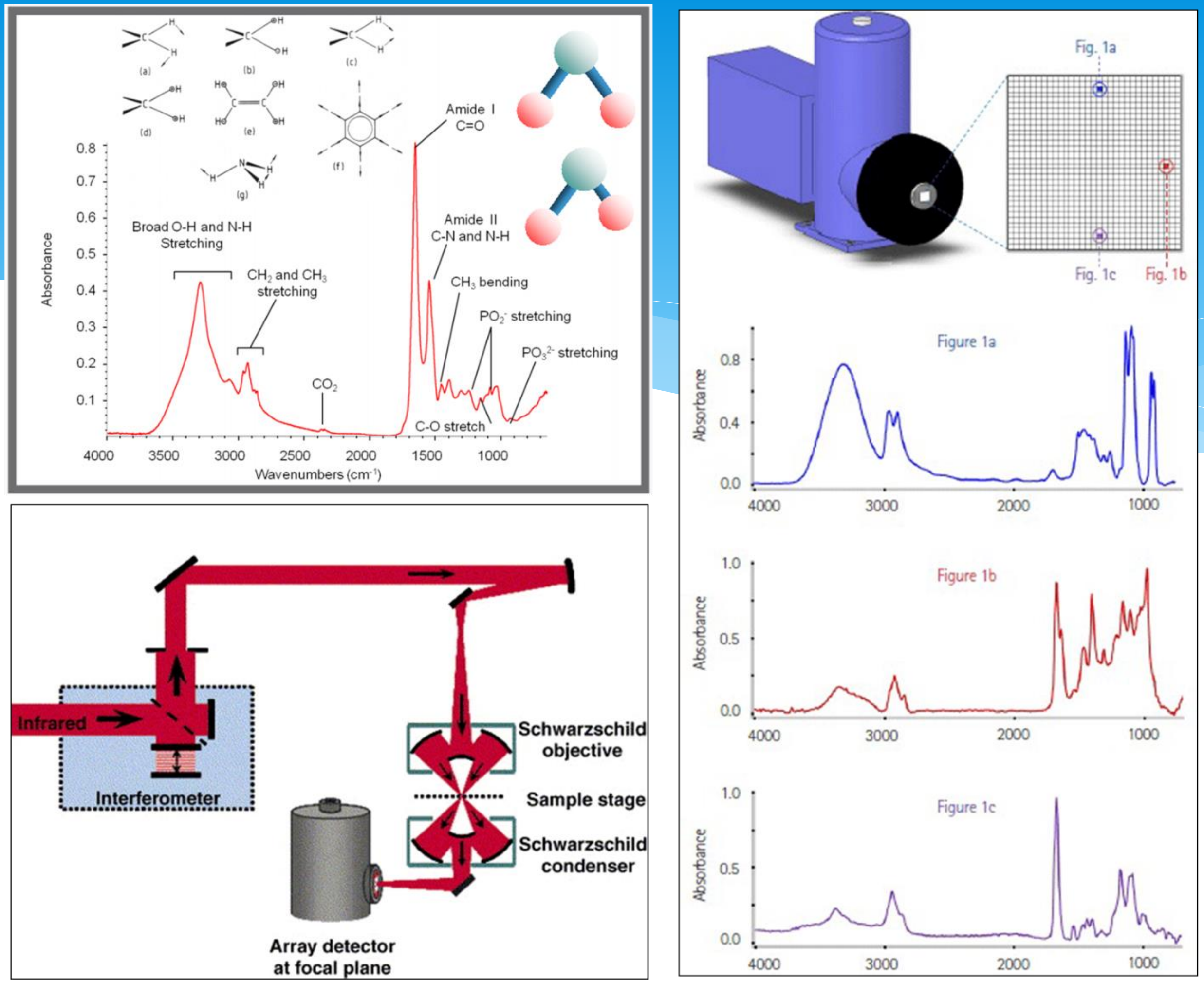
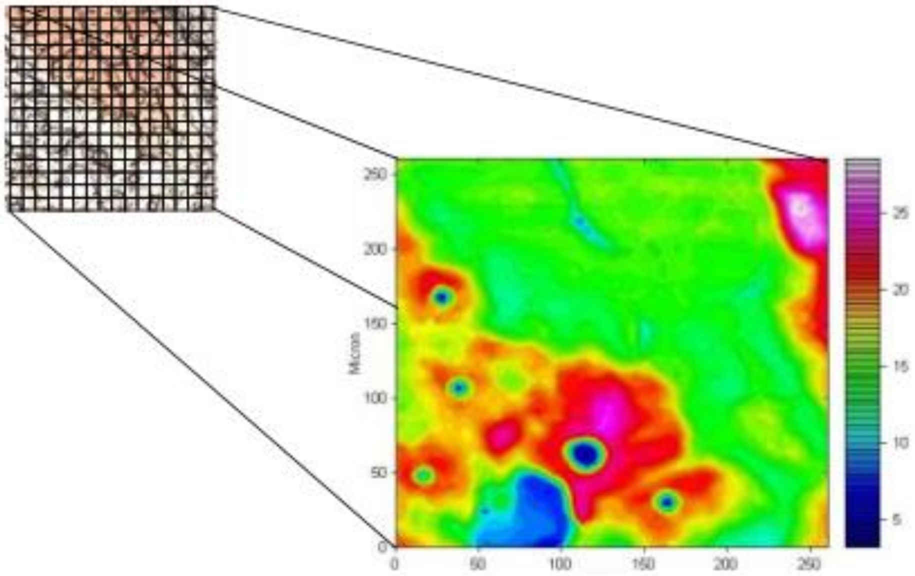


Figura 2: (a) Lo spettro IR di un composto organico mostra gli assorbimenti dovuti alle vibrazioni molecolari. (b) Schema ottico del microscopio IR accoppiato allo spettrometro ed al detector FPA. (c) Schema di funzionamento di un detector FPA.

