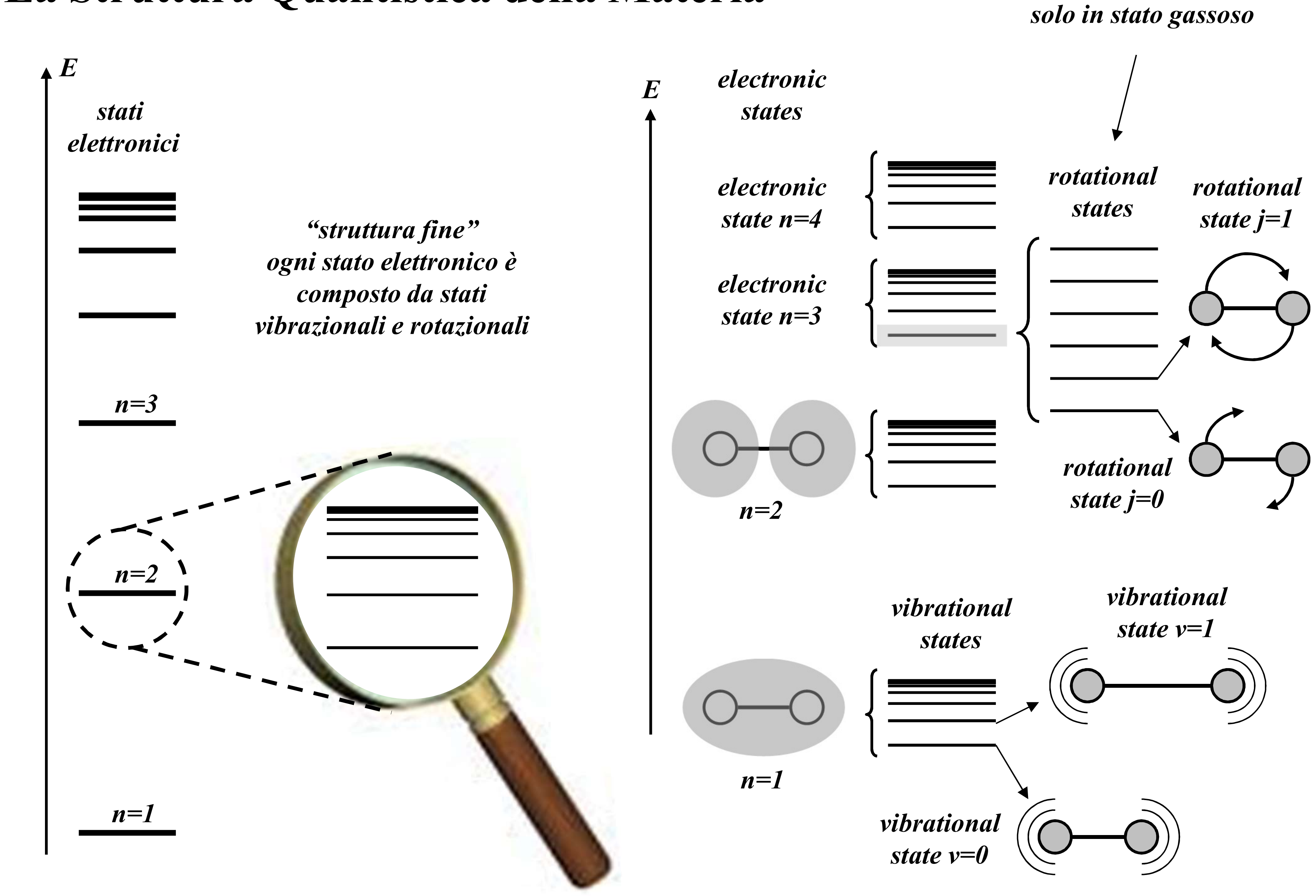
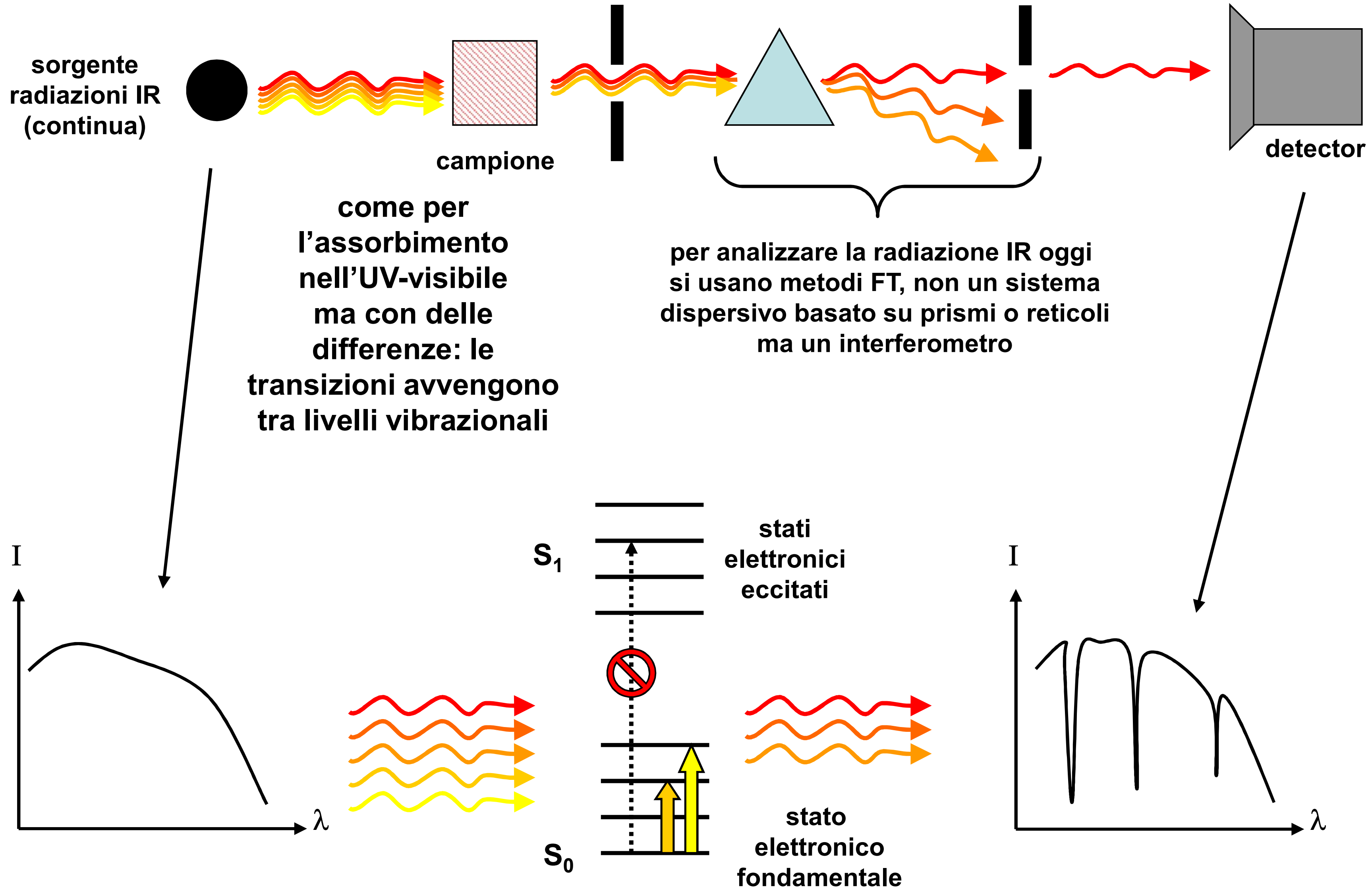
PARTE III

INFRAROSS
O

La Struttura Quantistica della Materia



La Spettroscopia IR

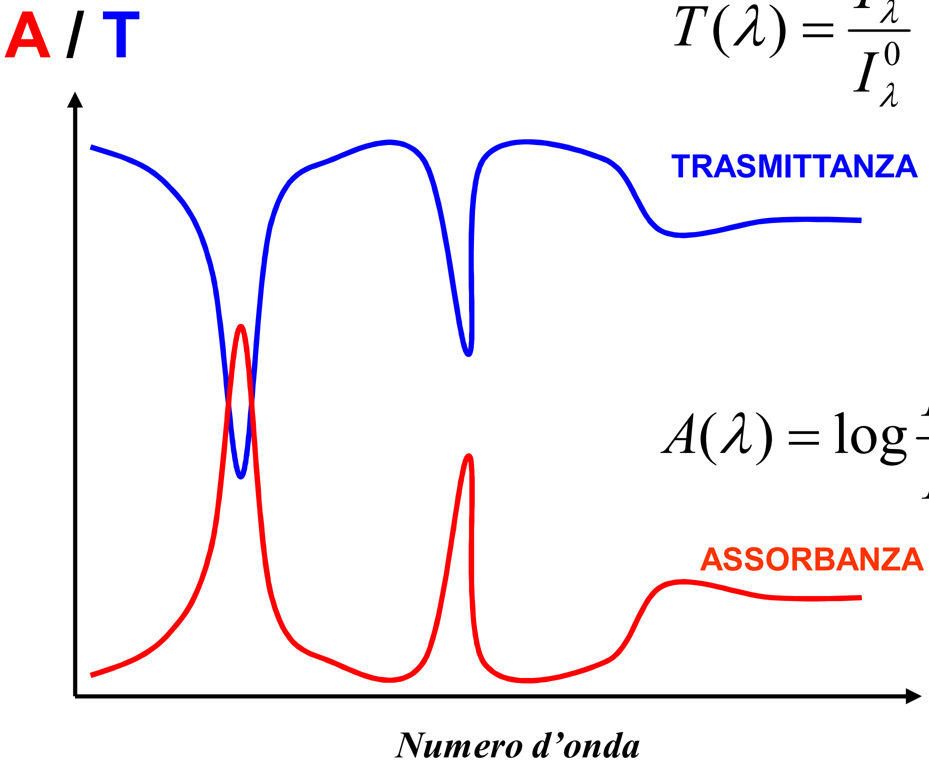


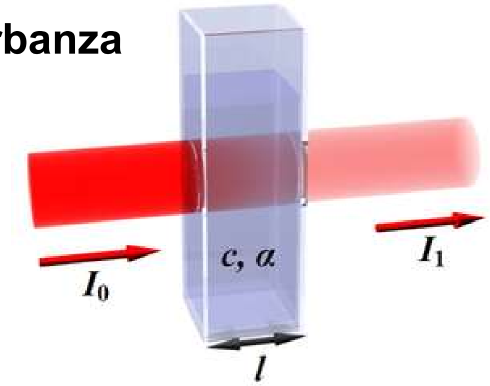
La Spettroscopia IR

Spettri IR presentati in forma diversa da quelli di assorbimento nell'UV-Vis (ma il principio è lo stesso):

- **invece della lunghezza d'onda in nm si usa il suo inverso in cm (numero d'onda, 1/cm)**
- **i dati sono presentati sia in Assorbanza che in Transmittanza, mentre nell'UV-Vis sono sempre presentati in Assorbanza**

$$T(\lambda) = \frac{I_\lambda^1}{I_\lambda^0}$$





$$A(\lambda) = \log \frac{I_\lambda^0}{I_\lambda^1} = -\log T(\lambda)$$

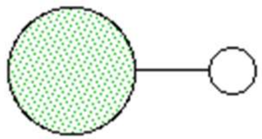
Far infrared <400 cm^{-1}
Mid infrared 4000-400 cm^{-1}
Near infrared 14000-4000 cm^{-1}

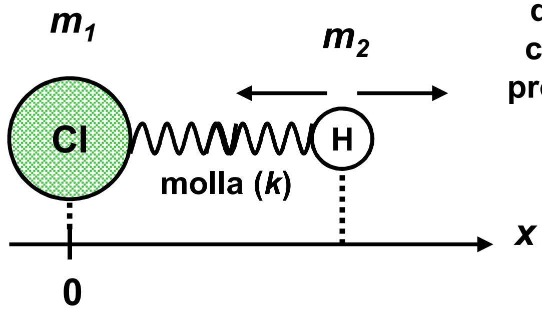
$$\tilde{\nu} = \frac{1}{\lambda} \left(\frac{1}{cm} = cm^{-1} \right)$$

La Spettroscopia IR

VIBRAZIONI MOLECOLARI
(approccio classico)

esempio H-Cl
(acido cloridrico)
2991 cm^{-1}





2 masse m1,m2 unite da una molla con costante di forza *k* problema meccanica classica

Legge di Hooke

$$F = -kx$$

Le molecole vibrano molto velocemente:
10^{12} -10^{13} vibrazioni al secondo (k=481N/s)

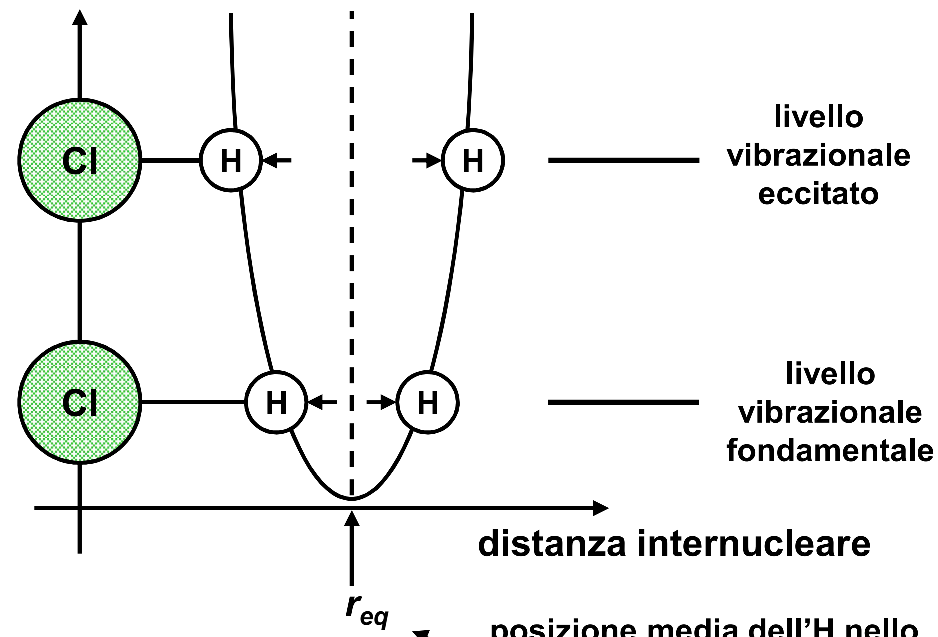
frequenza vibrazione

$$\nu(Hz) = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)}$$

$$\tilde{\nu}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\left(\frac{k}{\mu}\right)}$$

$$V(x) = \frac{1}{2}kx^2$$

Energia



posizione media dell'H nello stato fondamentale (lunghezza legame)

la frequenza della vibrazione

- **aumenta all'aumentare di *k* (forza legame)**
- **diminuisce all'aumentare delle masse m1 e m2 (μ)**

"massa ridotta μ"

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

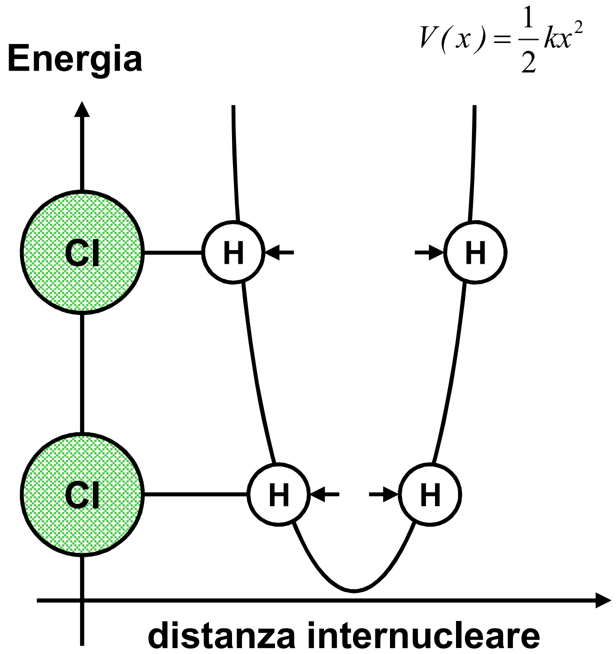
La Spettroscopia IR

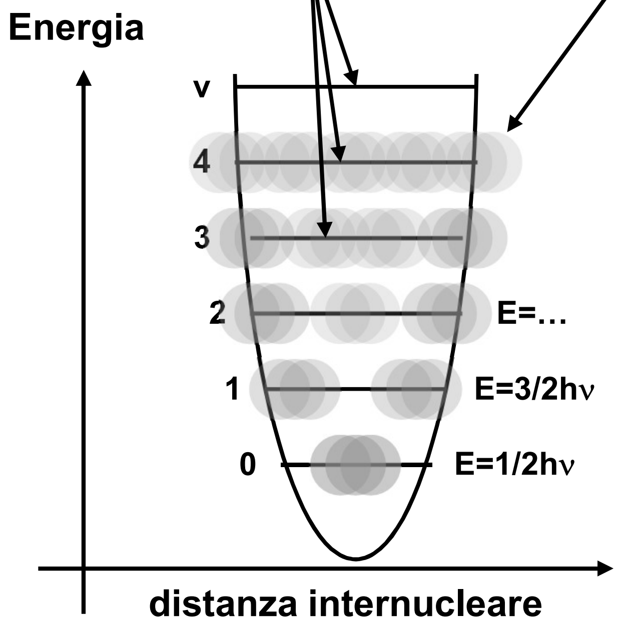
VIBRAZIONI MOLECOLARI
(approccio quantistico)

nell'approccio quantistico non tutte le energie sono accessibili

E = (v+1/2)hν
v num.quant.vibr.(v=0,1,2,3,..)

la posizione dell'atomo H non è più definita, ma è descritta da onde di probabilità (funzioni d'onda)





una molecola non può mai avere energia vibrazionale zero, cosa invece permessa dalla meccanica classica

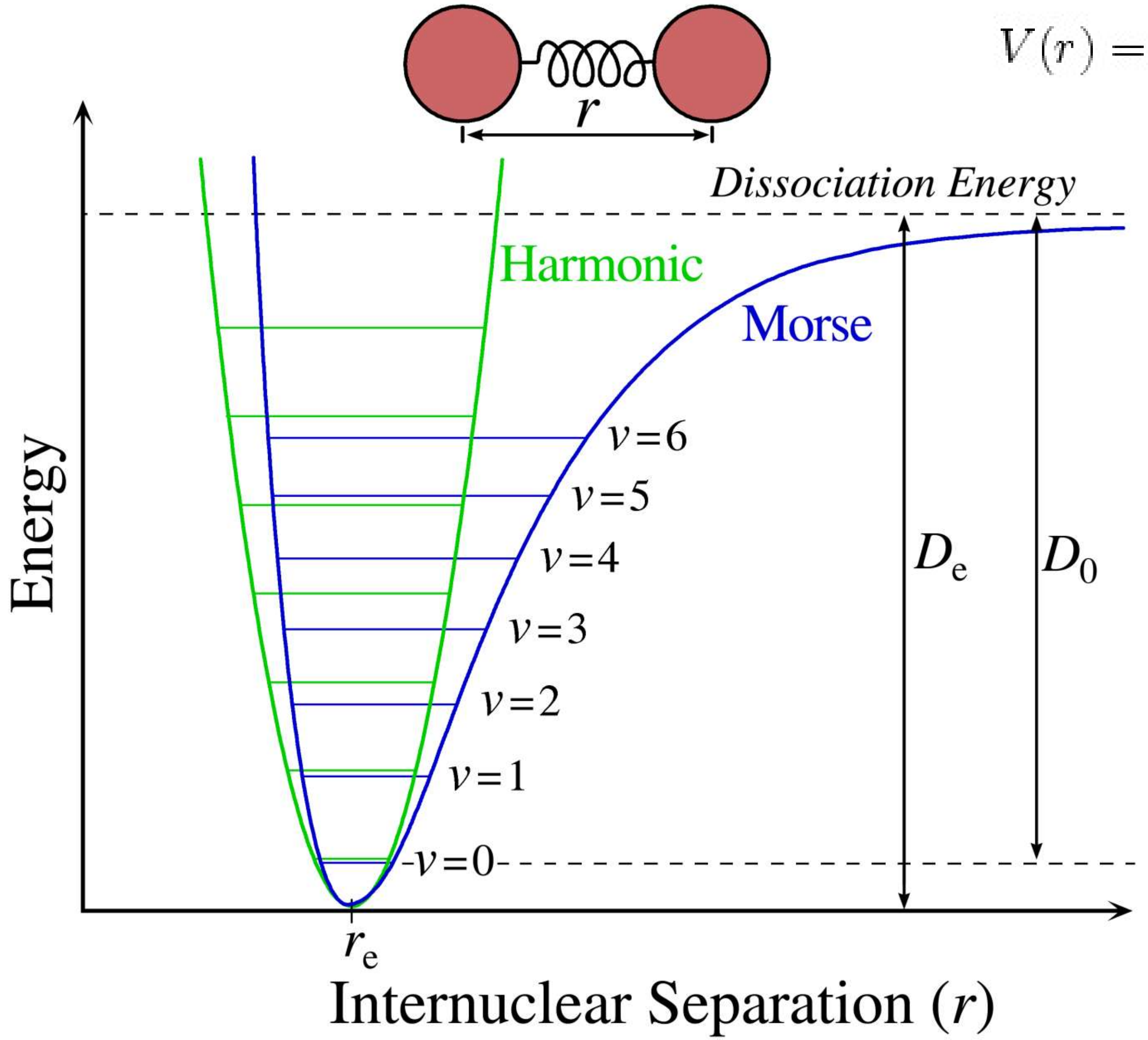
zero point vibration

potenziale armonico è un *caso ideale*: comportamento osservato sperimentalmente descritto meglio da altri potenziali

La Spettroscopia IR

Esempio potenziale *anarmonico*
Potenziale di Morse

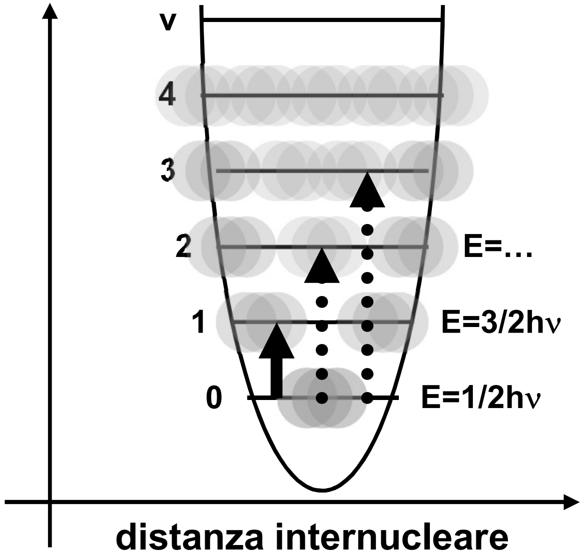
$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$



il potenziale di Morse contempla la possibilità che il legame si "spezzi", con conseguente dissociazione della molecola in due atomi distinti

La Spettroscopia IR

REGOLE DI SELEZIONE: quali transizioni sono permesse?



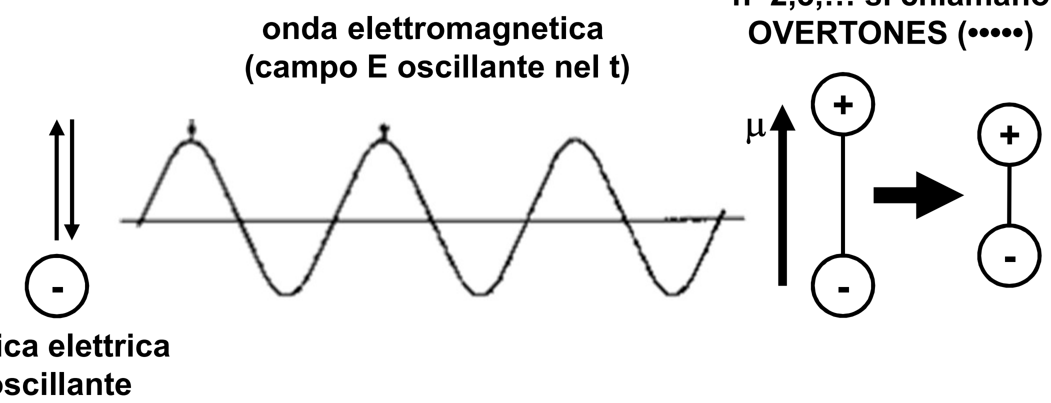
$E = (v+1/2)h\nu$
(v=0,1,2,3,..)

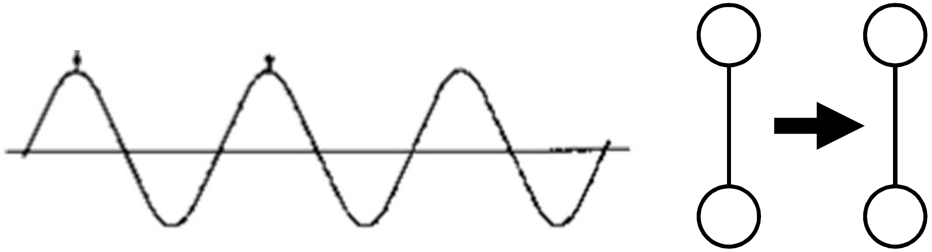
solo molecole con momento di dipolo μ danno spettri IR!!
(es. HCl sì, H_2 no)

Regole selezione IR

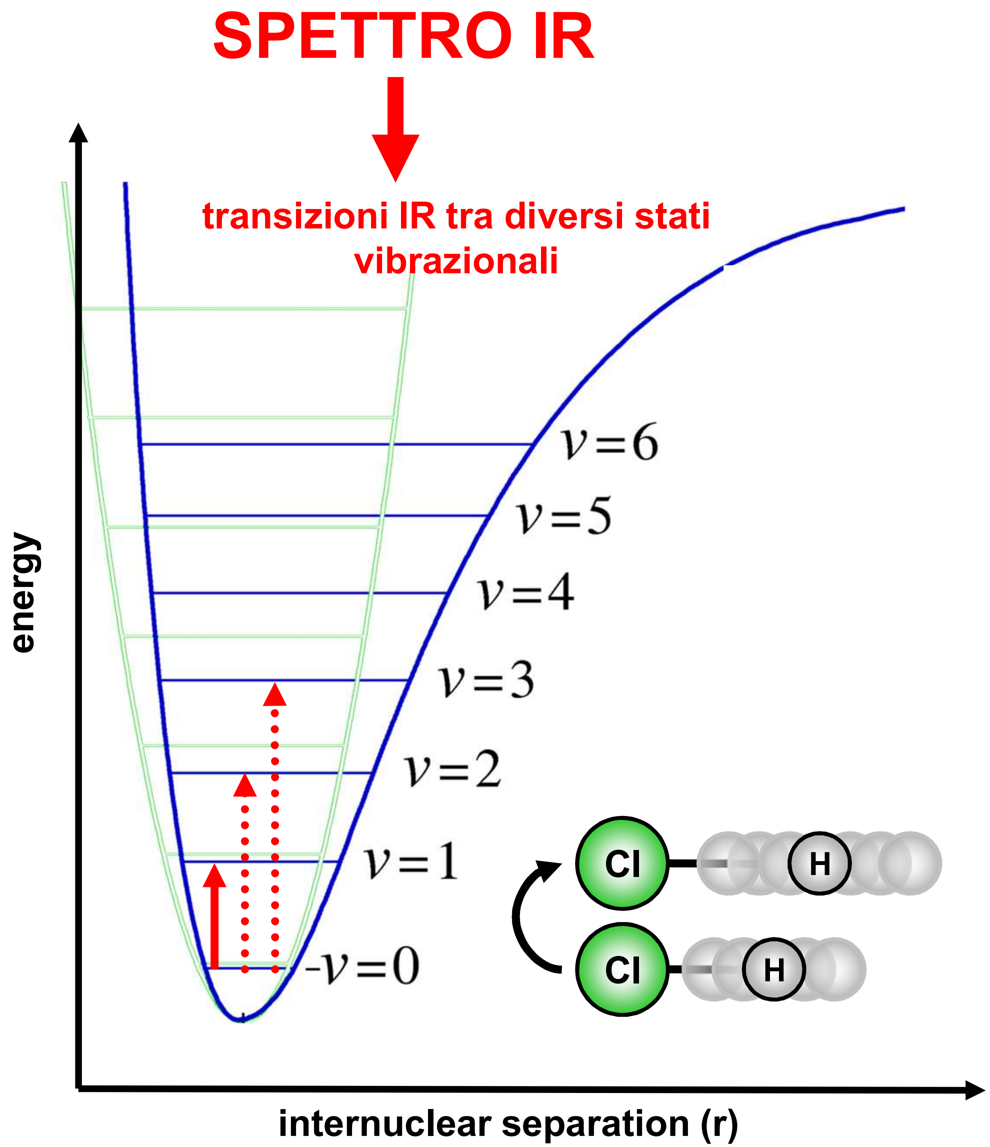
- **$\Delta n = \pm 1$**
- **la vibrazione deve cambiare il *momento di dipolo* μ**

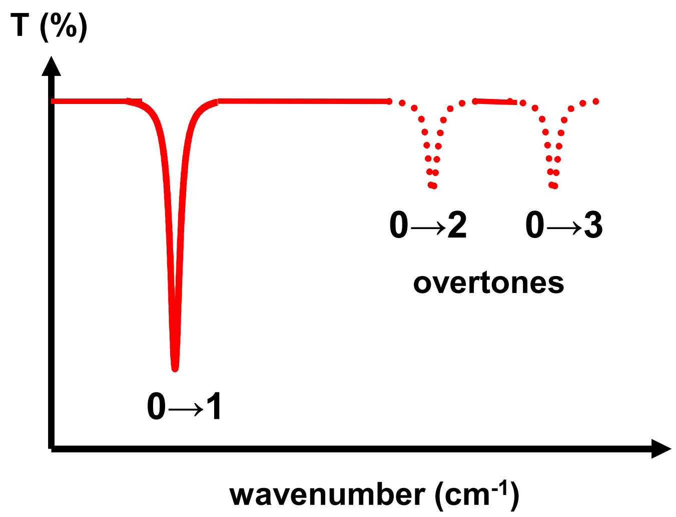
Questa regola non è strettamente osservata in realtà, visto che il potenziale non è armonico. Le transizioni da n=0 a n=2,3,… si chiamano OVERTONES (•••••)



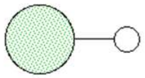


La Spettroscopia IR



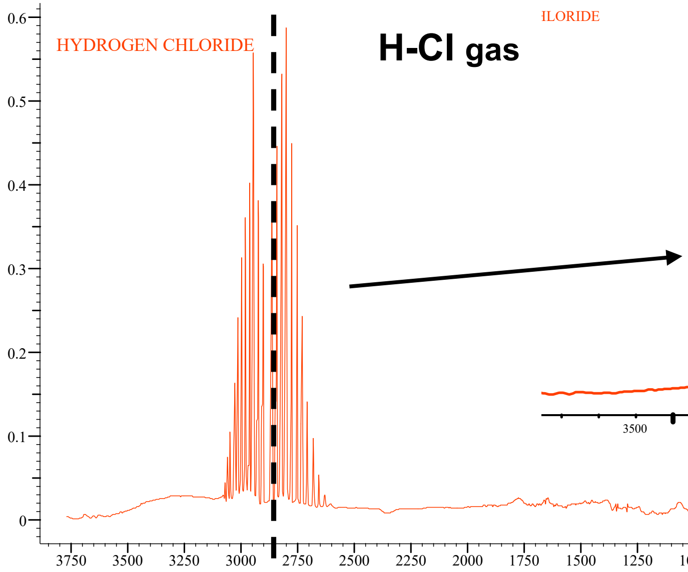


La Spettroscopia IR

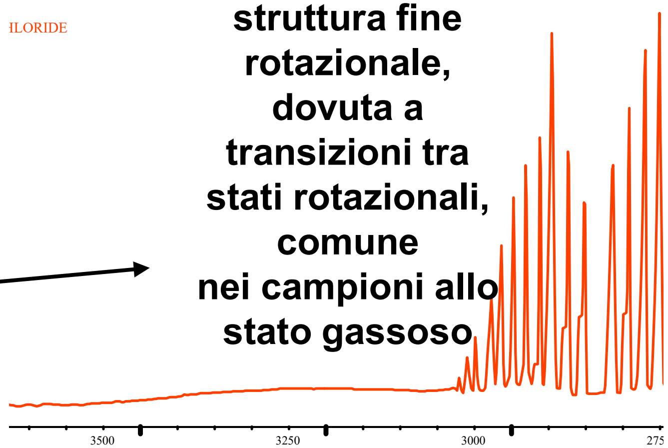


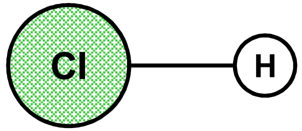
EFFETTO della MASSA

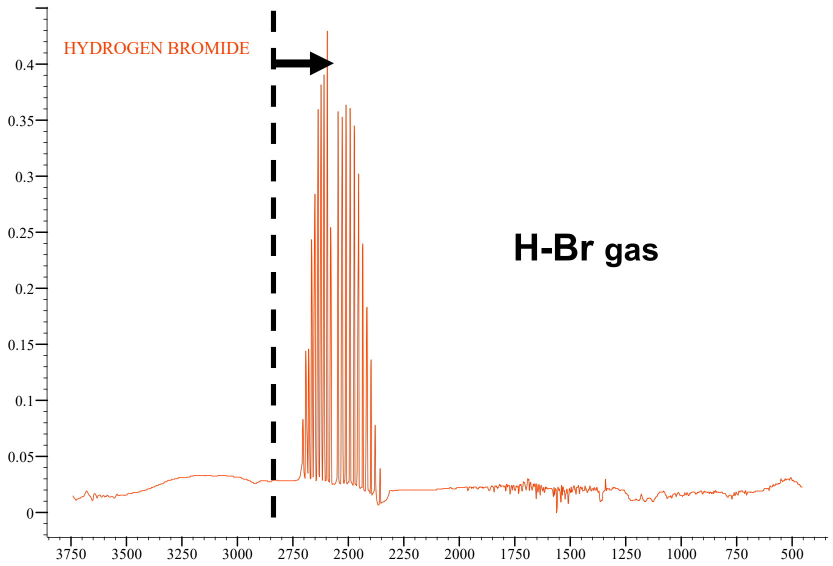
$$\tilde{\nu}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\left(\frac{k}{\mu}\right)}$$



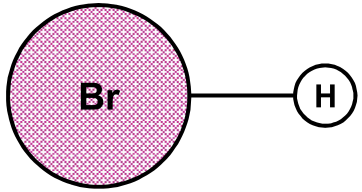
struttura fine rotazionale, dovuta a transizioni tra stati rotazionali, comune nei campioni allo stato gassoso







CAMBIA LA FREQUENZA per via della massa diversa



La Spettroscopia IR

VIBRAZIONI DI MOLECOLE POLIATOMICHE

numero di vibrazioni possibili (modi vibrazionali o modi normali di vibrazione) in molecole con *n* atomi

molecule	*degrees of freedom*
nonlinear	$3n - 6$
linear	$3n - 5$

Es. 3 atomi non-lineare H20

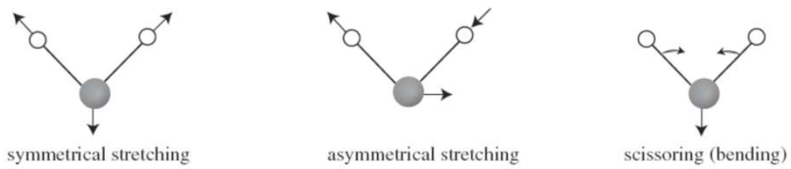
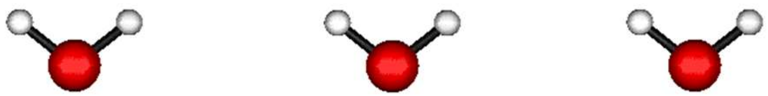


Figure 15.4 : Stretching and bending vibrational modes for H_2O



Es. 3 atomi lineare CO2

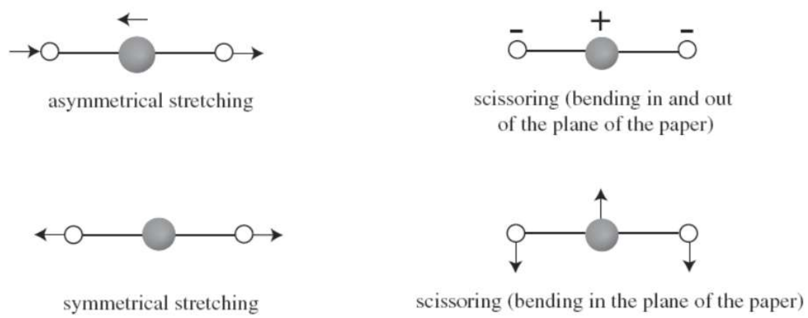
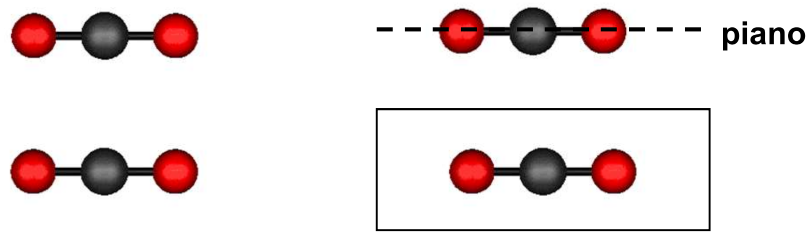
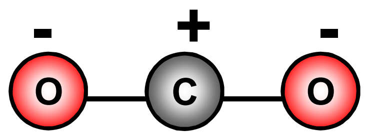


Figure 15.5 : Stretching and bending vibrational modes for CO_2

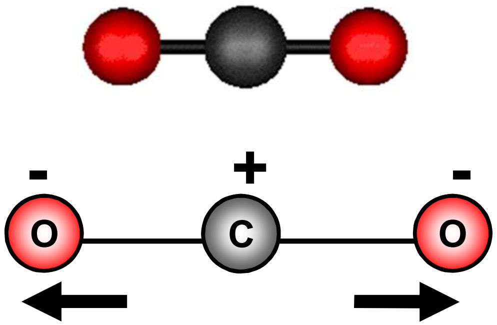


NON TUTTI I MODI VIBRAZIONALI SONO ATTIVI NELL'IR (SOLO QUELLI CON VARIAZIONE DEL MOMENTO DI DIPOLO!)