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

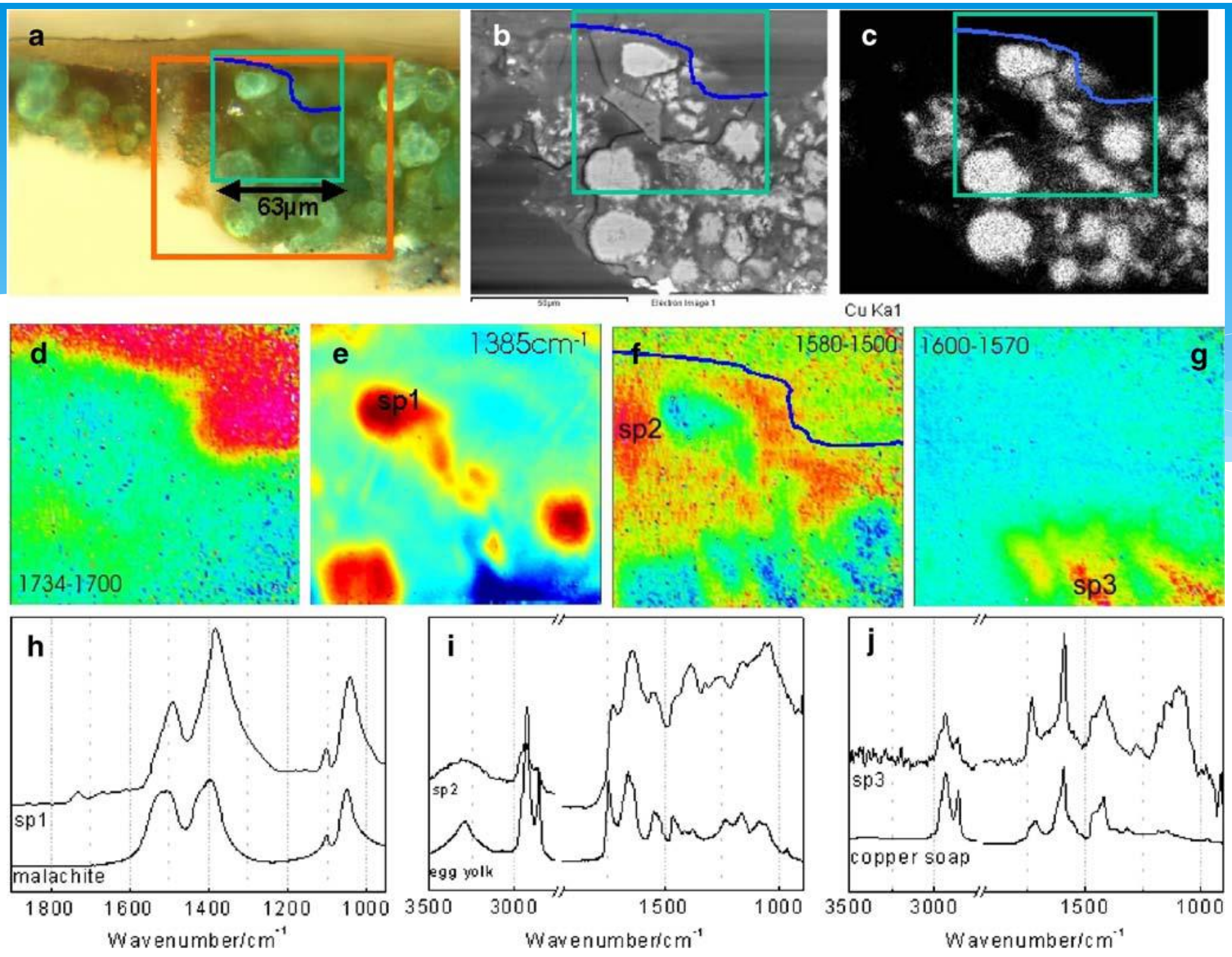


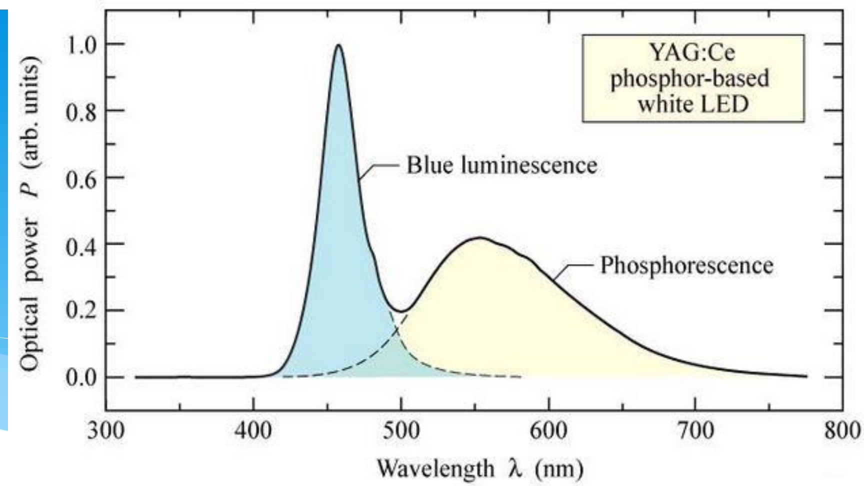
Figura 1. Sezione stratigrafica di un frammento prelevato dalla veste verde di un dipinto raffigurante la Madonna col Bambino: a) sezione stratigrafia al microscopio ottico in luce visibile; b) immagine ottenuta al microscopio elettronico (SEM); c) mappatura dell'elemento rame (Cu) eseguita mediante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

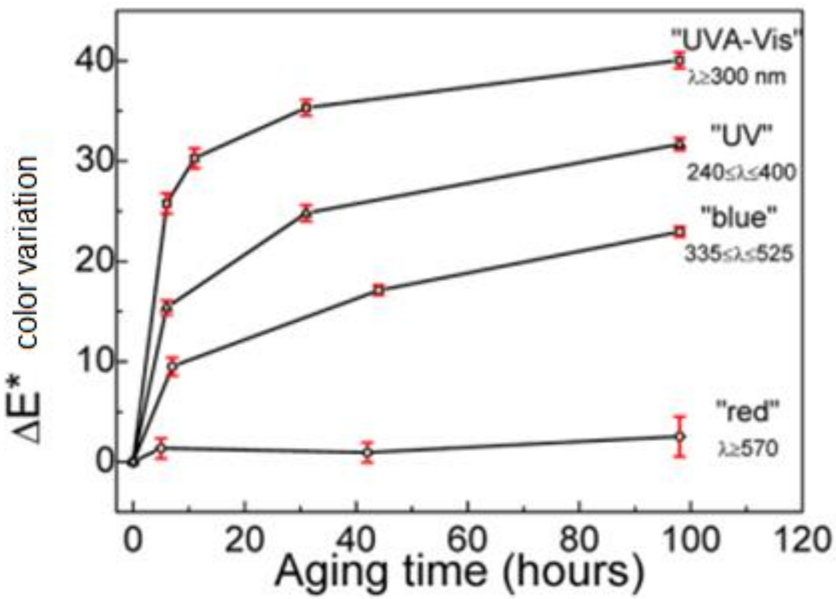
LED lights may be bad for *Van Gogh* Paintings