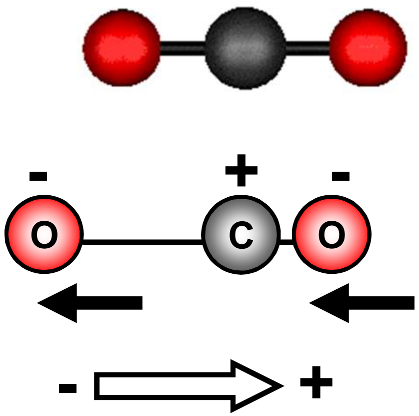
La Spettroscopia IR



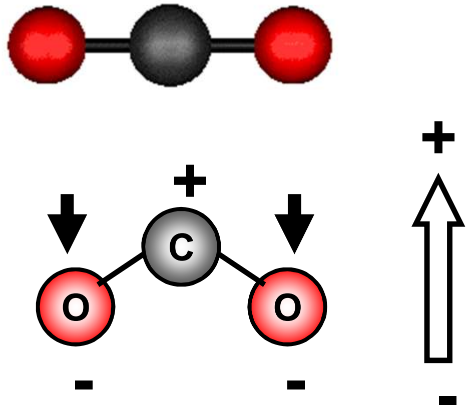
La molecola di CO_2 non ha di per sé un momento di dipolo



Il movimento di stretching simmetrico non cambia la situazione
VIBRAZIONE NON VISIBILE ALL'IR

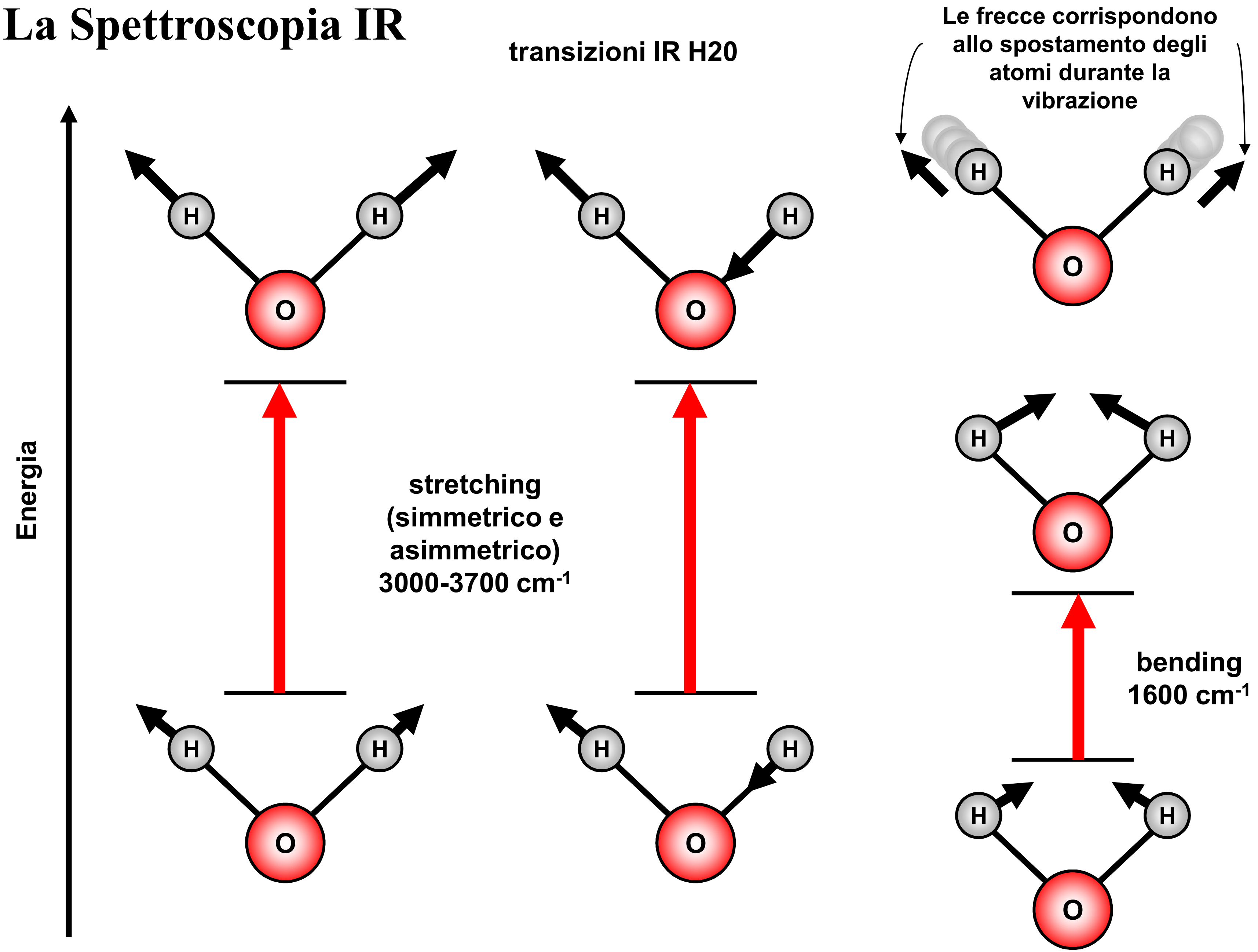


Il movimento di stretching asimmetrico introduce un'asimmetria ed una separazione di carica MOMENTO DI DIPOLO



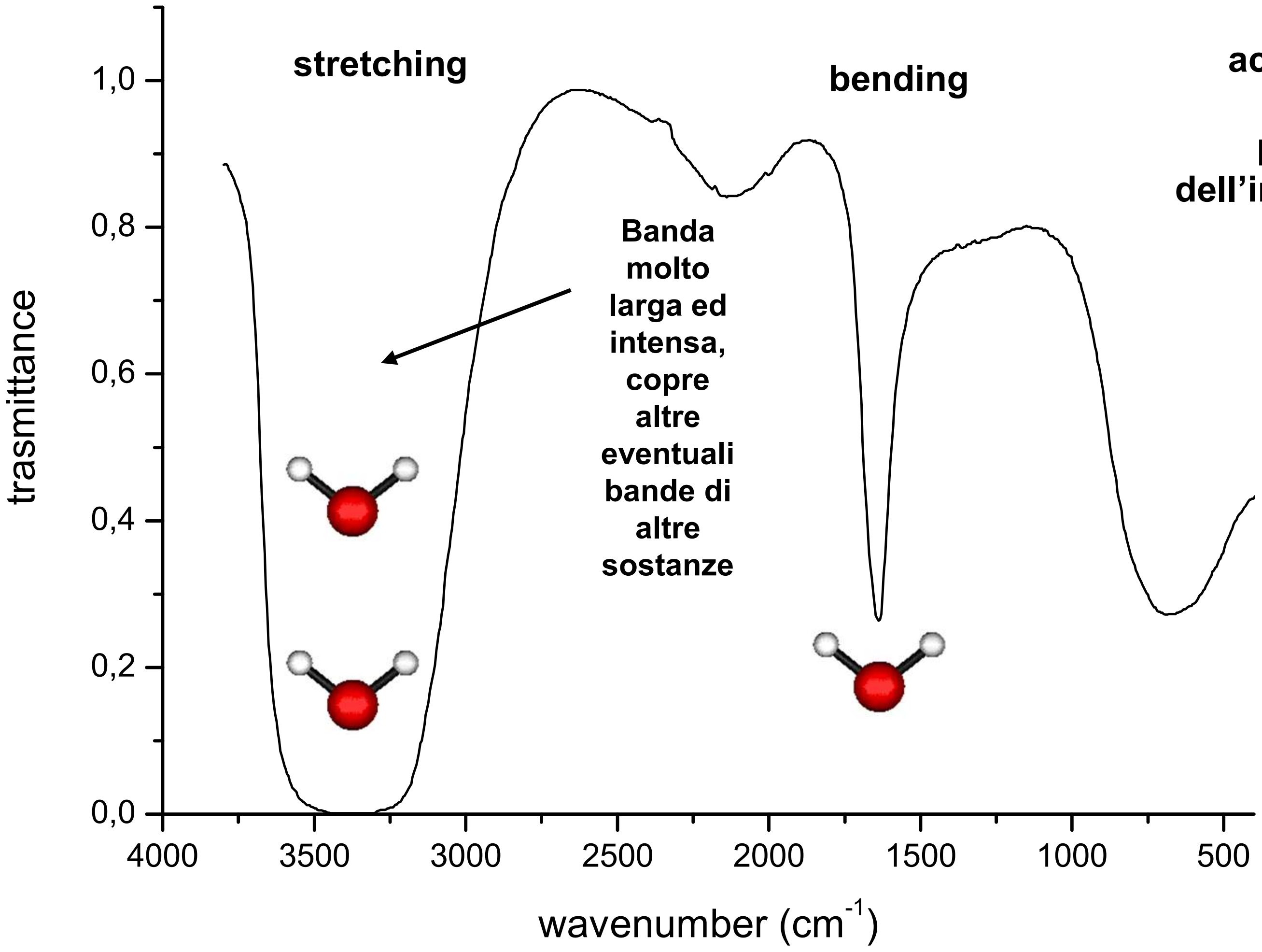
Movimenti di bending, introducono un'asimmetria e portano ad una separazione di carica MOMENTO DI DIPOLO

La Spettroscopia IR



La Spettroscopia IR

spettro IR acqua



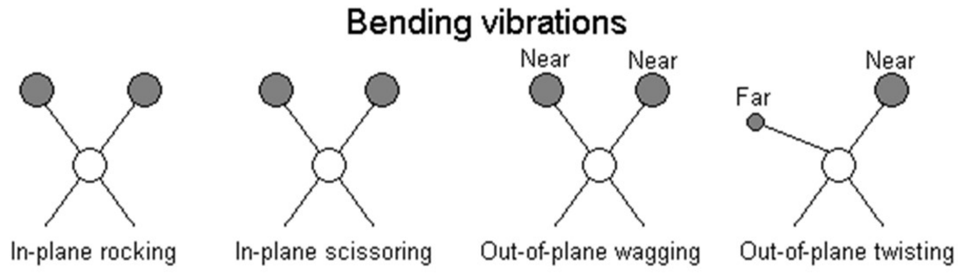
Lo stretching O-H da un segnale IR molto intenso, e compre una vasta regione spettrale

PROBLEMA:
acquisizione spettri IR di soluzioni acquose è problematica a causa dell'interferenza spettrale dello str O-H

La Spettroscopia IR

VIBRAZIONI MOLECOLE POLIATOMICHE con più di 3 atomi

Molecole con più atomi → **Geometrie più complesse** → **Altre vibrazioni oltre a stretching e bending nel piano**



ESEMPIO gruppo –CH2–

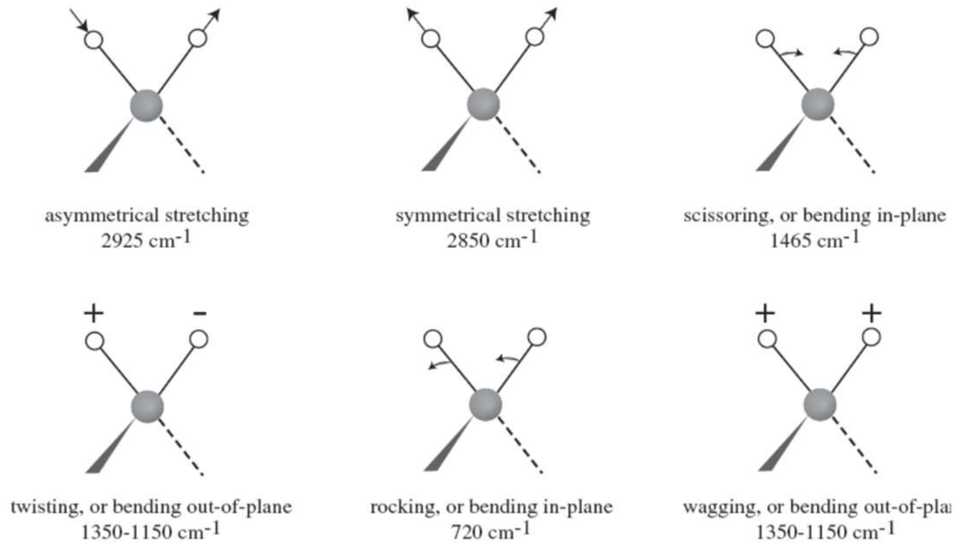
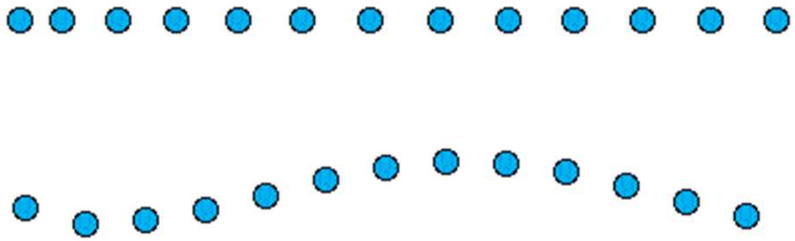


Figure 15.6 : Stretching and bending vibrational modes for a CH_2 group.

phonon (lattice vibration): collective vibration in a periodic, elastic arrangement of atoms or molecules in a solid

- **Transverse / Longitudinal**
- **Acoustic (in phase) / Optical (out of phase)**



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TA

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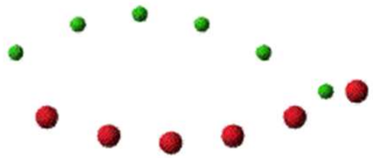


TO

3D crystal with N atoms/cell : 3 acoustic and 3N-3 optical phonons

La Spettroscopia IR

SPETTRI IR di 3 SOSTANZE DIVERSE (STRUTTURA CHIMICA DIFFERENTE)

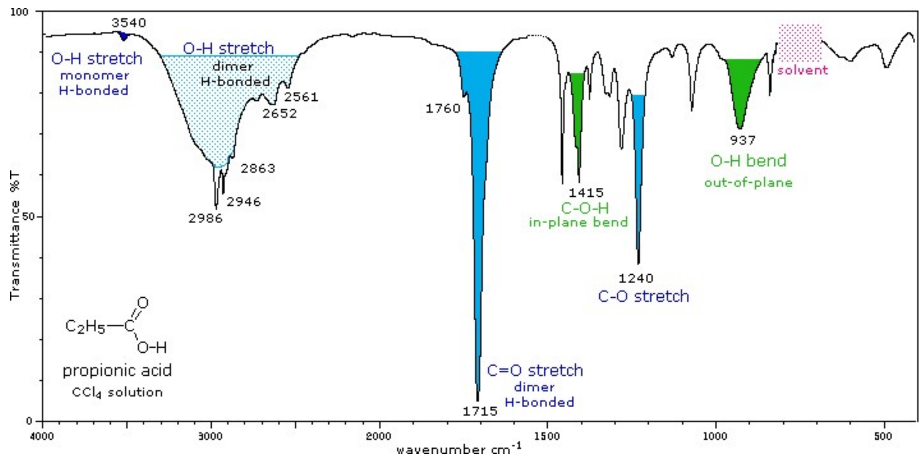
ALCUNE BANDE (O GRUPPI DI BANDE) IN POSIZIONI "SIMILI" – IN COMUNE

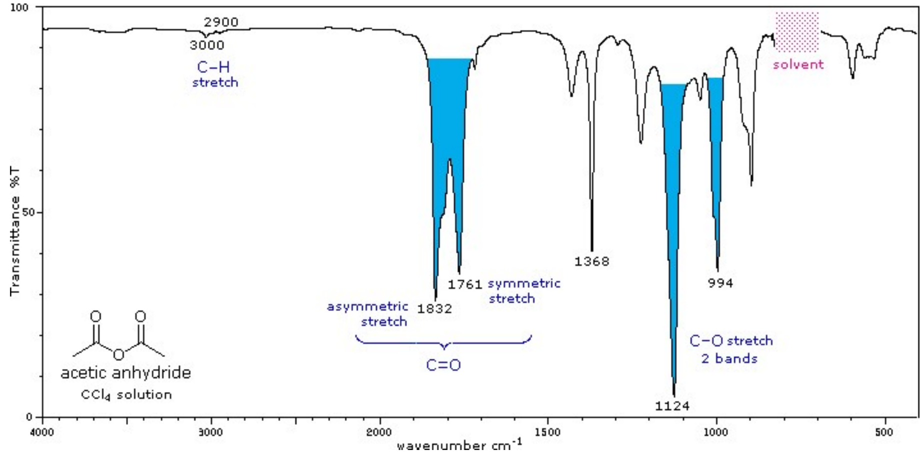
<u>stretching C=0 e C-O</u>

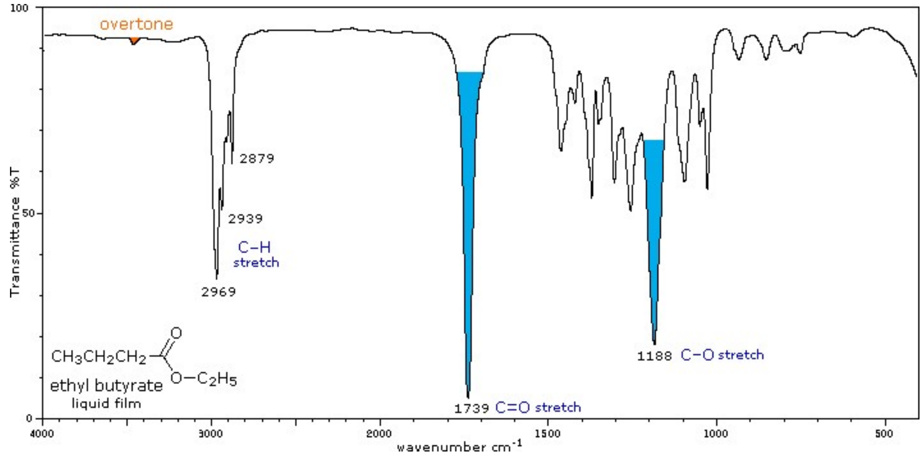
riflettono la condivisione di alcuni gruppi funzionali

Si noti l'EFFETTO COSTANTE DI FORZA k sulla frequenza C=O>C-O
k legame doppio > k legame singolo

$$\tilde{\nu}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\left(\frac{k}{\mu}\right)}$$

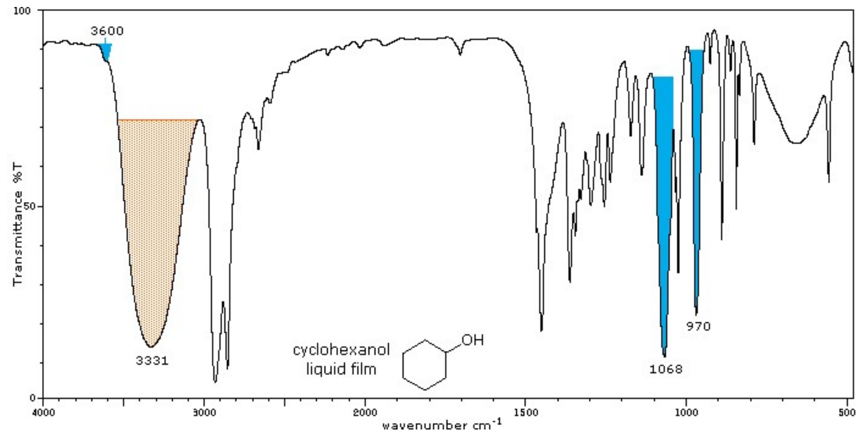


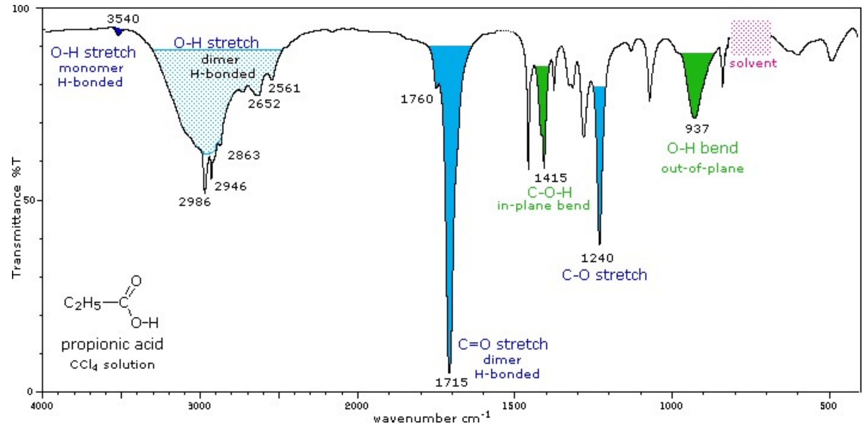




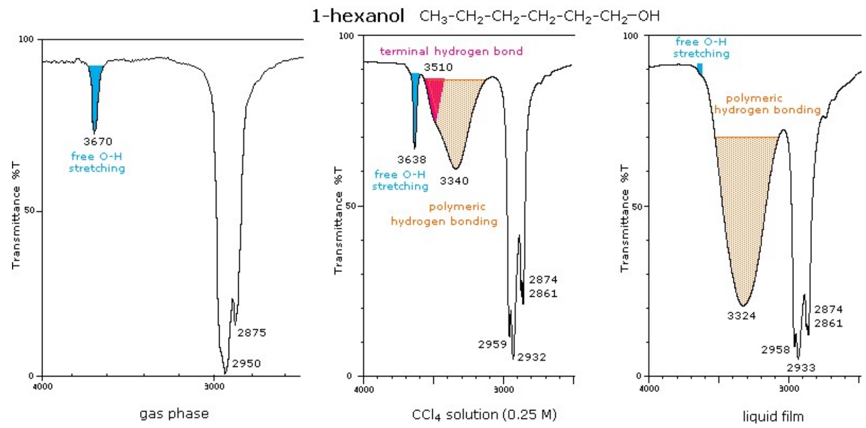
La Spettroscopia IR

SPETTRI IR di 2 SOSTANZE DIVERSE AVENTI IN COMUNE IL GRUPPO -OH





stretching O-H presente in entrambi gli spettri IR

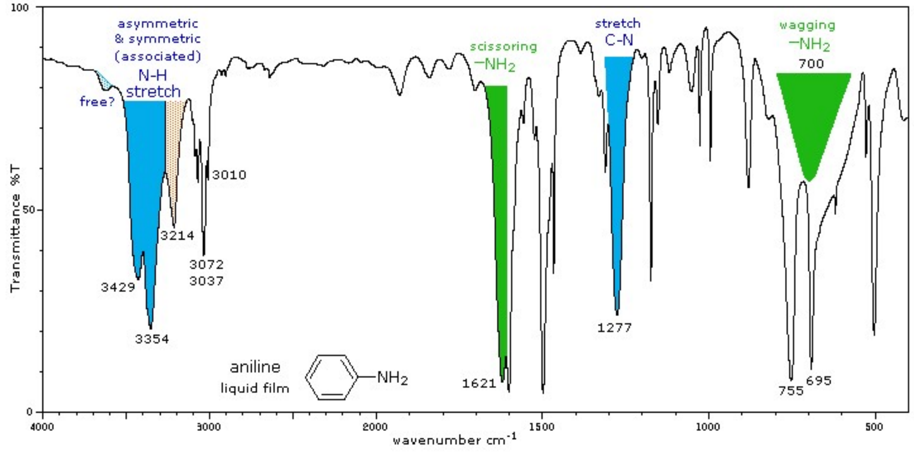


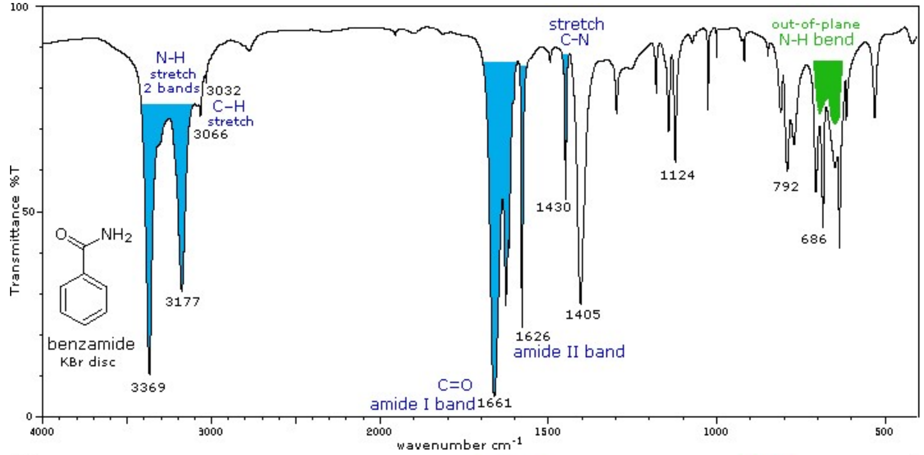
La Spettroscopia IR

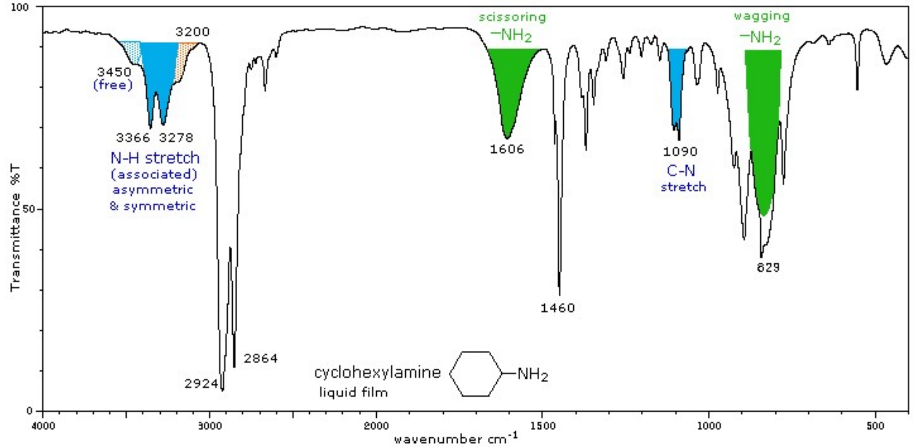
SPETTRI IR di 3 SOSTANZE DIVERSE AVENTI IN COMUNE IL GRUPPO –NH2

vibrazioni -NH2 presente in tutti gli spettri IR

RAGIONAMENTO VALIDO PER MOLTI ALTRI GRUPPI FUNZIONALI





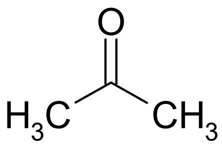


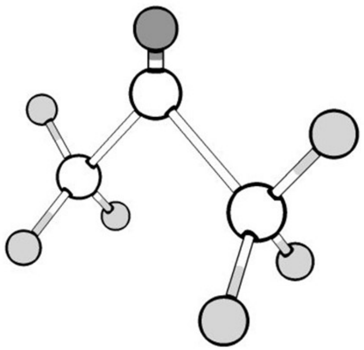
La Spettroscopia IR

VIBRAZIONI CARATTERISTICHE DI GRUPPO - APPROSSIMAZIONE

Per quanto estesa e complessa sia la struttura di una molecola organica, alcuni modi vibrazionali saranno localizzati sui suoi eventuali gruppi funzionali (es. C=O) e daranno origine a bande IR che cadranno in intervalli di frequenze caratteristici dei modi vibrazionali di quel gruppo funzionale

es. modo di vibrazione dell'acetone a 1750 cm^{-1} modo complesso dominato dallo stretching C=O



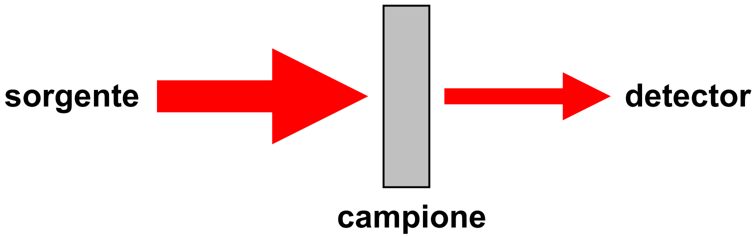


Functional Group	*Characteristic Absorption(s)* (cm^{-1})
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

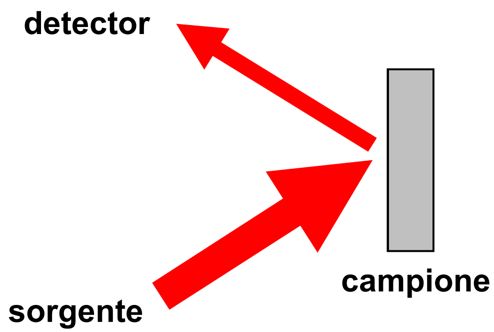
La Spettroscopia IR

Metodi di campionamento IR

In TRASMISSIONE
tradizionali, routine

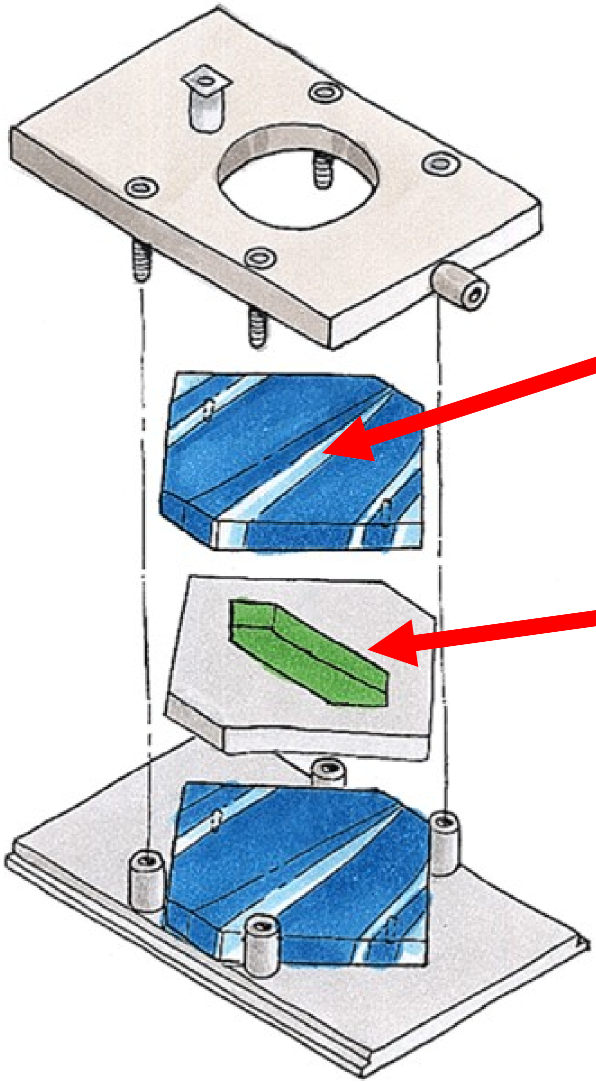


In RIFLESSIONE



La Spettroscopia IR

Metodi di campionamento IR in trasmissione: liquidi e soluzioni

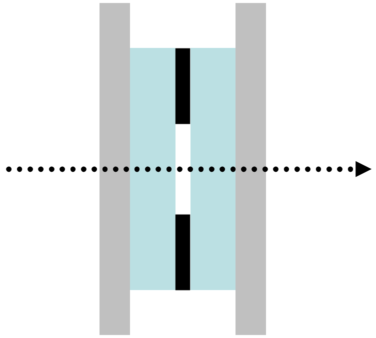


Finestre di materiale che non assorbe (transparente) nell'IR

esempi materiali comuni

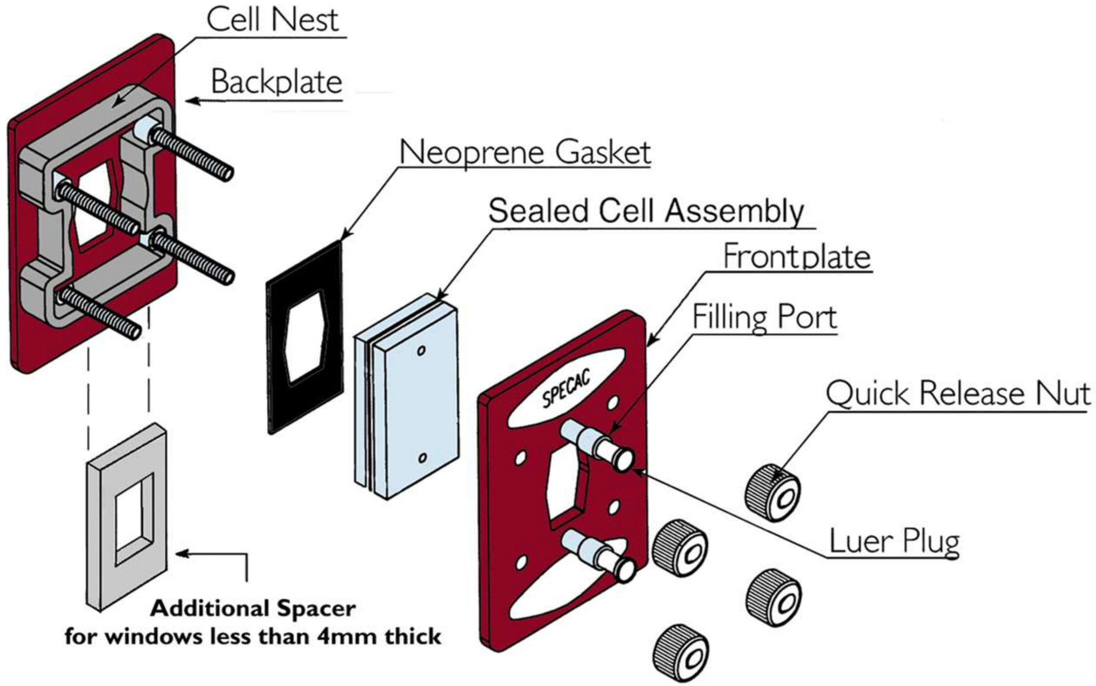
- **NaCl 40000-600 cm^{-1}**
- **KBr 43500-400 cm^{-1}**
- **CaF_2 77000-900 cm^{-1}**

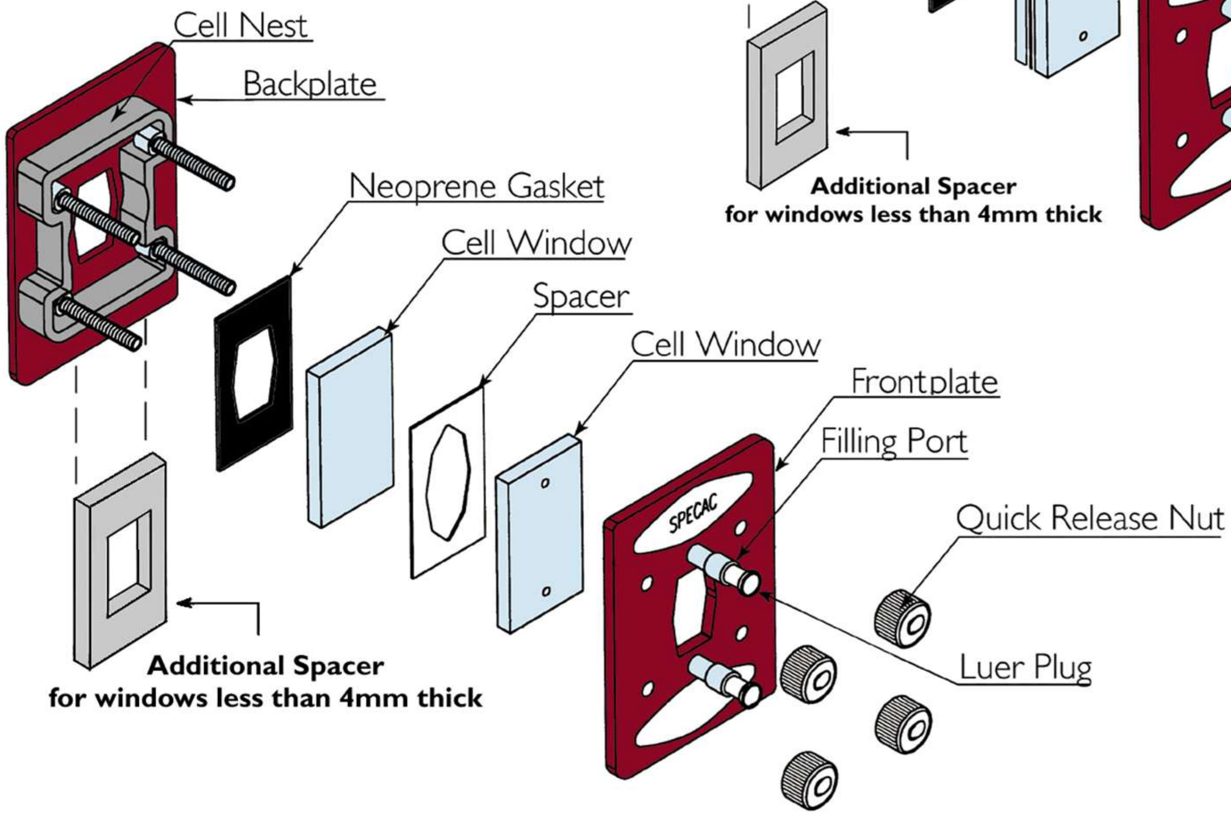
Interstizio per il campione liquido



La Spettroscopia IR

Metodi di campionamento IR in trasmissione: liquidi e soluzioni



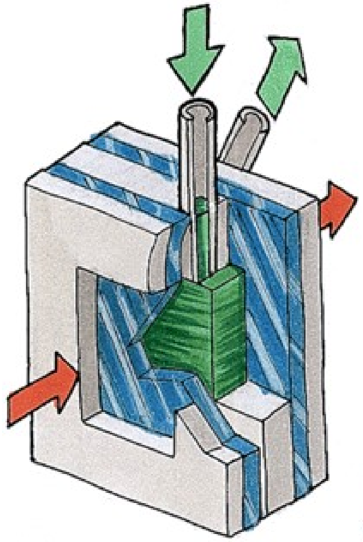


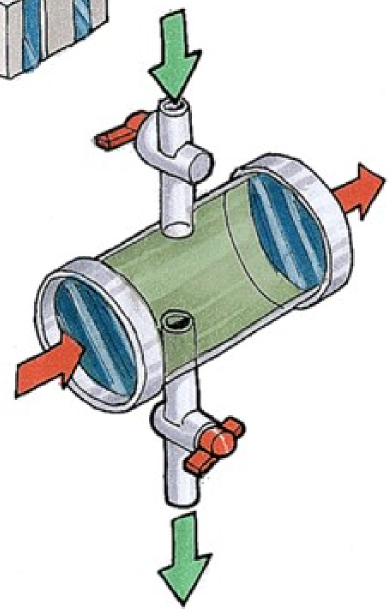
Cella per film sottili (<0.01mm) di liquidi (H_2O)

La Spettroscopia IR

Metodi di campionamento IR in trasmissione: liquidi e soluzioni

celle con diverso cammino ottico



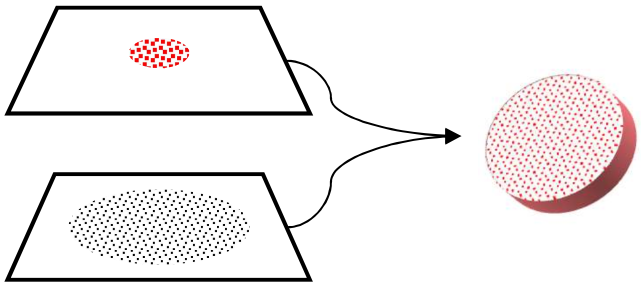


La Spettroscopia IR

Metodi di campionamento IR in trasmissione: solidi

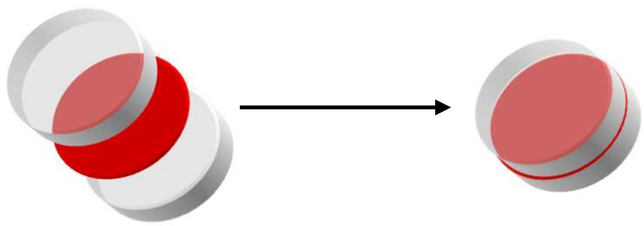
pastiglie preparate con l'analita + KBr

pochi mg



100-200 mg KBr

film di nujol (paraffina liquida) + analita (emulsione) tra due finestre di materiale trasparente all'IR

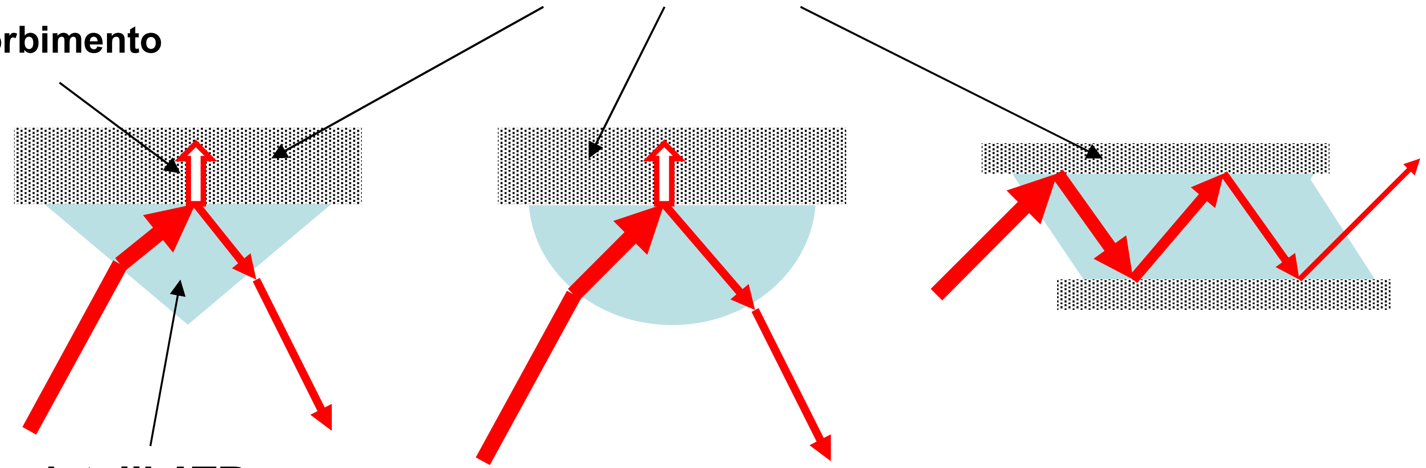


La Spettroscopia IR

Metodi di campionamento IR in riflessione

campioni solidi o liquidi

assorbimento



cristalli ATR di materiale particolare, poco solubile e con alto indice di rifrazione (Ge, ZnSe,…)

Attenuated Total Reflection (ATR)

Sfrutta il principio della riflessione totale

MOLTO USATO

Diffuse reflectance infrared technique (DRIFT)