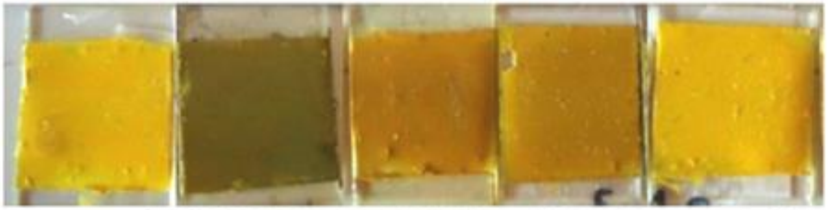
http://www.vangogh.ua.ac.be/

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







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**

$PbCrO_4$ → **$PbCr_{1-x}S_xO_4$**

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

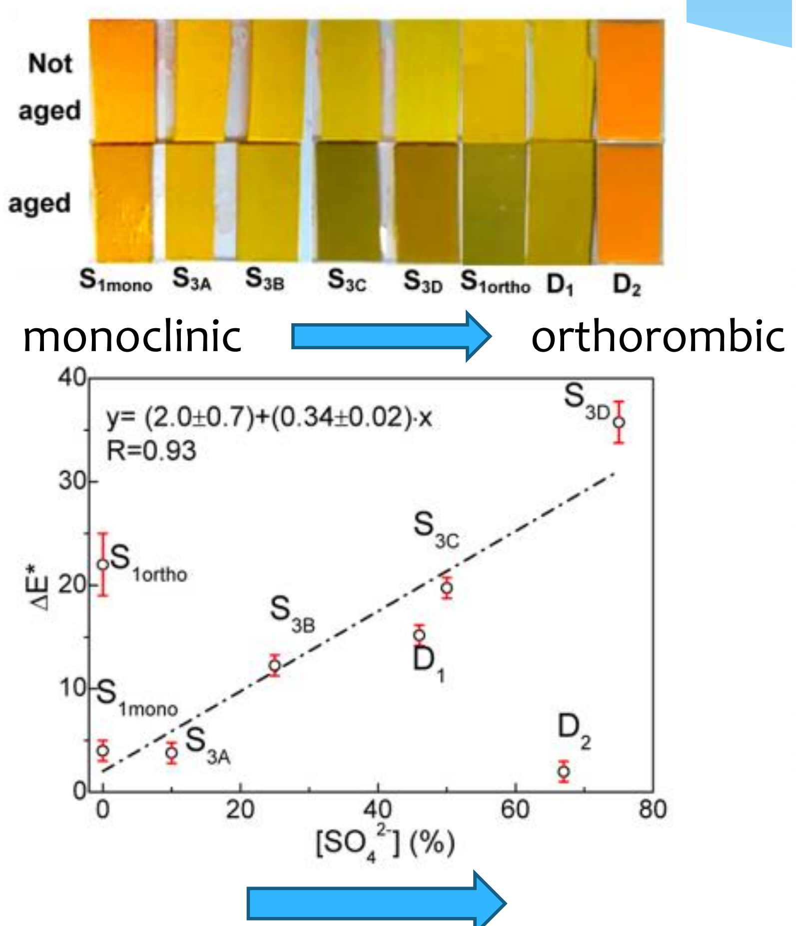
INFN Istituto Nazionale di Fisica Nucleare

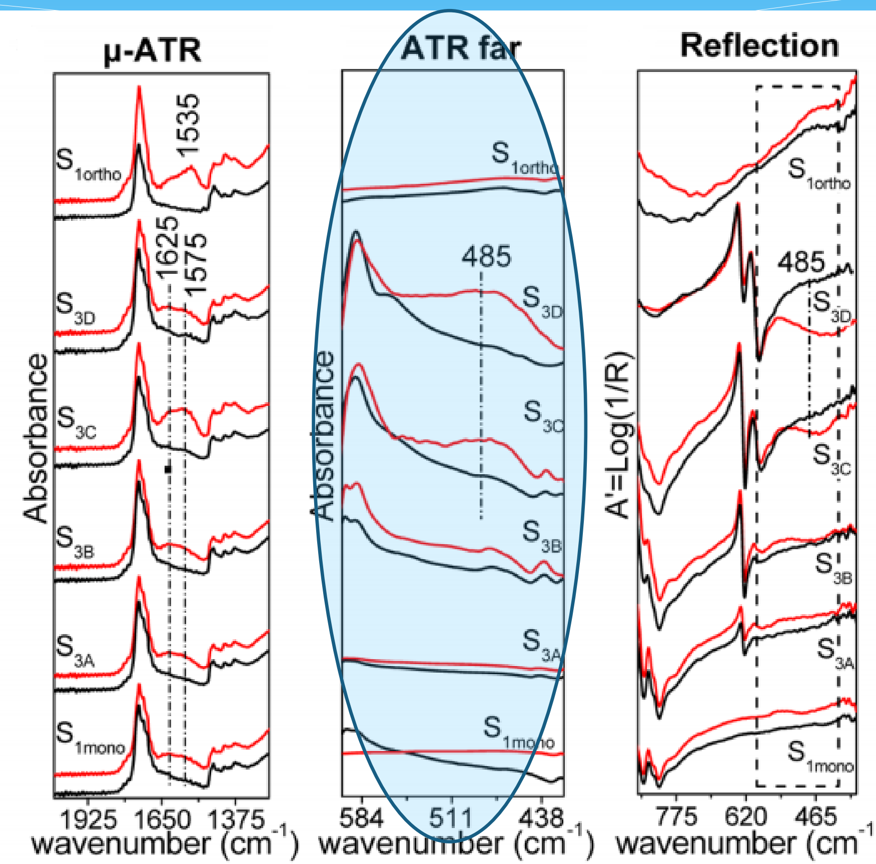
Micro-X-ray Fluorescence

What is the alteration mechanism of the chrome yellow pigments?

Micro-X-ray Absorption Near-Edge

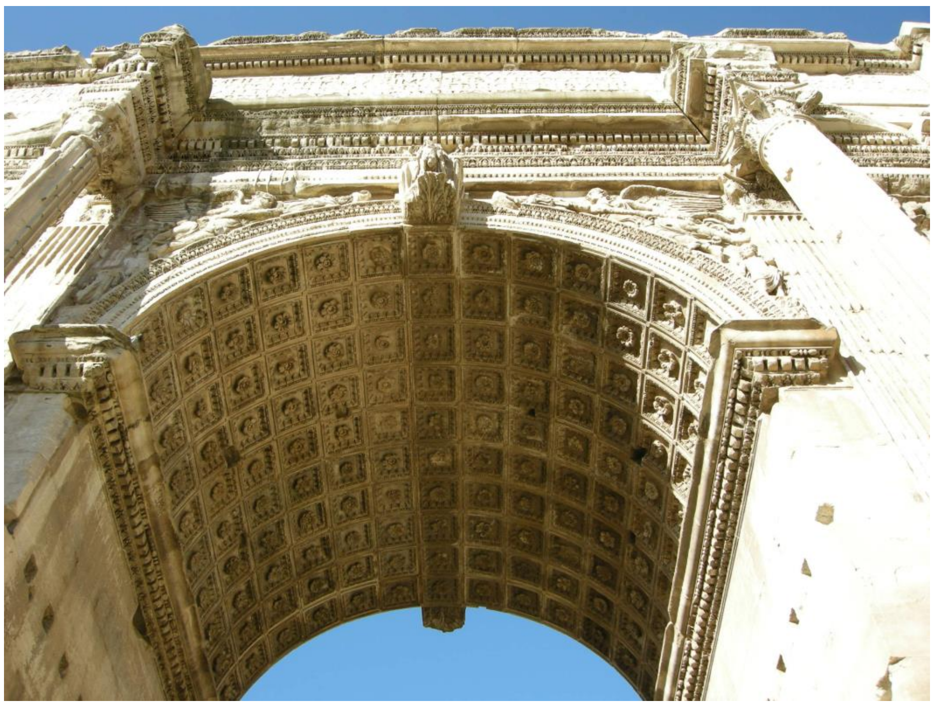
Fourier Transform Infrared Spectroscopy (FT-IR) @ LNF

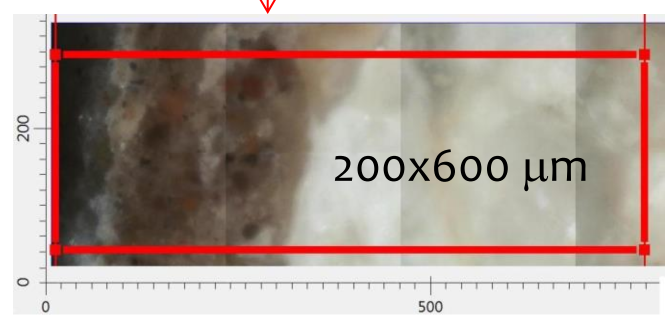




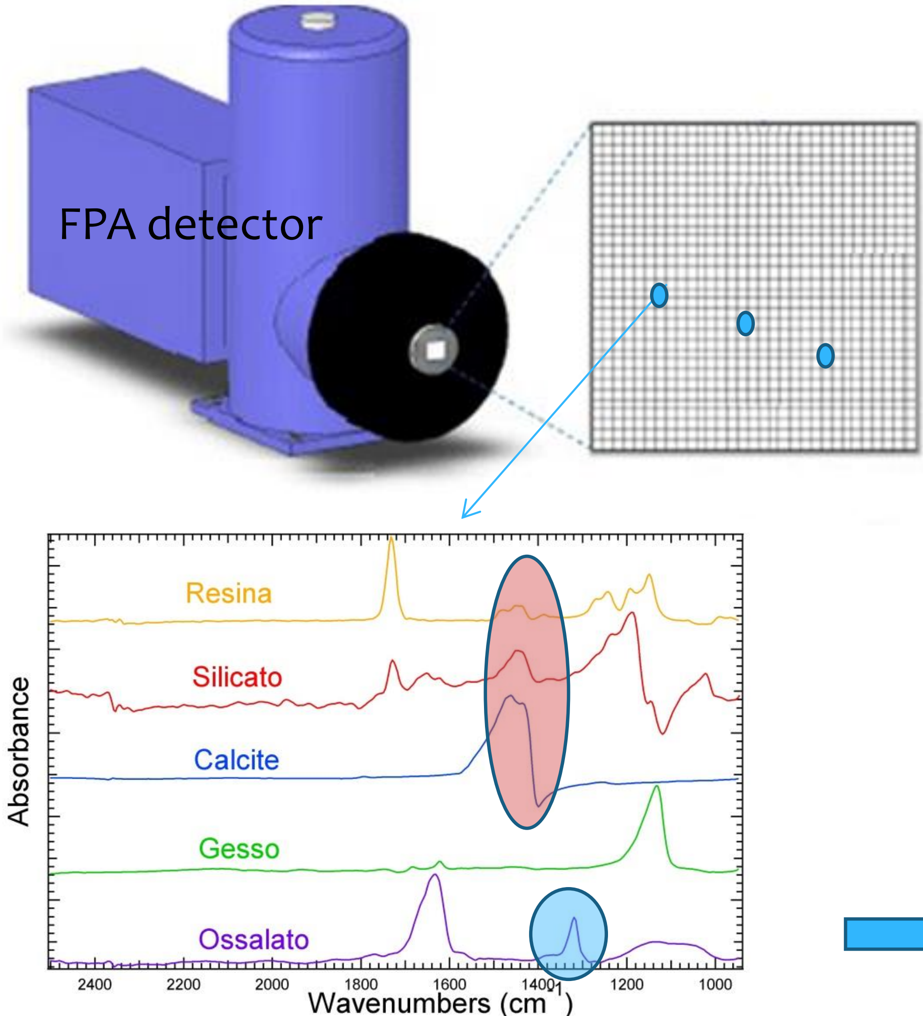
Sulphate [SO_4^{2-}] content

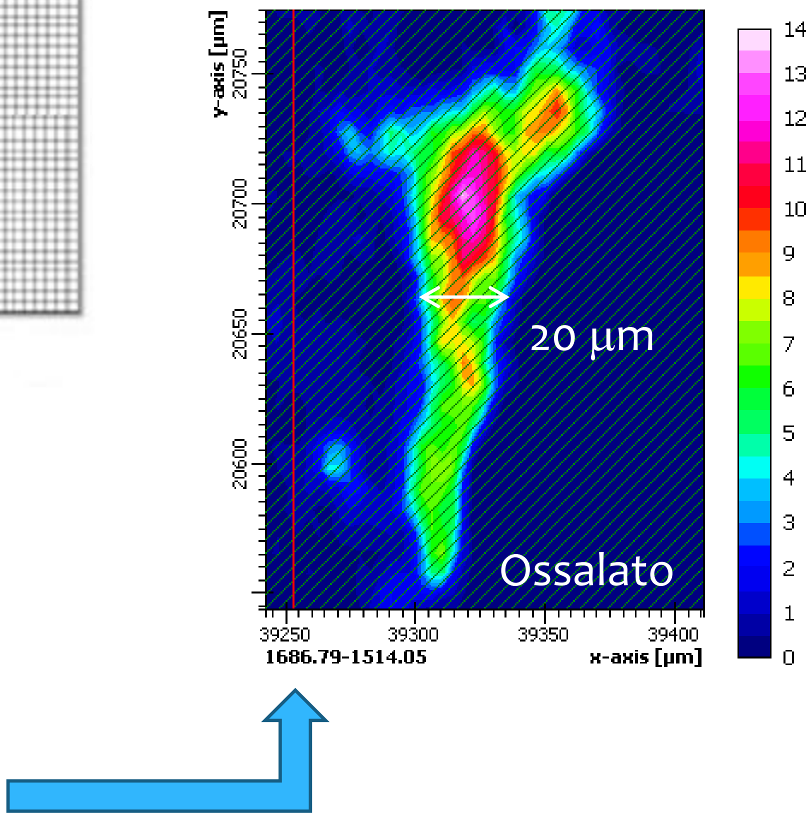
Septimius Severus's Arch degradation products