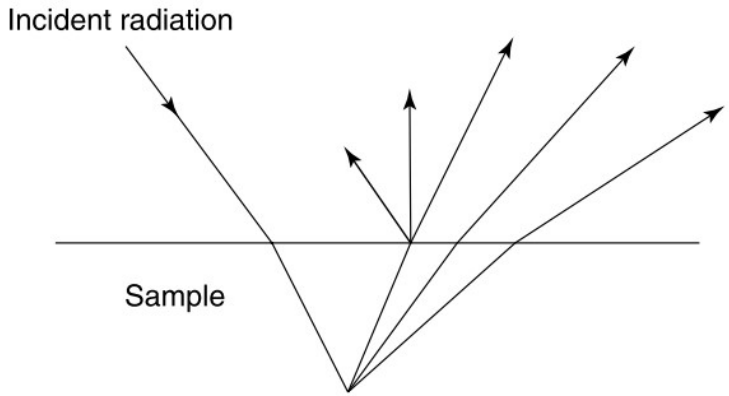
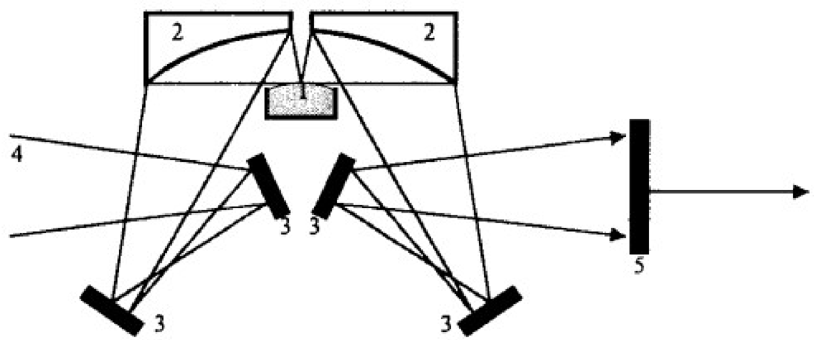


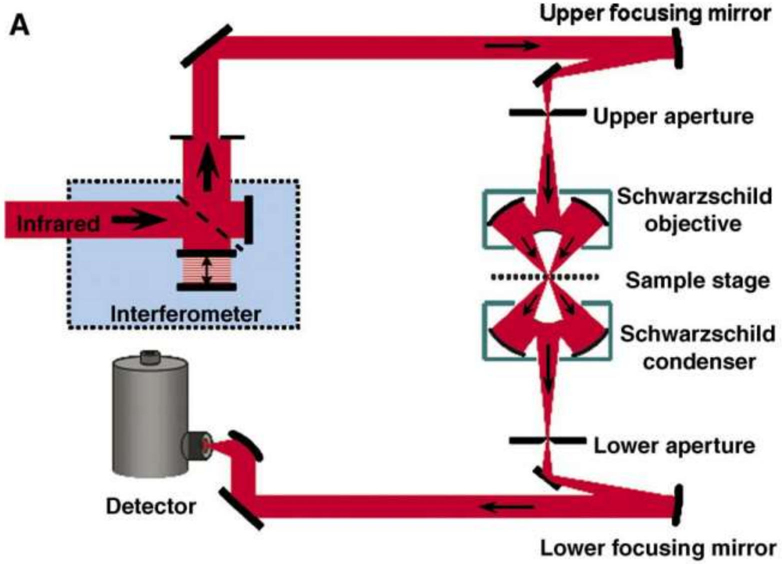
Figure 2.17 Illustration of diffuse reflectance.



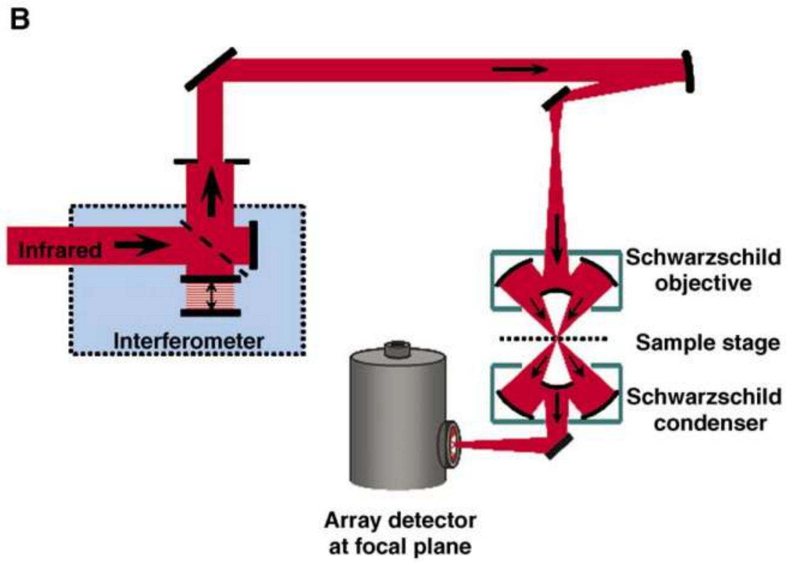
1: sample; 2: concave mirror; 3: mirror; 4: infrared beam; 5: detector
Fig.3: DRIFT-technique

FT-IR microscopy

FT-IR Microspectroscopy (FTIRM)



FT-IR Imaging (FTIRI)



Focal Plane Array (FPA)

Biochimica et Biophysica Acta 1758 (2006) 846 – 857

mid-infrared 3-10 μm

$$r = \frac{0.5\ \lambda}{NA} = \frac{0.5\ \lambda}{n\ sin(\theta)}$$

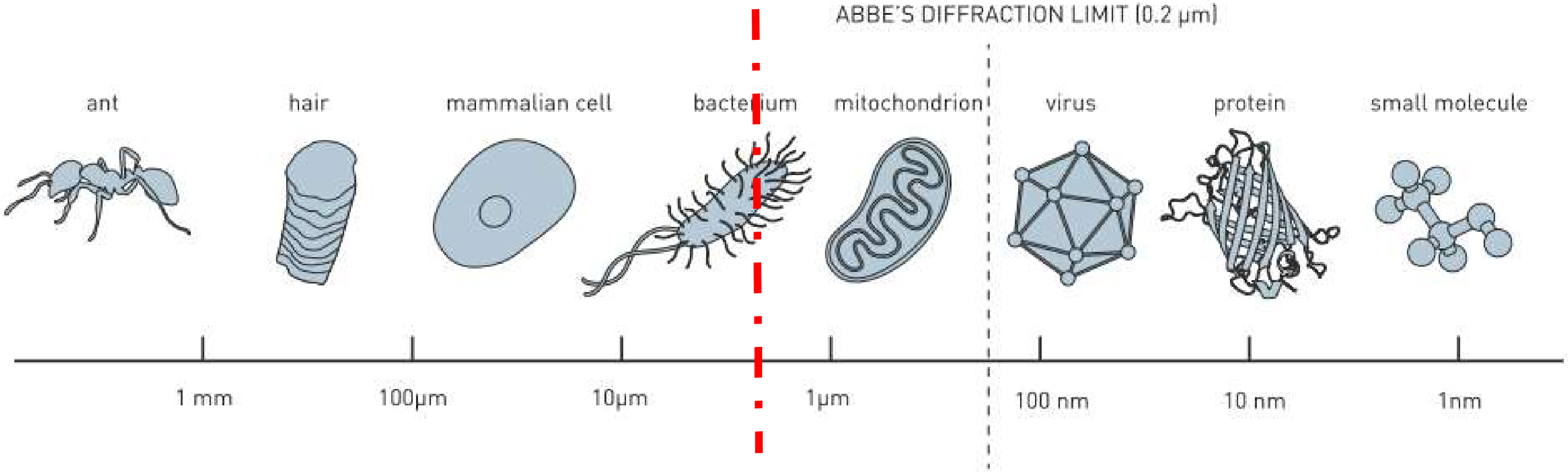
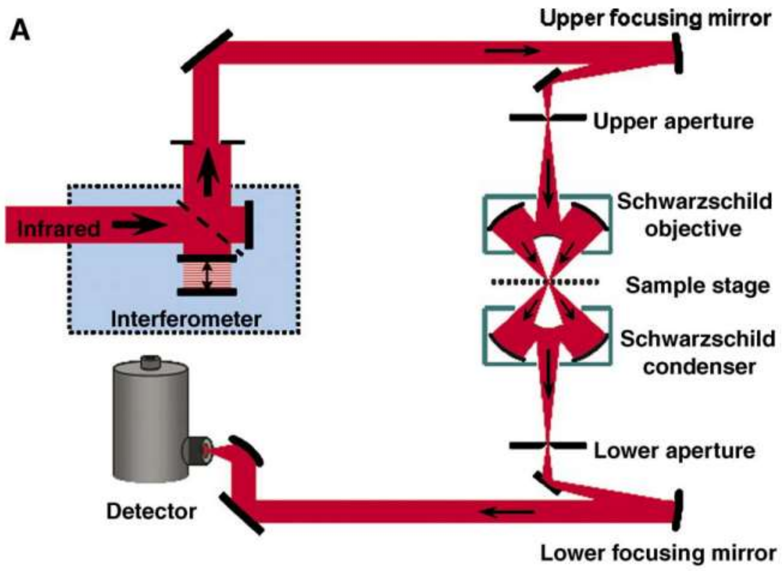
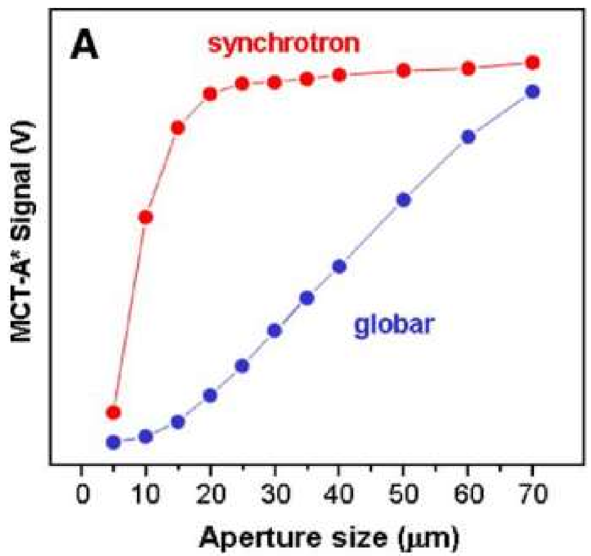
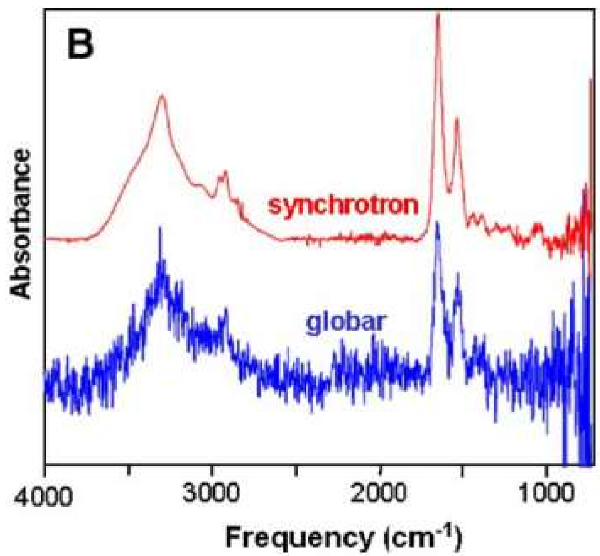


Figure 1. At the end of the 19th century, Ernst Abbe defined the limit for optical microscope resolution to roughly half the wavelength of light, about 0.2 micrometre. This meant that scientists could distinguish whole cells, as well as some parts of the cell called organelles. However, they would never be able to discern something as small as a normal-sized virus or single proteins.



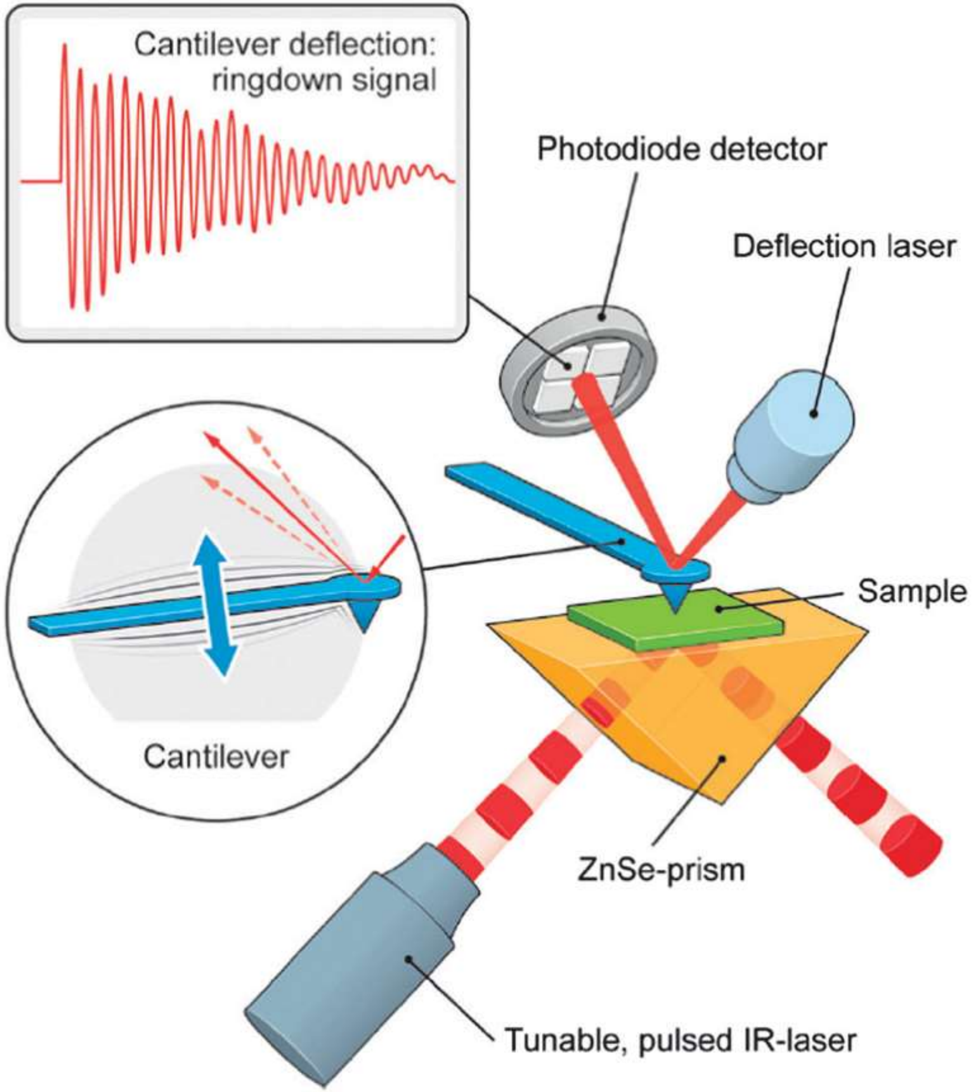
synchrotron radiation useful especially for high-resolution (cells)





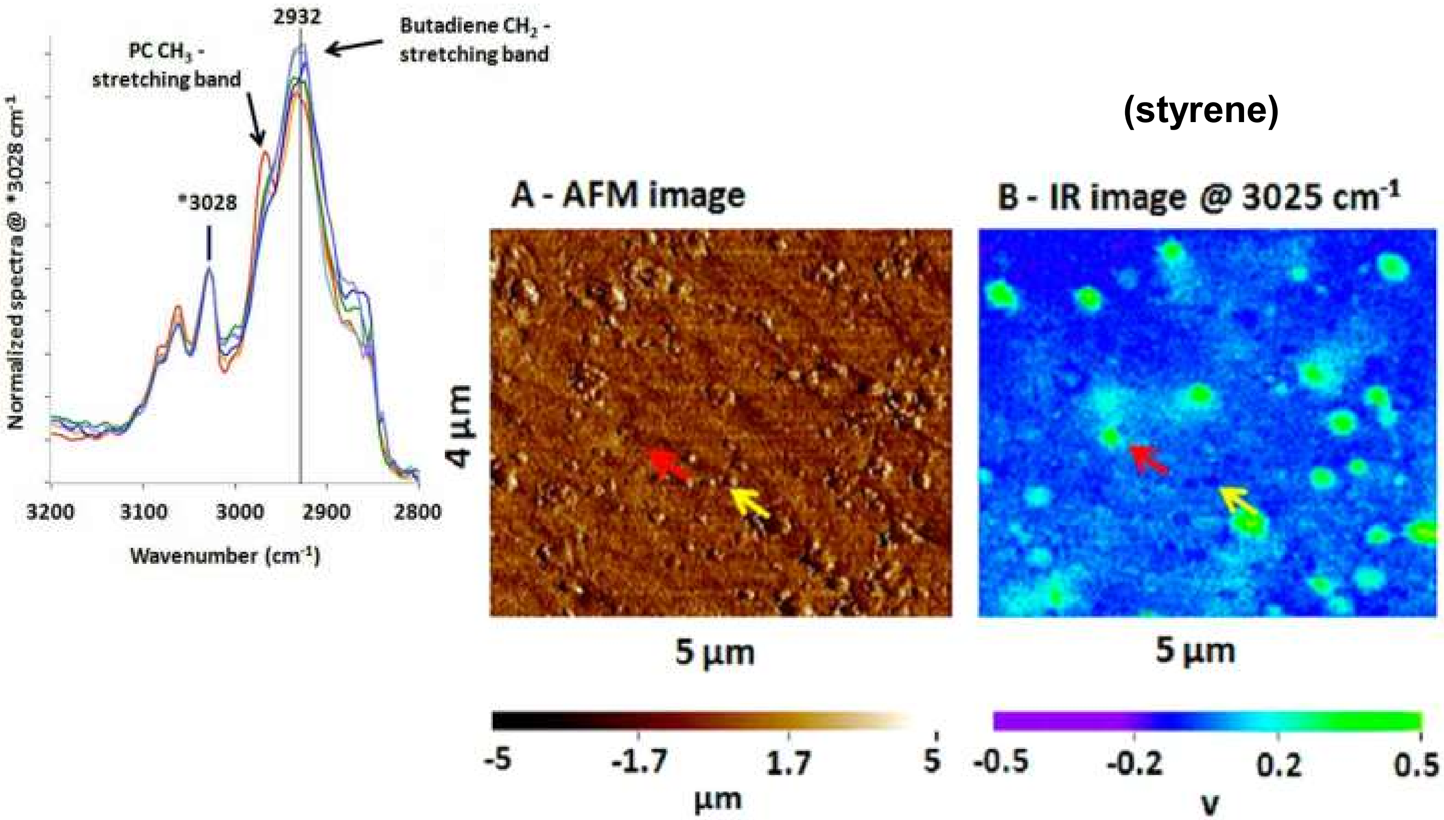
Biochimica et Biophysica Acta 1758 (2006) 846 – 857

AFM-IR



Cantilever deflection:
ringdown signal
Photodiode detector
Deflection laser
Sample
Cantilever
ZnSe-prism
Tunable, pulsed IR-laser

Nanoimaging of acrilonitrile-butadiene-stirene (ABS) polymer



(49) Ye, J.; Midorikawa, H.; Awatani, T.; Marcott, C.; Lo, M.; Kjoller, K.; Shetty, R. Nanoscale Infrared Spectroscopy and AFM Imaging of a Polycarbonate/Acrylonitrile-Styrene/Butadiene Blend. *Microscopy and Analysis* **2012**, *April*, 24−27.