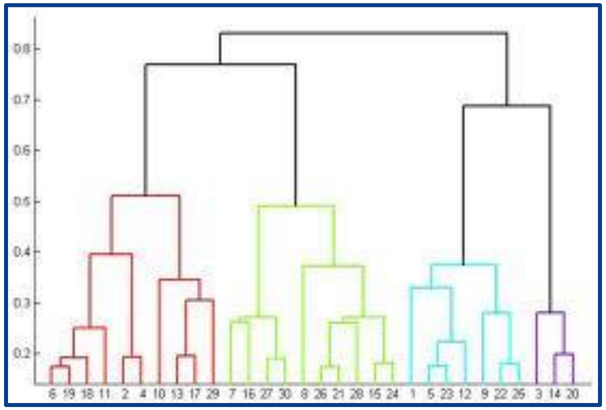


MICRO FT-IR chemical imaging

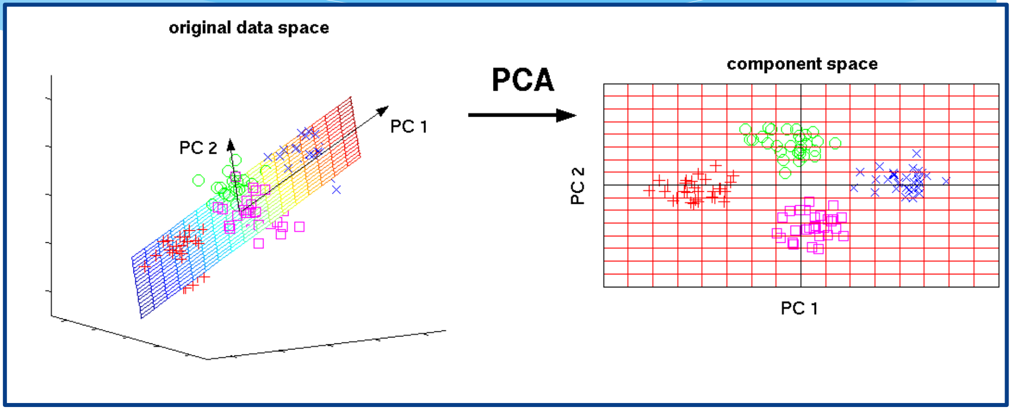




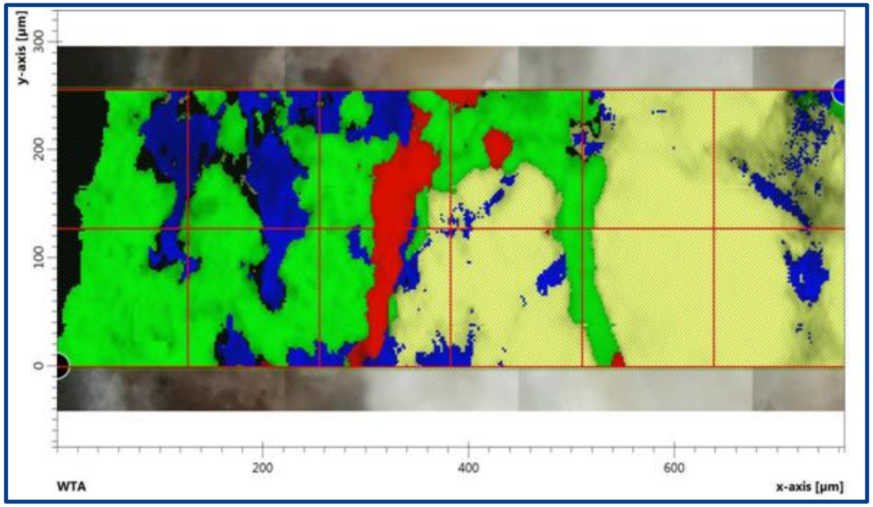
Multivariate analysis combined with FT-IR



Cluster Analysis



Principal Component Analysis



RGB map of the sample composition

Centro Conservazione e Restauro
La Venaria Reale

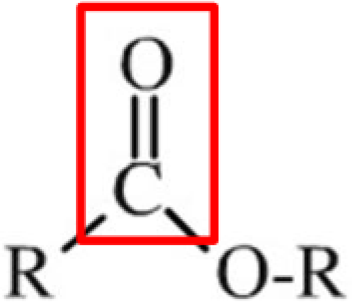
Il carbonile

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

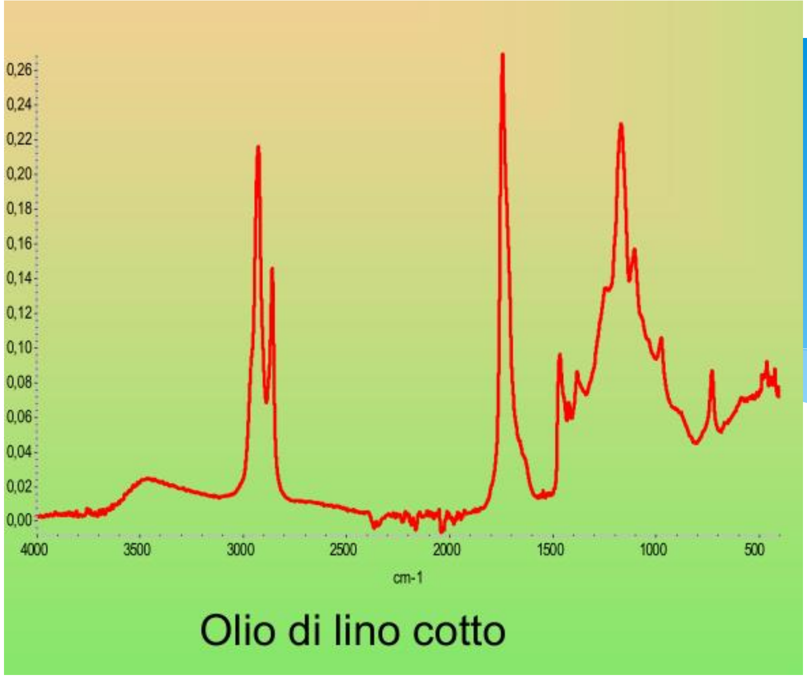
Solventi
Leganti
Vernici
Fibre

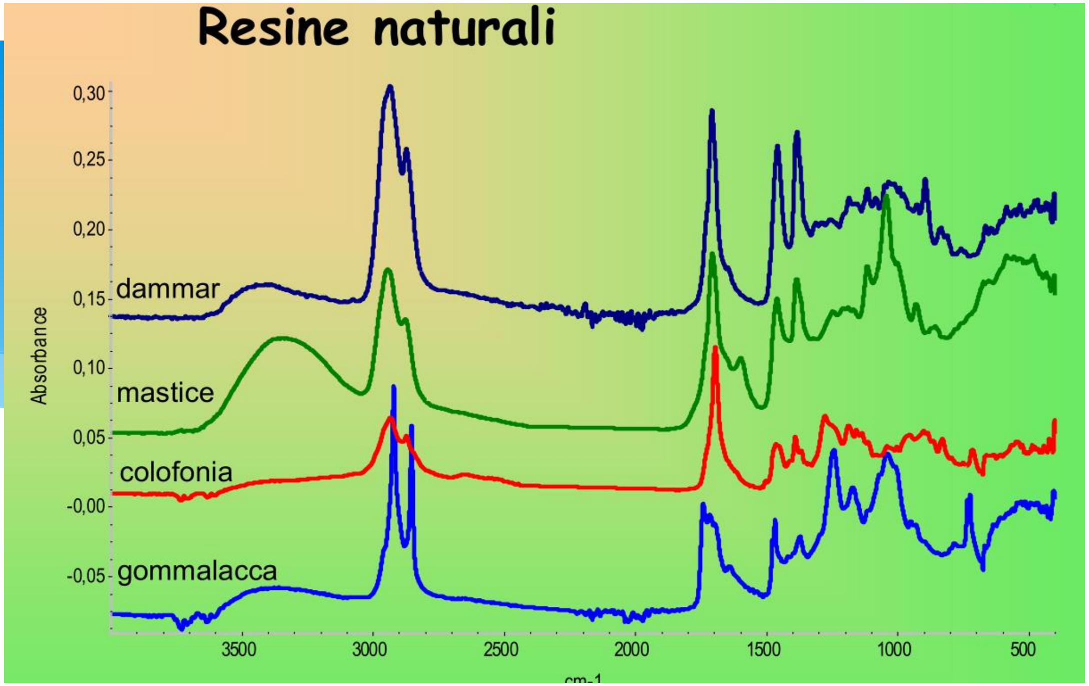
Ma anche in alcuni pigmenti inorganici

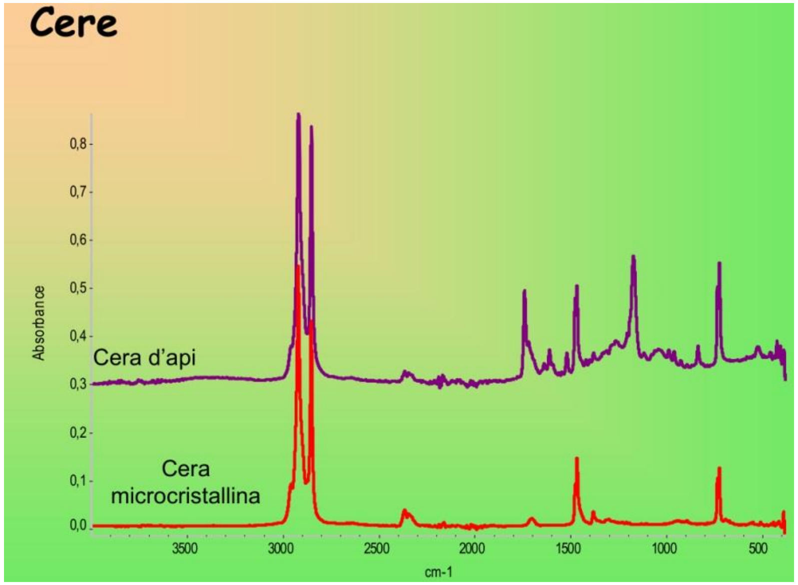
Gli esteri

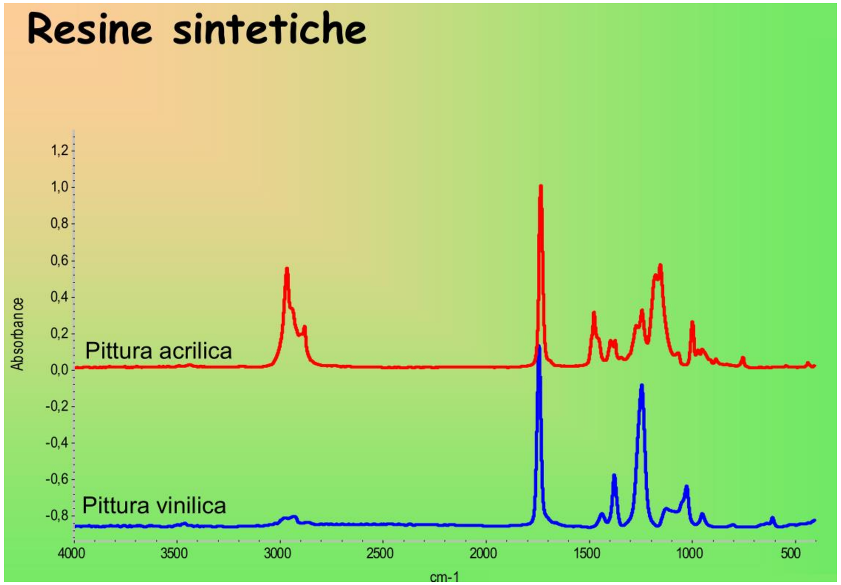


Olii siccativi
Resine naturali
Cere
Resine sintetiche
Additivi
Plastiche

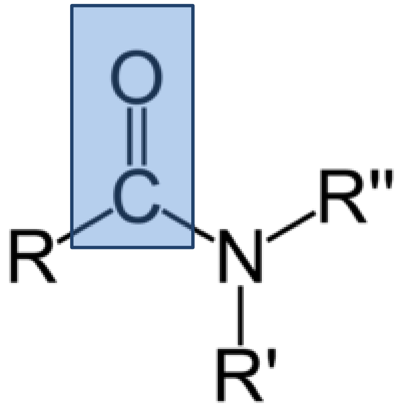

0,26
0,24
0,22
0,20
0,18
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
4000
3500
3000
2500
2000
1500
1000
500
cm-1
Olio di lino cotto


Resine naturali
0,30
0,25
0,20
0,15
0,10
0,05
-0,00
-0,05
Absorbance
dammar
mastice
colofonia
gommalacca
3500
3000
2500
2000
1500
1000
500


Cere
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
Absorbance
Cera d'api
Cera
microcristallina
3500
3000
2500
2000
1500
1000
500
cm-1

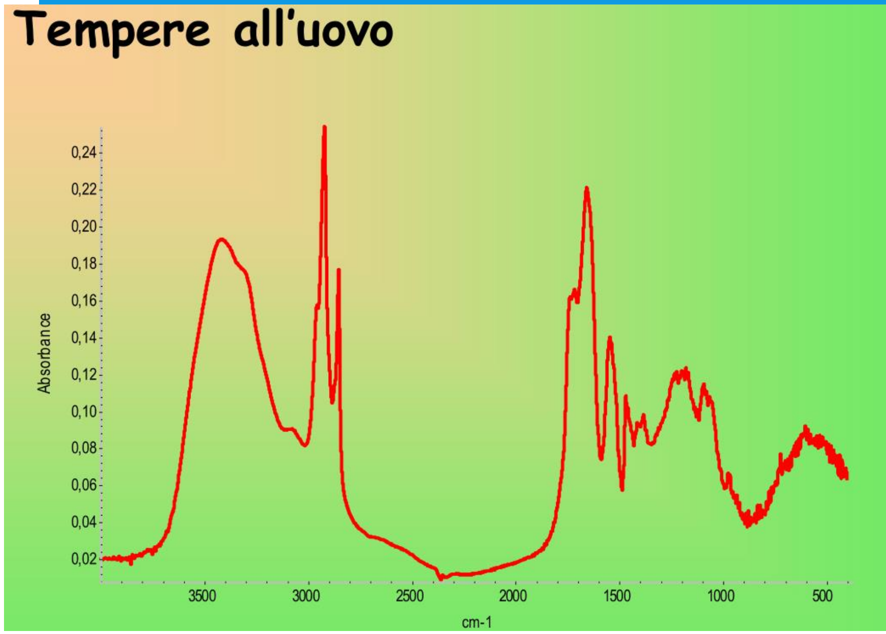

Resine sintetiche
1,2
1,0
0,8
0,6
0,4
0,2
0,0
-0,2
-0,4
-0,6
-0,8
Absorbance
Pittura acrilica
Pittura vinilica
4000
3500
3000
2500
2000
1500
1000
500
cm-1