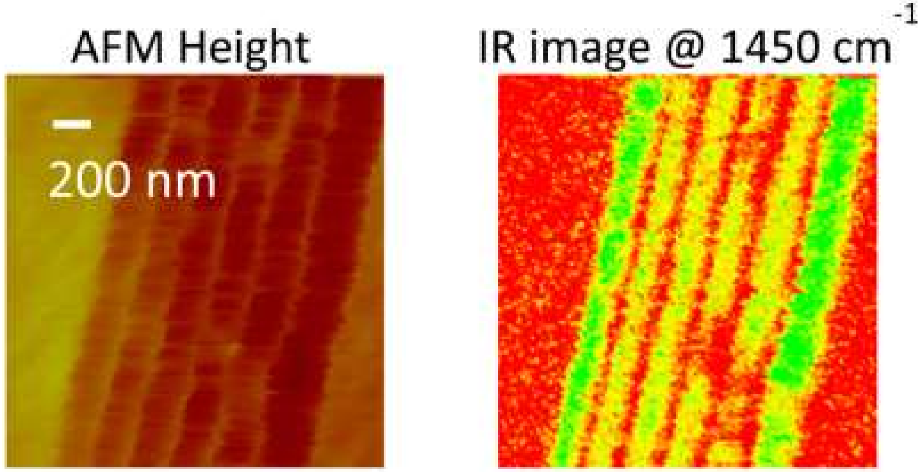
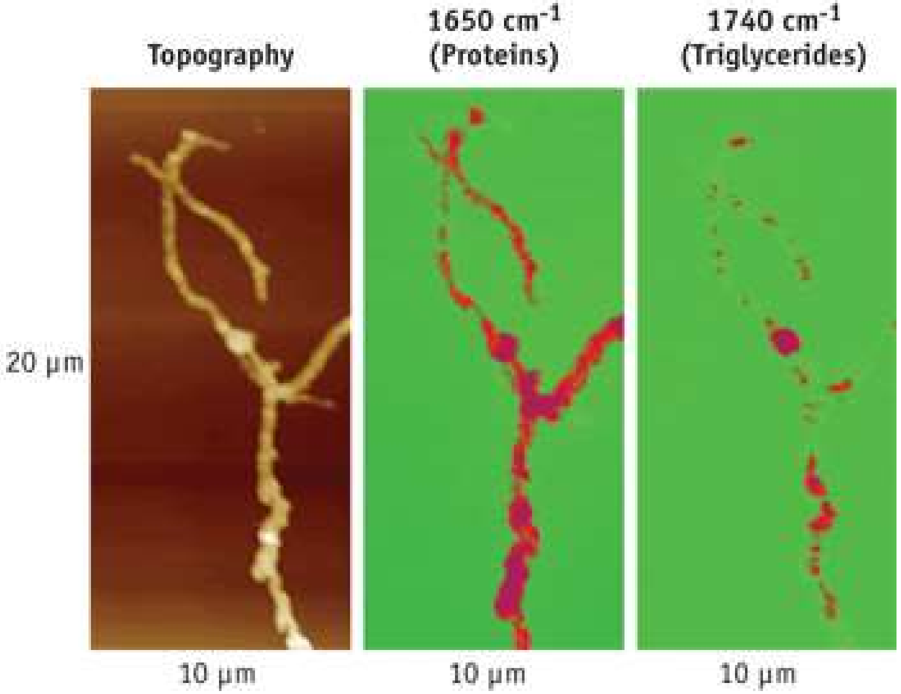


Figure 10. AFM (left) and AFM-IR absorption image (right) of a multilayer laminate film. The AFM-IR absorption image clearly reveals nonuniformity in the layers as well as localized defects. Reprinted with permission. Copyright 2014 Anasys Instruments.



Both AFM (a) and AFM-IR (b, c) images show that the topography of the cell is readily linked to the chemical composition of the energy storage sacks in *Streptomyces* bacteria. At 1650 cm^{-1} (b), the proteinaceous materials are highlighted for most of the cell. With the IR laser tuned to 1740 cm^{-1} (c), only certain locations light up, showing infrared absorption related to triglyceride energy.

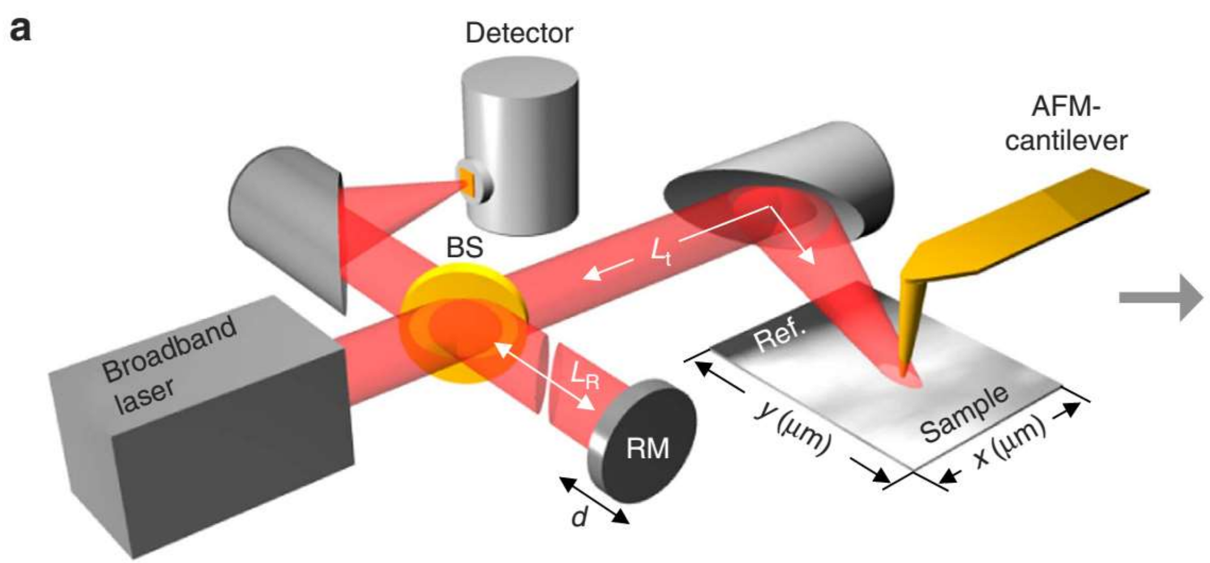
scattering scanning near-field optical microscopy (sSNOM)

ARTICLE

Received 13 Jun 2016 | Accepted 22 Dec 2016 | Published 15 Feb 2017 DOI: 10.1038/ncomms14402 OPEN

Hyperspectral infrared nanoimaging of organic samples based on Fourier transform infrared nanospectroscopy

Iban Amenabar[1], Simon Poly[1,2], Monika Goikoetxea[1,3], Wiwat Nuansing[1], Peter Lasch[4] & Rainer Hillenbrand[5,6]



ARTICLE

Received 12 Jul 2013 | Accepted 7 Nov 2013 | Published 4 Dec 2013 DOI: 10.1038/ncomms3890 OPEN

Structural analysis and mapping of individual protein complexes by infrared nanospectroscopy

Iban Amenabar[1], Simon Poly[1], Wiwat Nuansing[1], Elmar H. Hubrich[2], Alexander A. Govyadinov[1], Florian Huth[1,3], Roman Krutokhvostov[1], Lianbing Zhang[1], Mato Knez[1,4], Joachim Heberle[2], Alexander M. Bittner[1,4] & Rainer Hillenbrand[1,4]

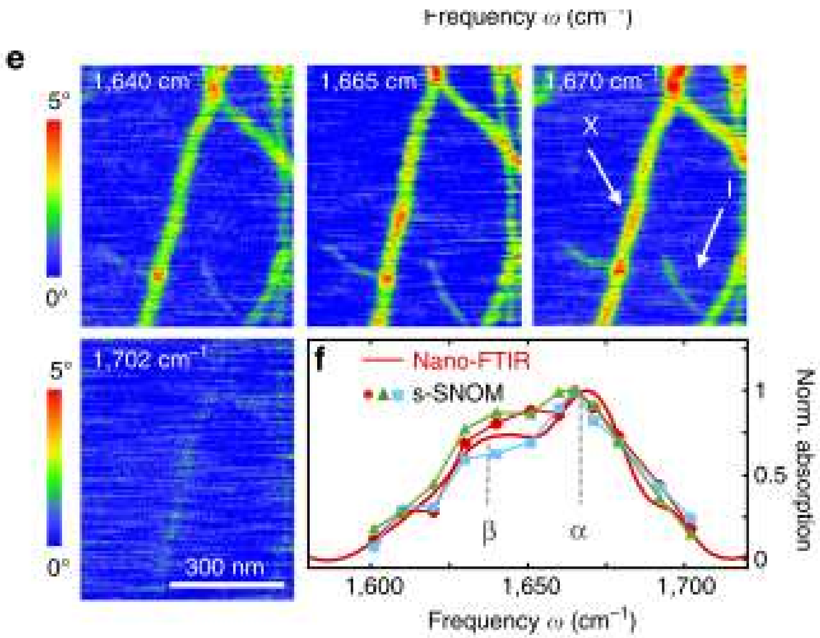


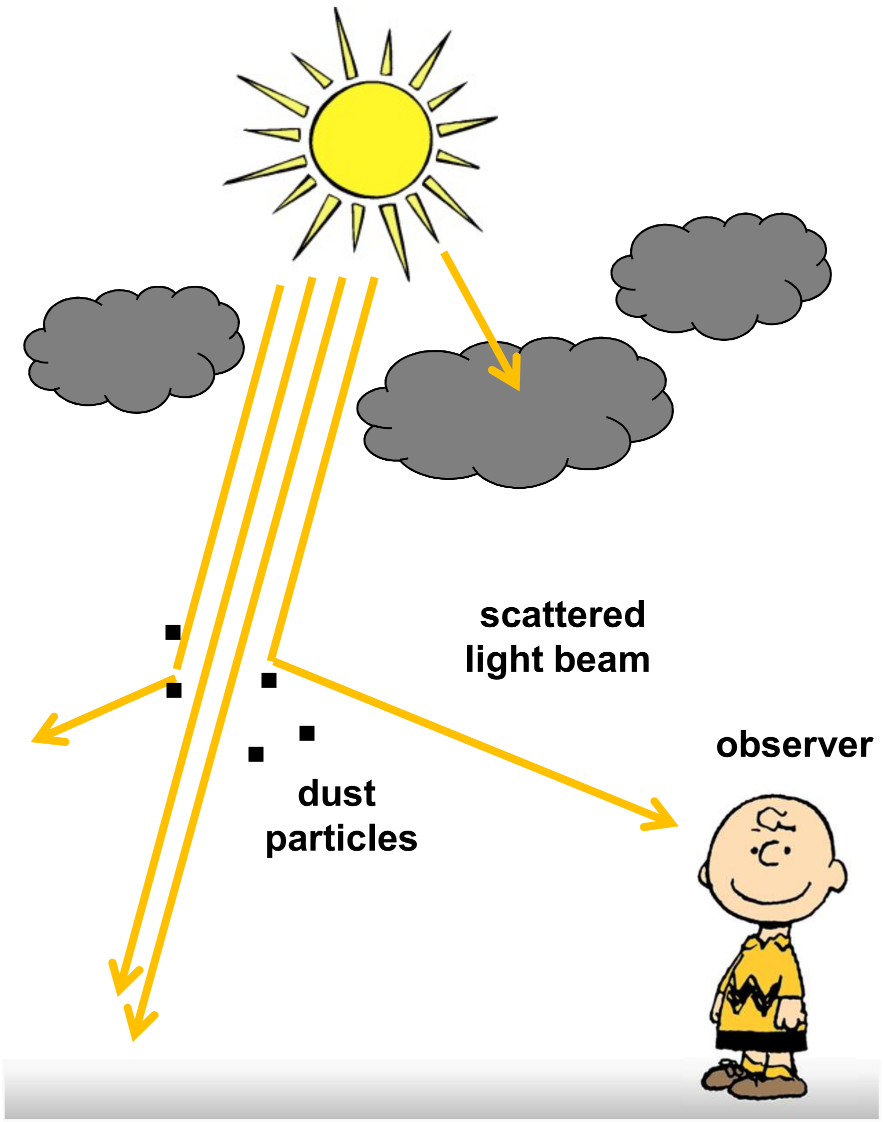
Figure 6 | Infrared nanospectroscopy and nanoimaging of secondary structure in individual insulin fibrils. (**a**) Topography of insulin fibrils on a silicon substrate. Scale bar, 200 nm. The arrows indicate a type I fibril (I) and a 9-nm-thick fibril composed of several protofilaments (X),

RAMAN

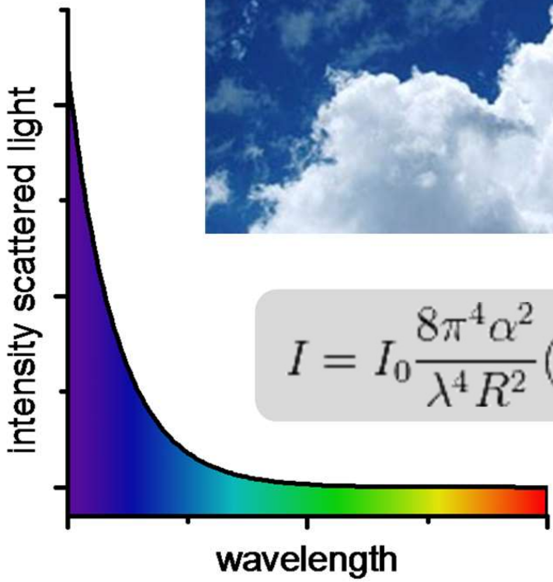
Light scattering: what is it?

scatter (verb)
To (cause to) move far apart in different directions.

(from the Cambrigde Advanced Learner's Dictionary)

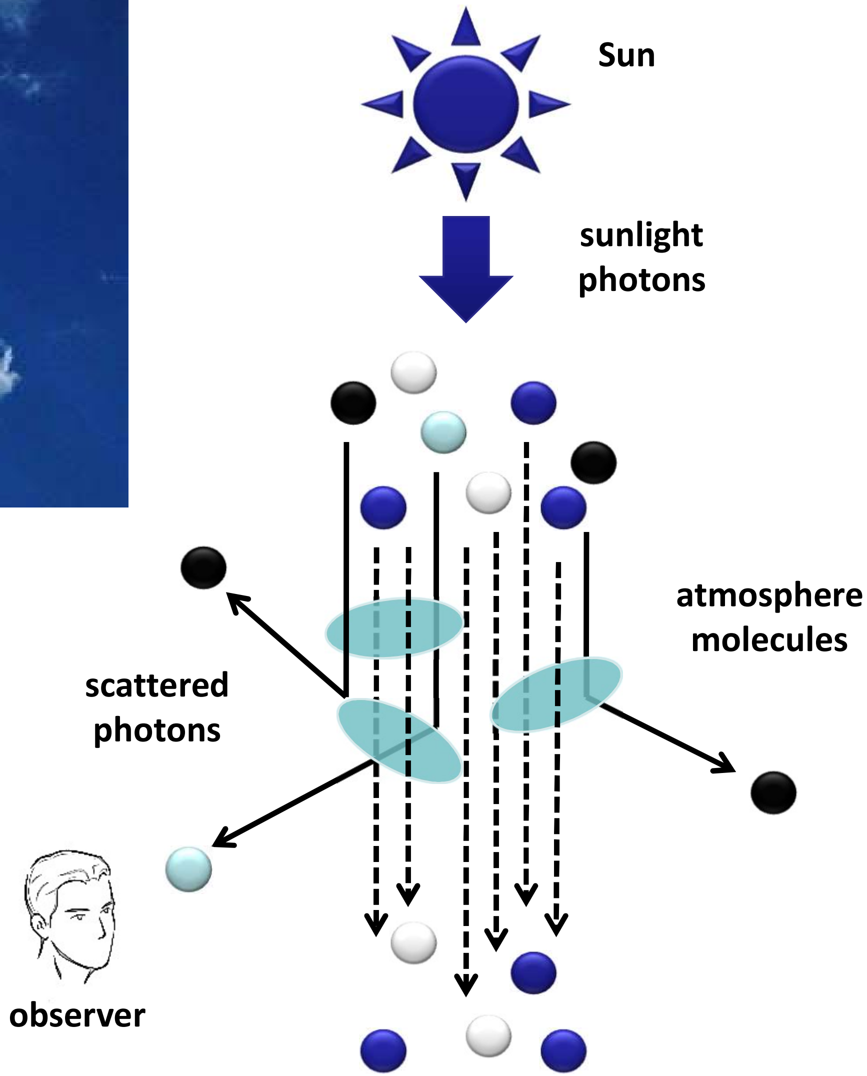


Light scattering and blue sky



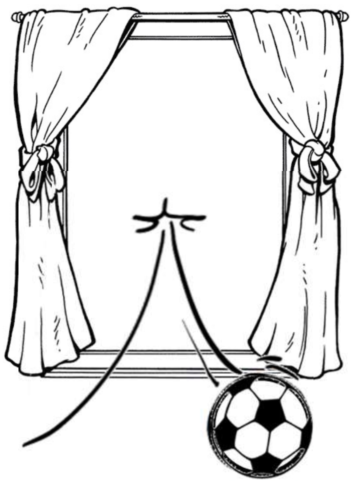
$$I = I_0 \frac{8\pi^4\alpha^2}{\lambda^4 R^2}(1+\cos^2\theta).$$

The scattering at 400 nm is 9.4 times as great as that at 700 nm for equal incident intensity

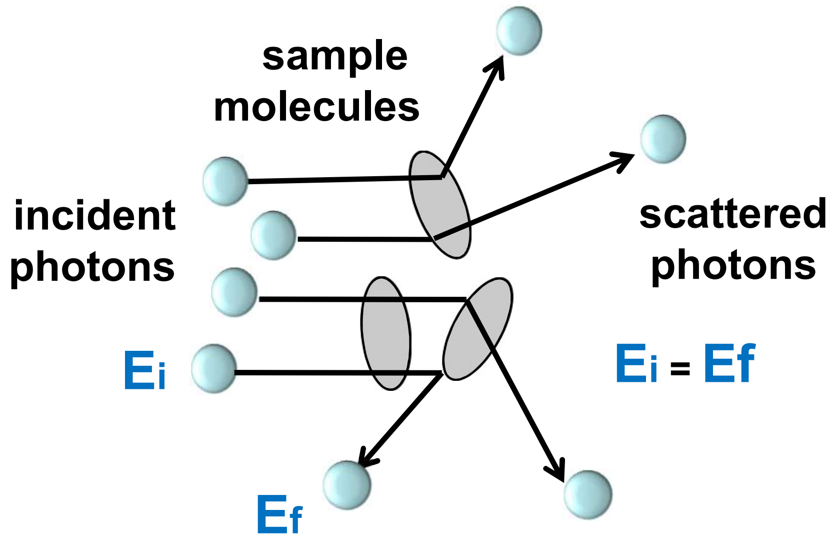


“Elastic” and “inelastic” scattering

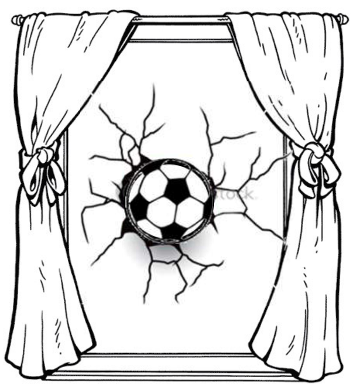
elastic process



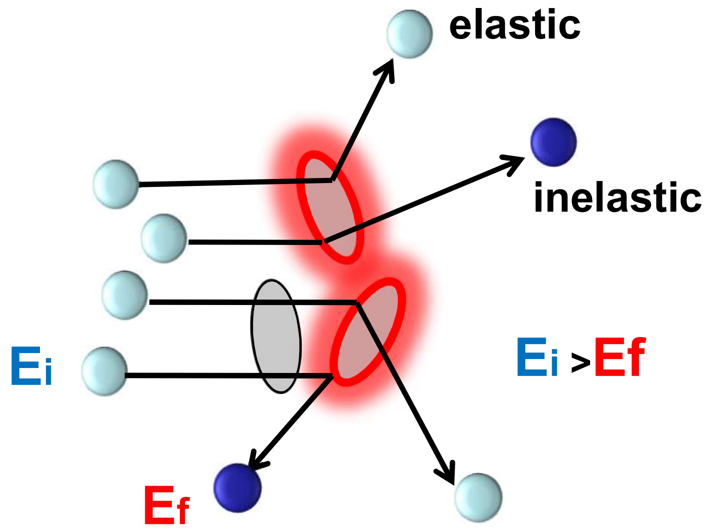
no energy is exchanged



*in*elastic process



energy is exchanged!



1928: a "new type of radiation"

A New Type of Secondary Radiation.