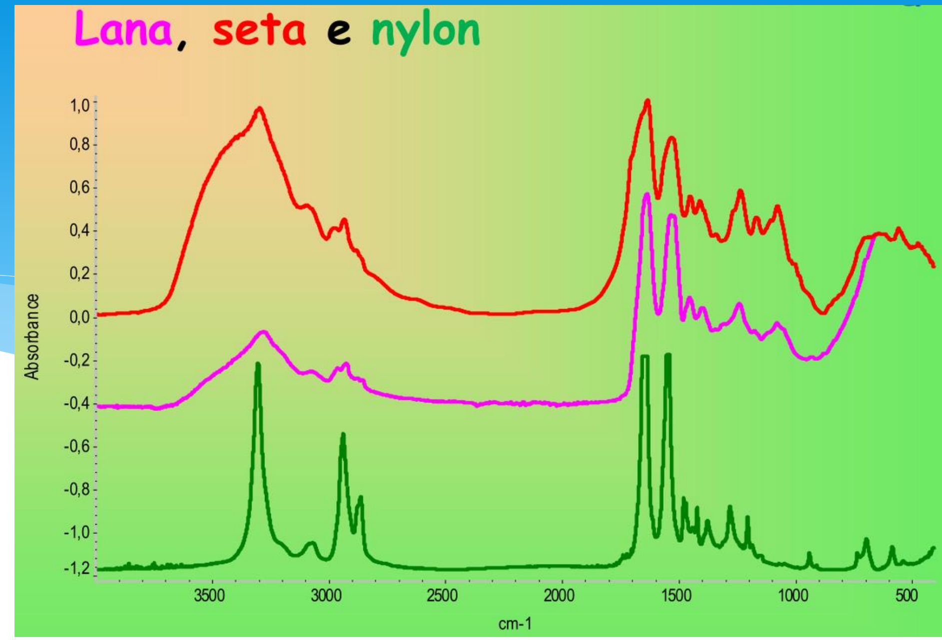
Le ammidi

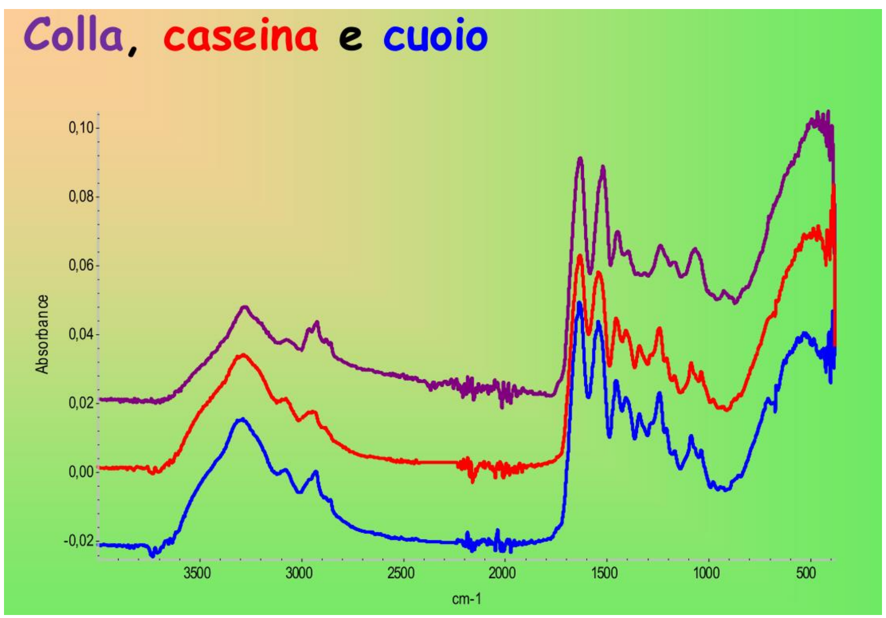


Struttura generale di un'ammide. Se R' e R" sono idrogeni l'ammide si dice primaria, se solo uno fra R' ed R" è un H, si dice secondaria, se R' ed R" non sono idrogeni, l'ammide si dice terziaria

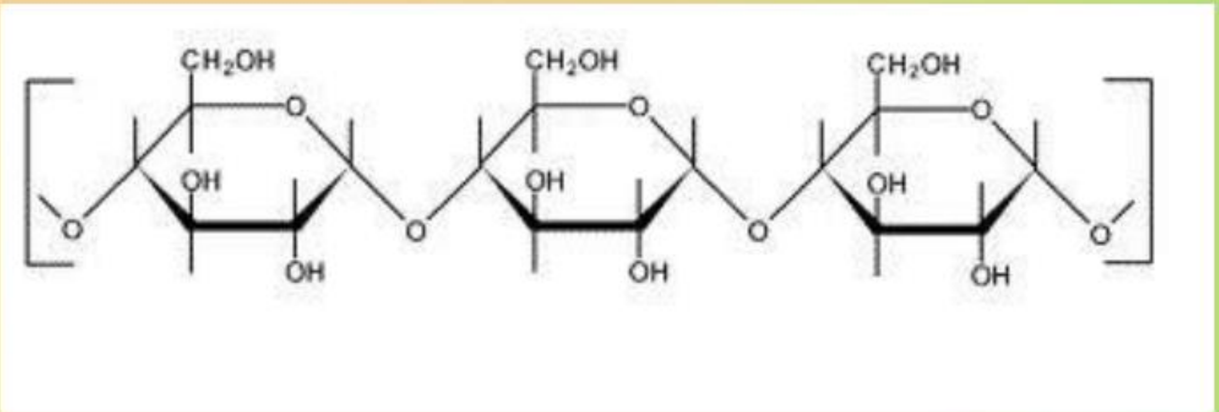
Tempere all’uovo
Tempera grassa
Lana e seta
Colle animali
Cuoio e pelle
Caseina
Plastica


Tempere all'uovo
Absorbance
0,24
0,22
0,20
0,18
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
3500
3000
2500
2000
1500
1000
500
cm-1


Lana, seta e nylon
Absorbance
1,0
0,8
0,6
0,4
0,2
0,0
-0,2
-0,4
-0,6
-0,8
-1,0
-1,2
3500
3000
2500
2000
1500
1000
500
cm-1


Colla, caseina e cuoio
Absorbance
0,10
0,08
0,06
0,04
0,02
0,00
-0,02
3500
3000
2500
2000
1500
1000
500
cm-1