IF we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and

N 2

track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

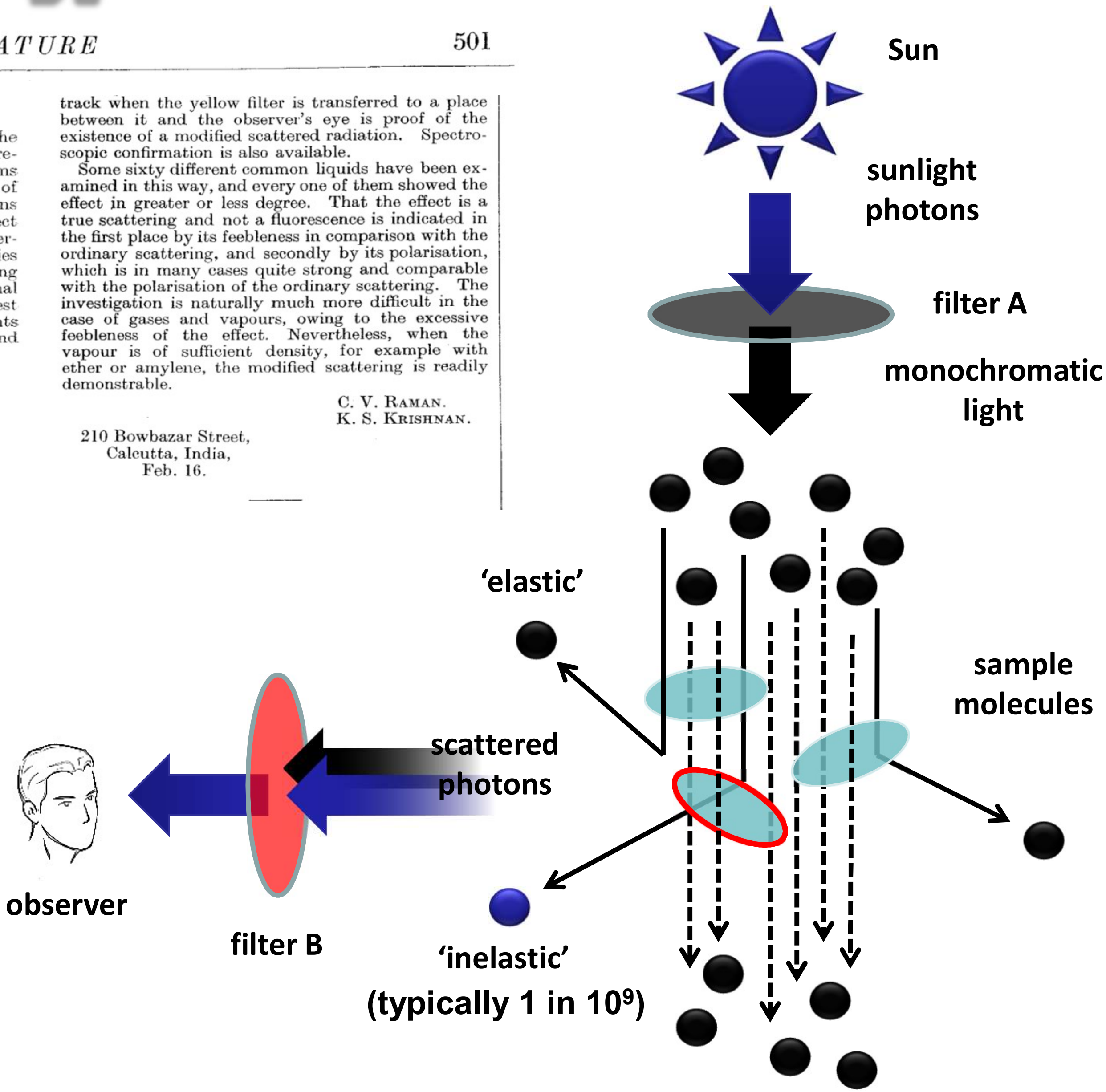
Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. RAMAN.
K. S. KRISHNAN.

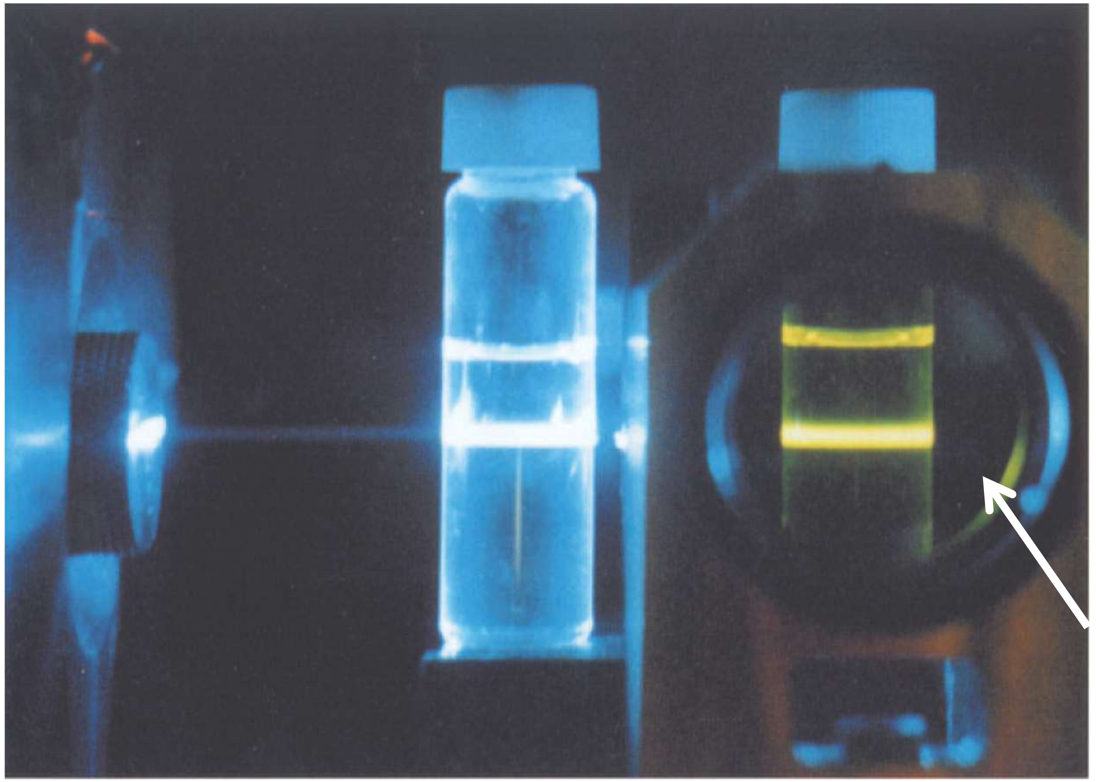
210 Bowbazar Street,
Calcutta, India,
Feb. 16.

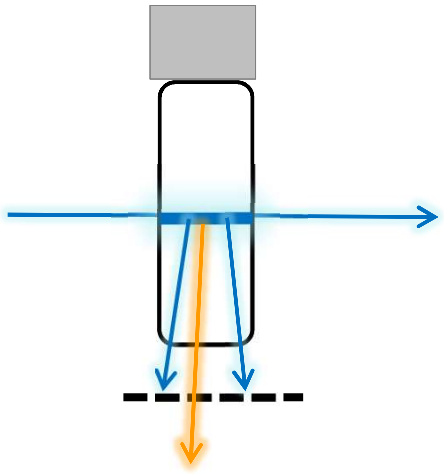
Chandrasekhar Venkata Raman
(1888-1970)

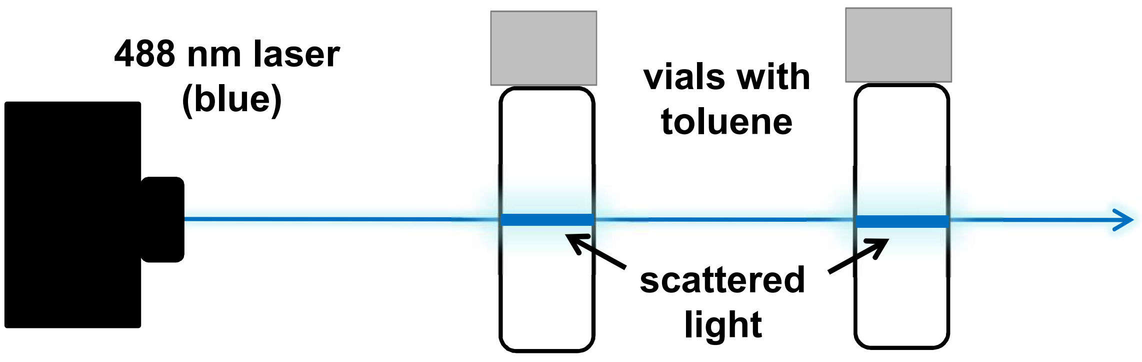
Nobel Prize for
Physics in 1930



Observing the Raman effect (nowadays)







Raman scattering involves vibrational transition

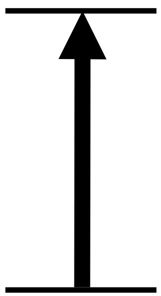
Raman scattering

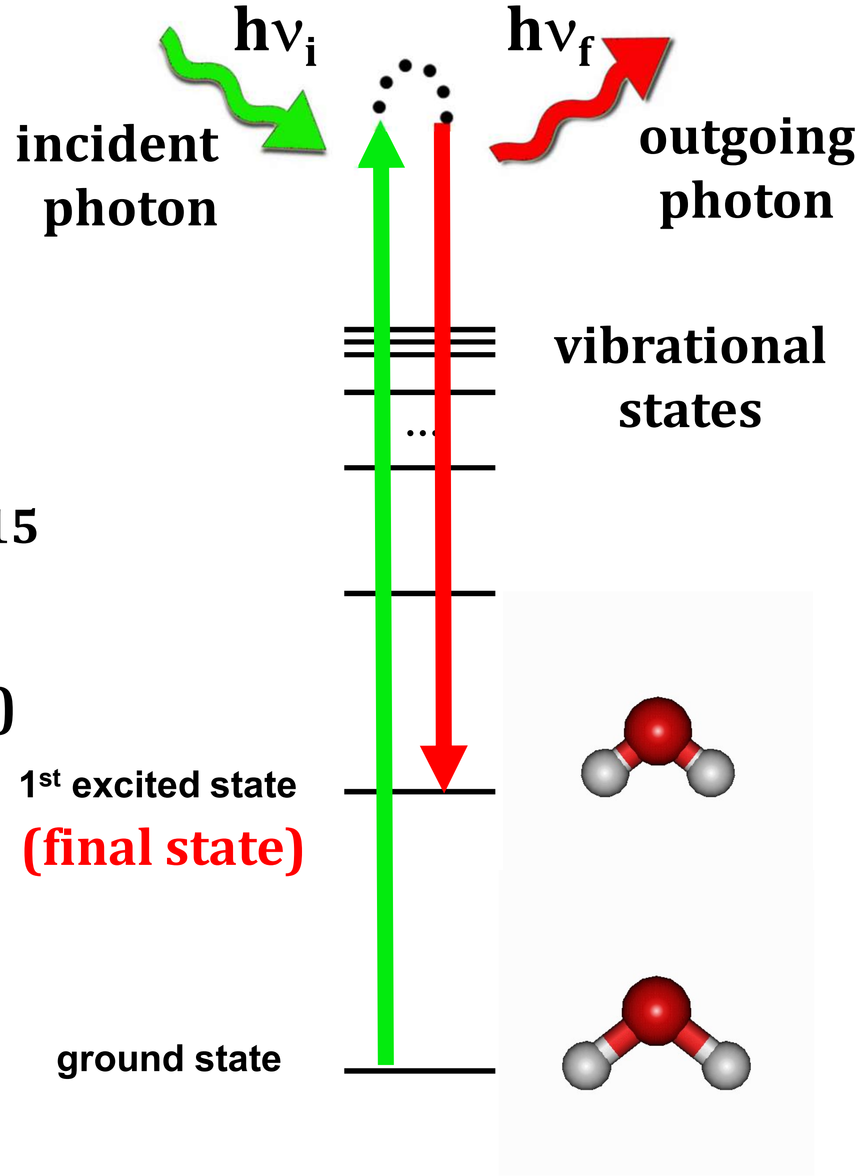
is a "*two photons*" process

instantaneous (10^{-15} s)

(fluorescence is just 10^{-9} s)

resulting transition is from ground to 1st excited state





The "economy" of Raman processes

according to A. Einstein (?)

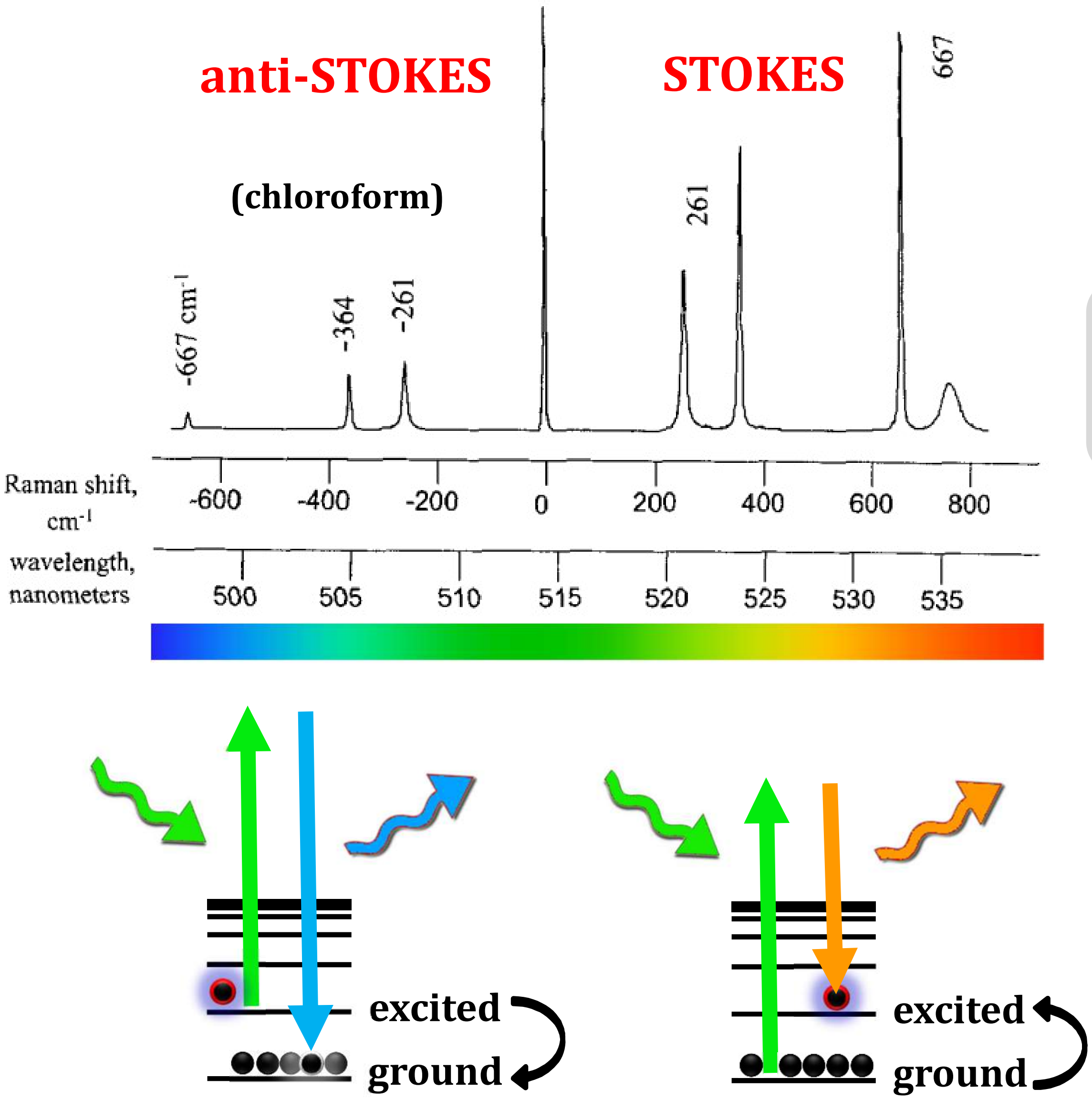
IR

is analogous to putting 10¢ in a Coke machine and getting a Coke

Raman

is analogous to putting $1.00 in a Coke machine and getting a Coke plus 90¢ change

Raman Stokes and Anti-Stokes



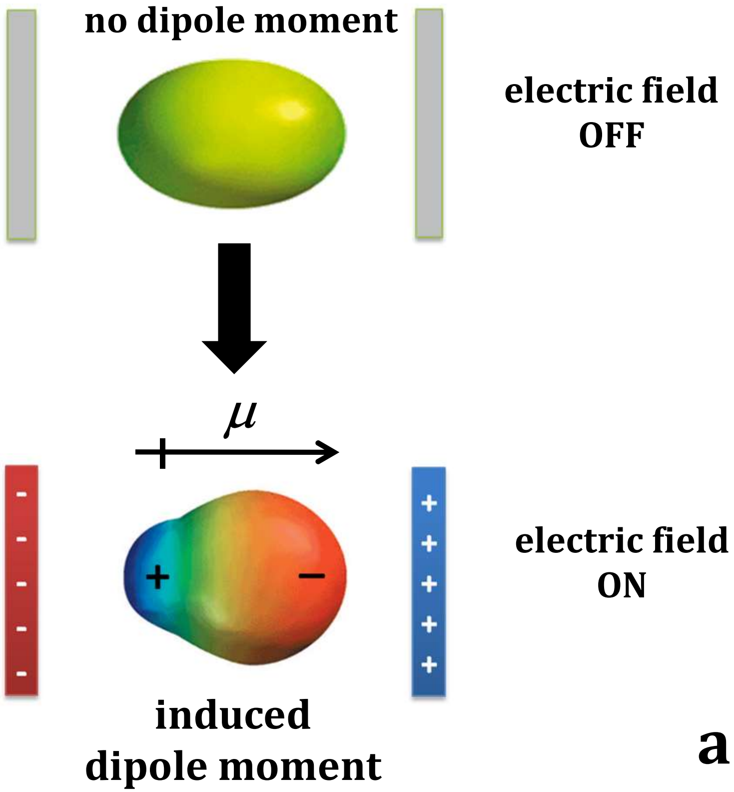
intensity ratio between Stokes and anti-Stokes bands

$$\frac{I_{Stokes}}{I_{A-Stokes}} \propto \exp\left(\frac{-hc\tilde{\nu}_i}{kT}\right)$$

Boltzmann!