I polisaccaridi



Acquerello

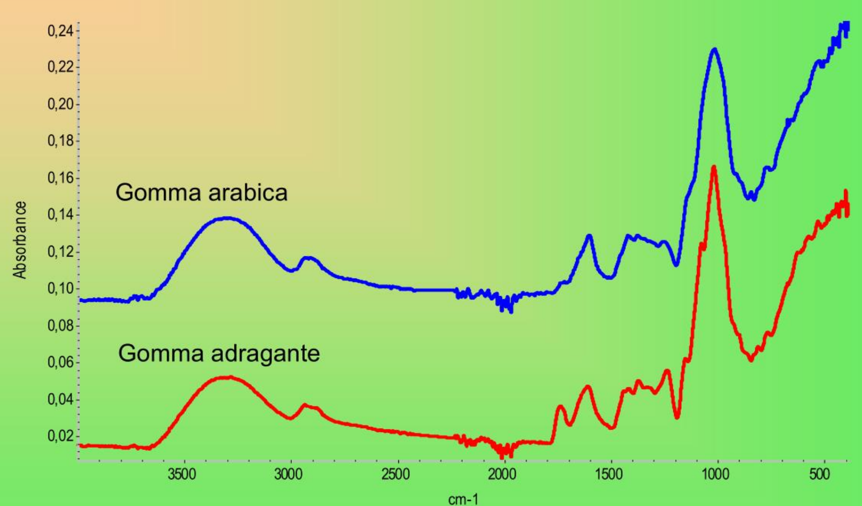
Gomme naturali

Legno

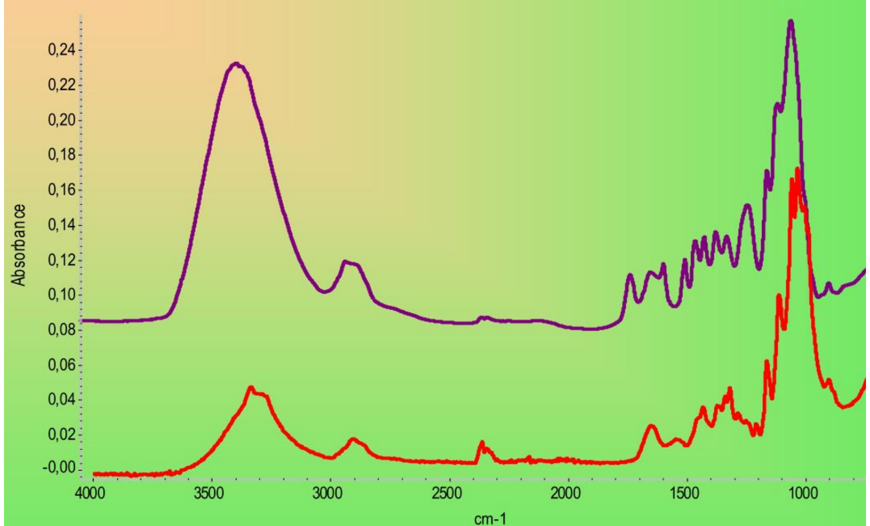
Carta

Fibre vegetali

Acquerello

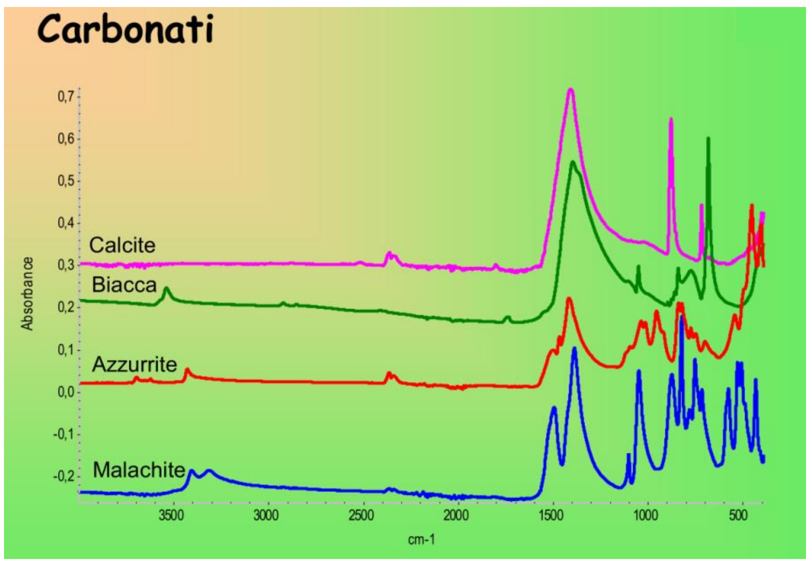


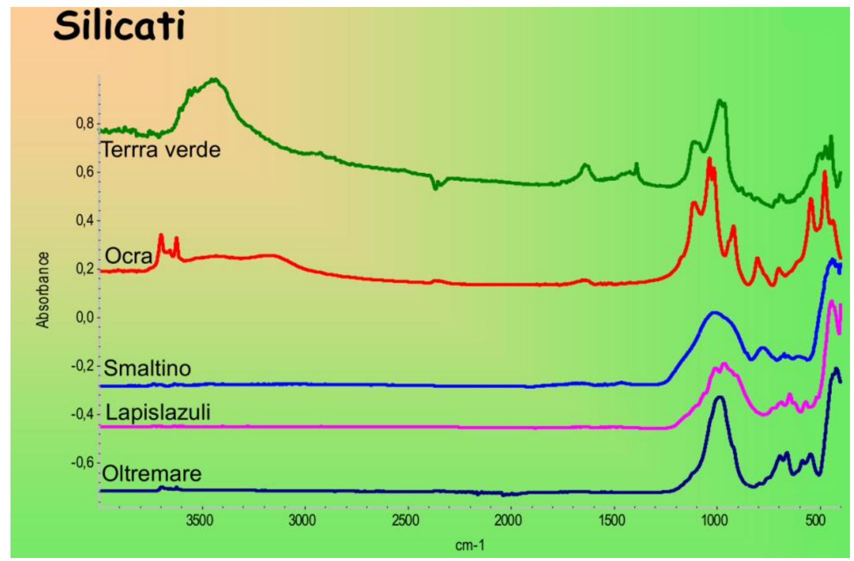
Legno e carta



I pigmenti

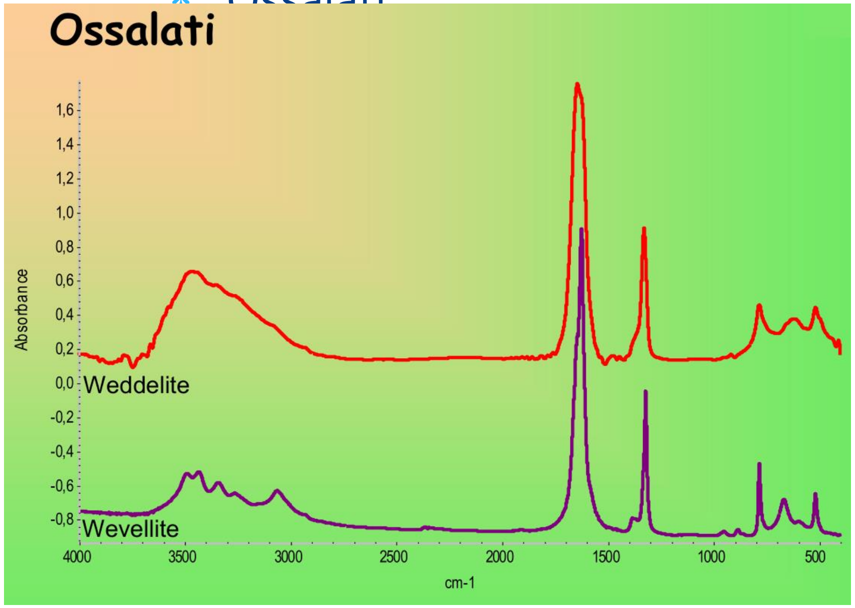
* Carbonati
* Silicati
* Solfati
* Pigmenti organici

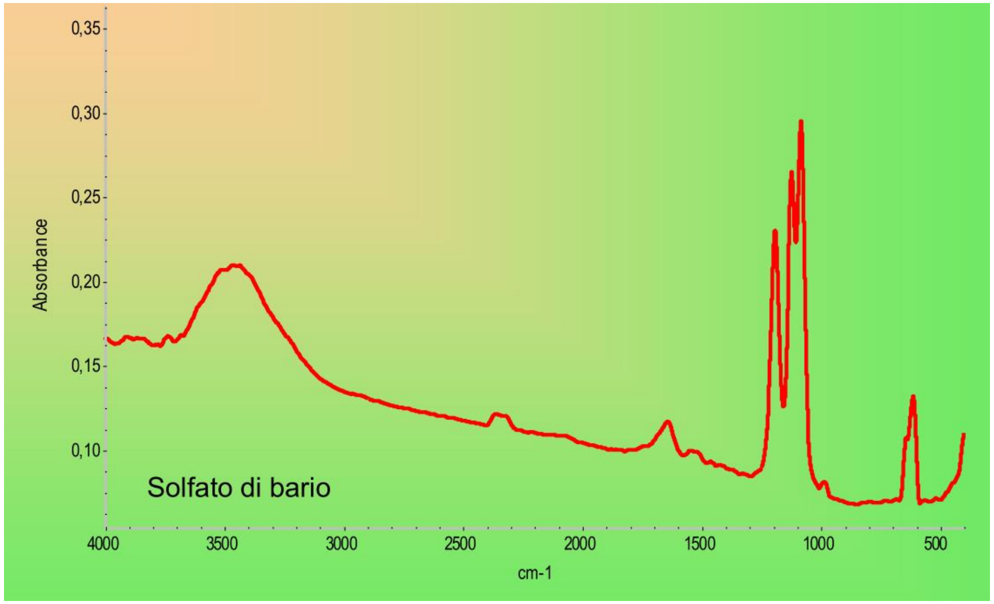




Prodotti di degrado comuni

* Solfati
* Ossalati





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

cestelli@lnf.infn.it