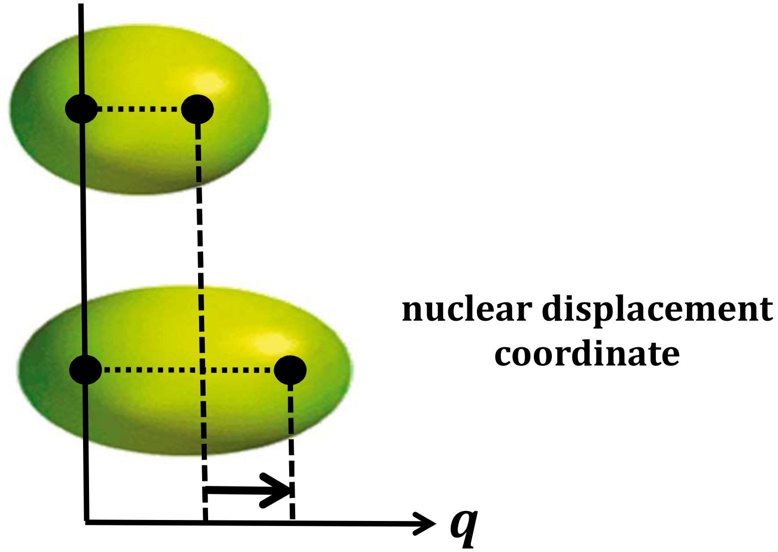
at RT, the ground state is much more populated than the excited state

Are all vibrations “Raman active”?



$$\mu = \alpha \cdot E$$

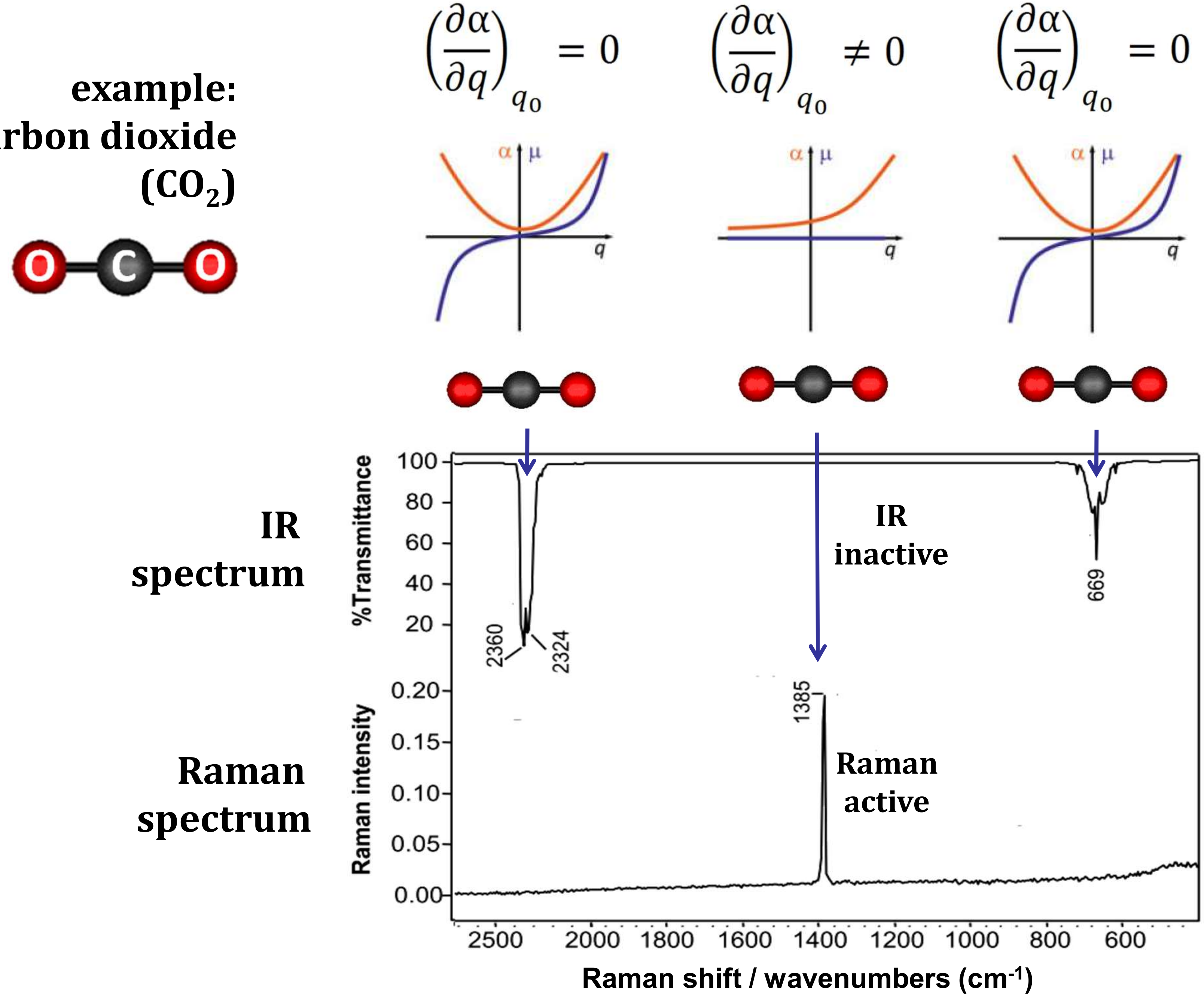
↑
molecular polarizability



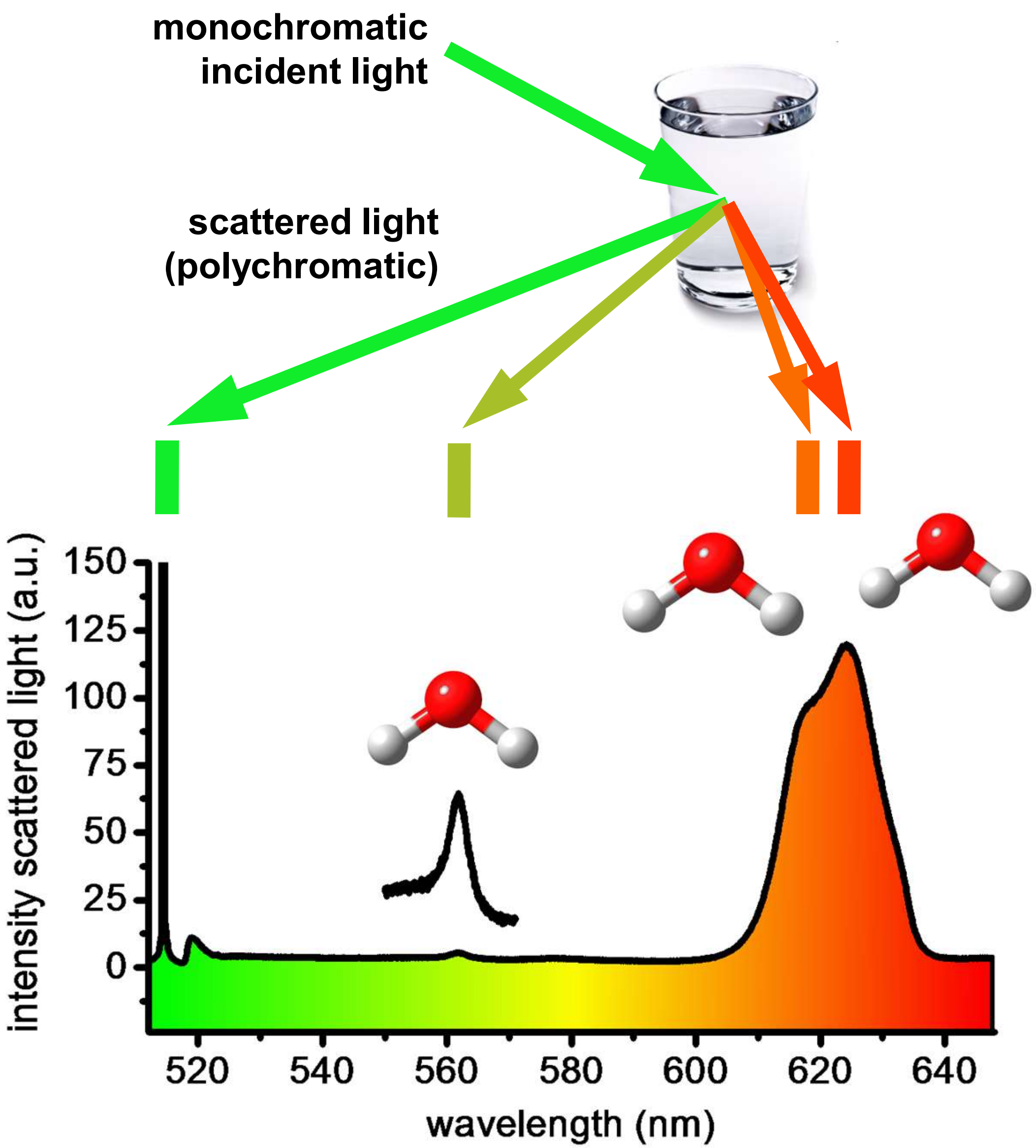
a vibration is Raman active **if** $\left(\frac{\partial \alpha}{\partial q}\right)_{q_0} \neq 0$

... if during the vibration the polarizability changes in a “definite” way

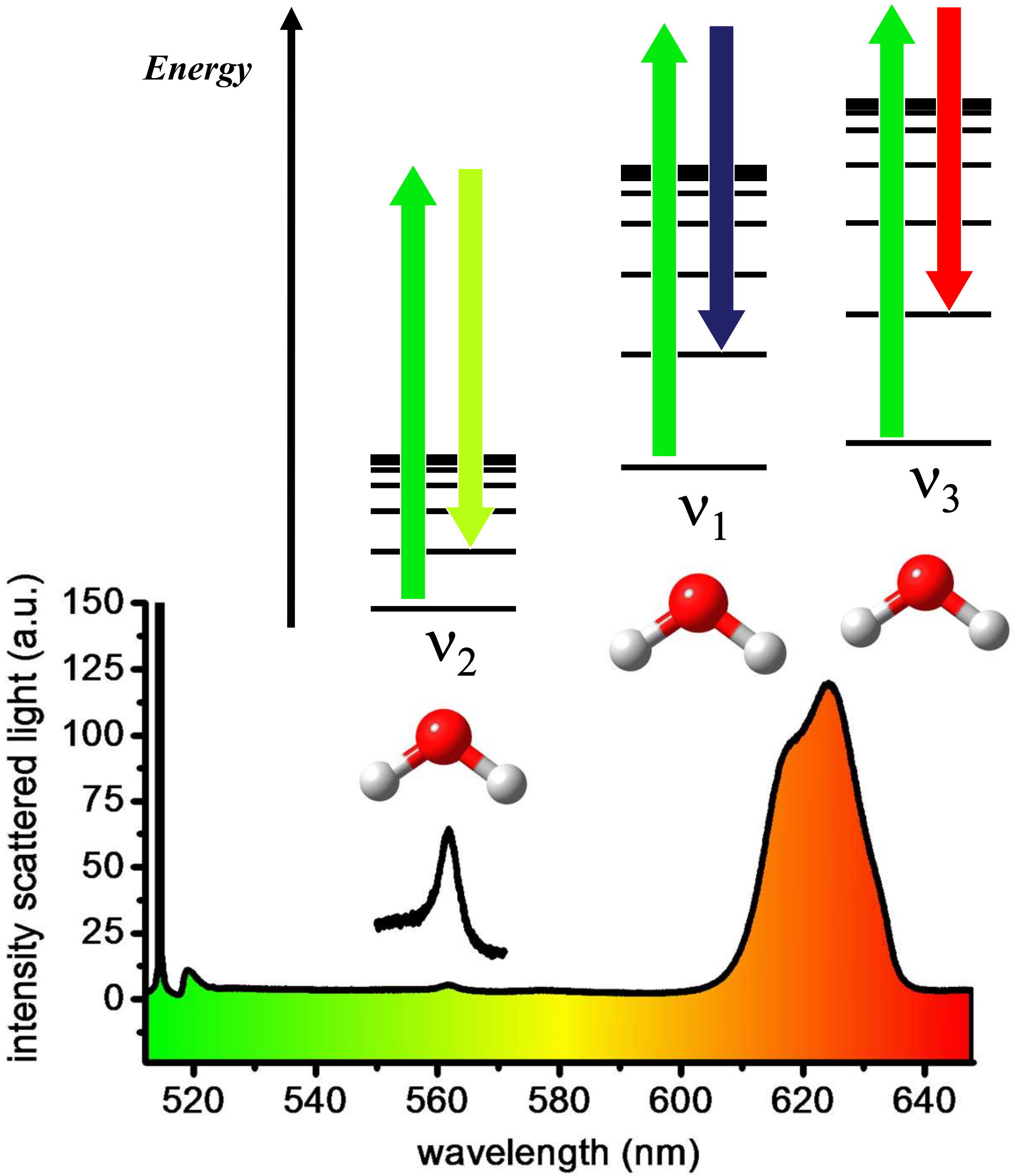
example: carbon dioxide (CO_2)



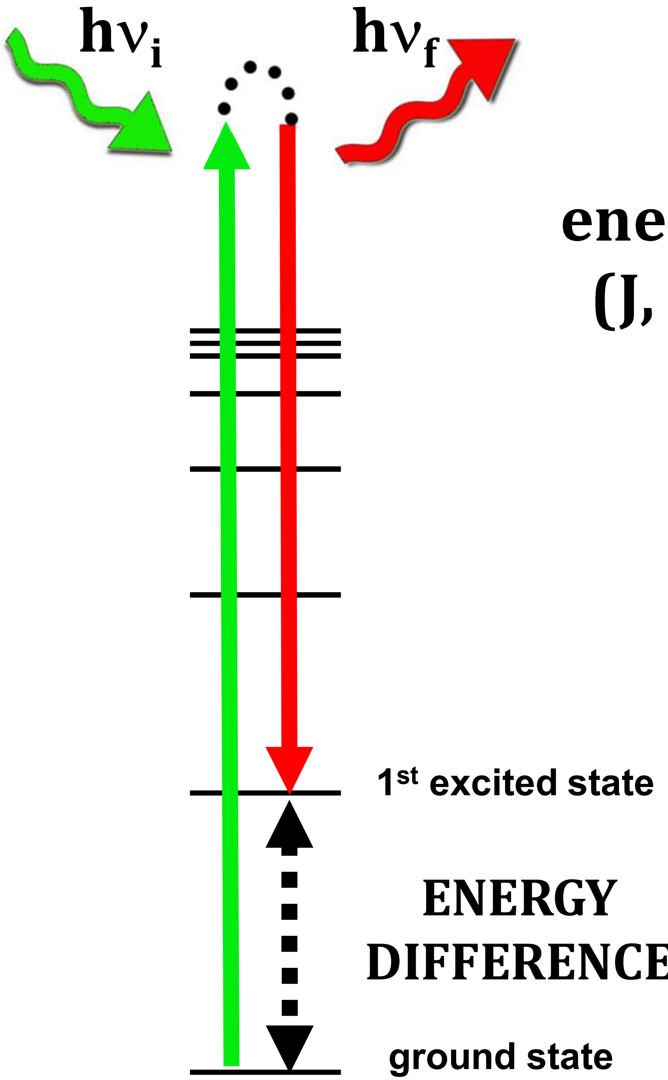
Raman spectra and molecular vibrations



Raman spectra and molecular vibrations



nergy, frequency, wavelengths and wavenumbe



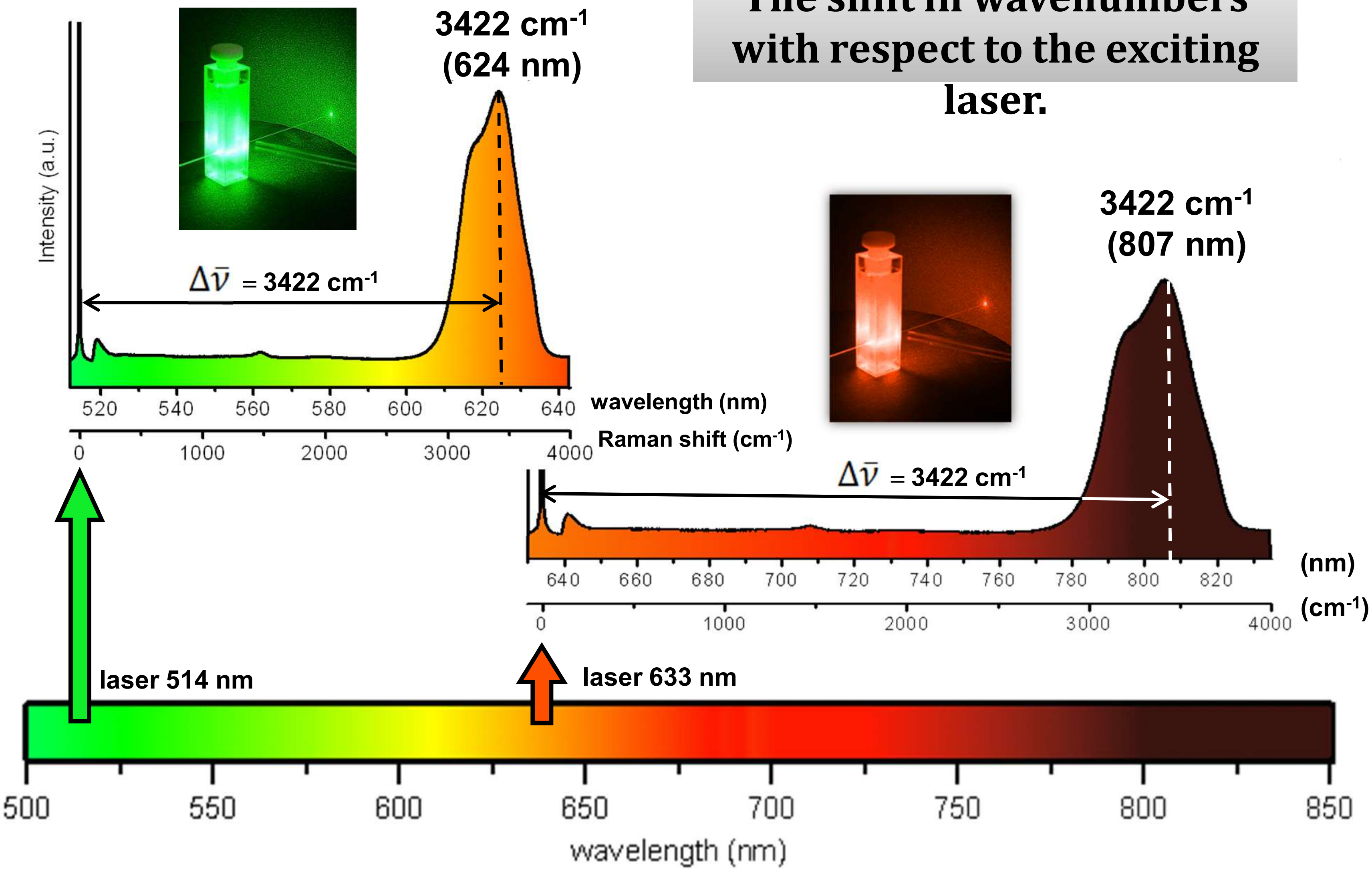
energy ⇄ radiation (waves)

energy E (J, eV)	$E = h\nu$	frequency ν (Hz, GHz)
	$\downarrow \; \nu = \frac{c}{\lambda}$	
	$E = \frac{hc}{\lambda}$	wavelength λ (nm)
	$\downarrow \; \frac{1}{\lambda} = \tilde{\nu}$	
	$E = hc\tilde{\nu}$	wavenumber $\tilde{\nu}$ (cm^{-1}) number of λ in 1 cm

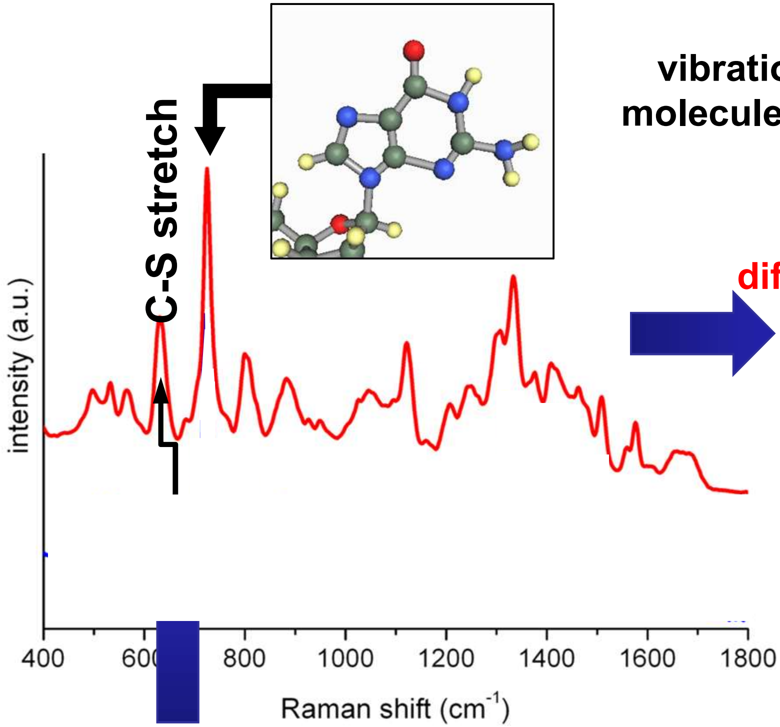
(e.g. 1000 cm^{-1} = 0.15 eV = $2.4 \cdot 10^{-20}$ J)

The Raman shift

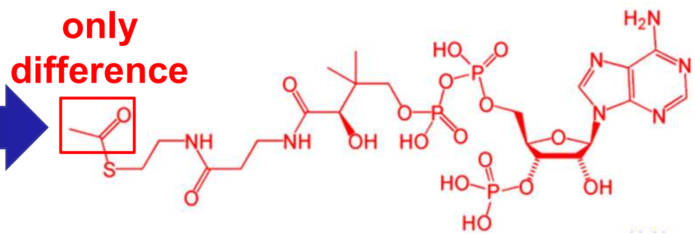
The shift in wavenumbers with respect to the exciting laser.



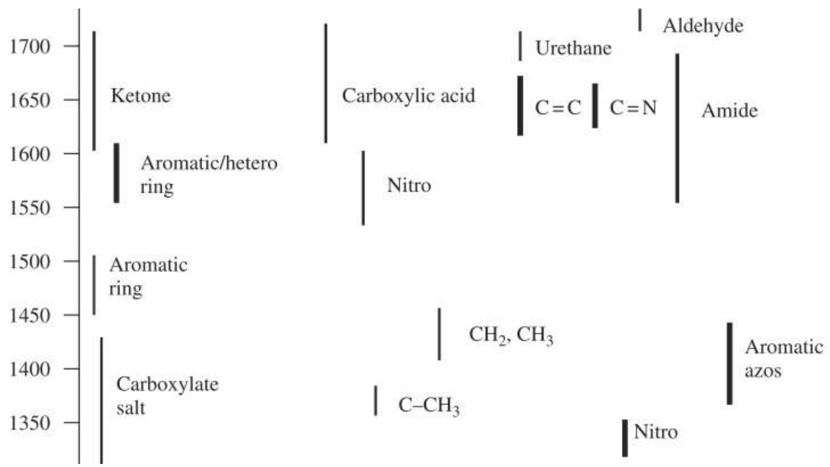
We do have a Raman spectrum, so what?



vibrations of larger molecules are complex



molecular “fingerprint”

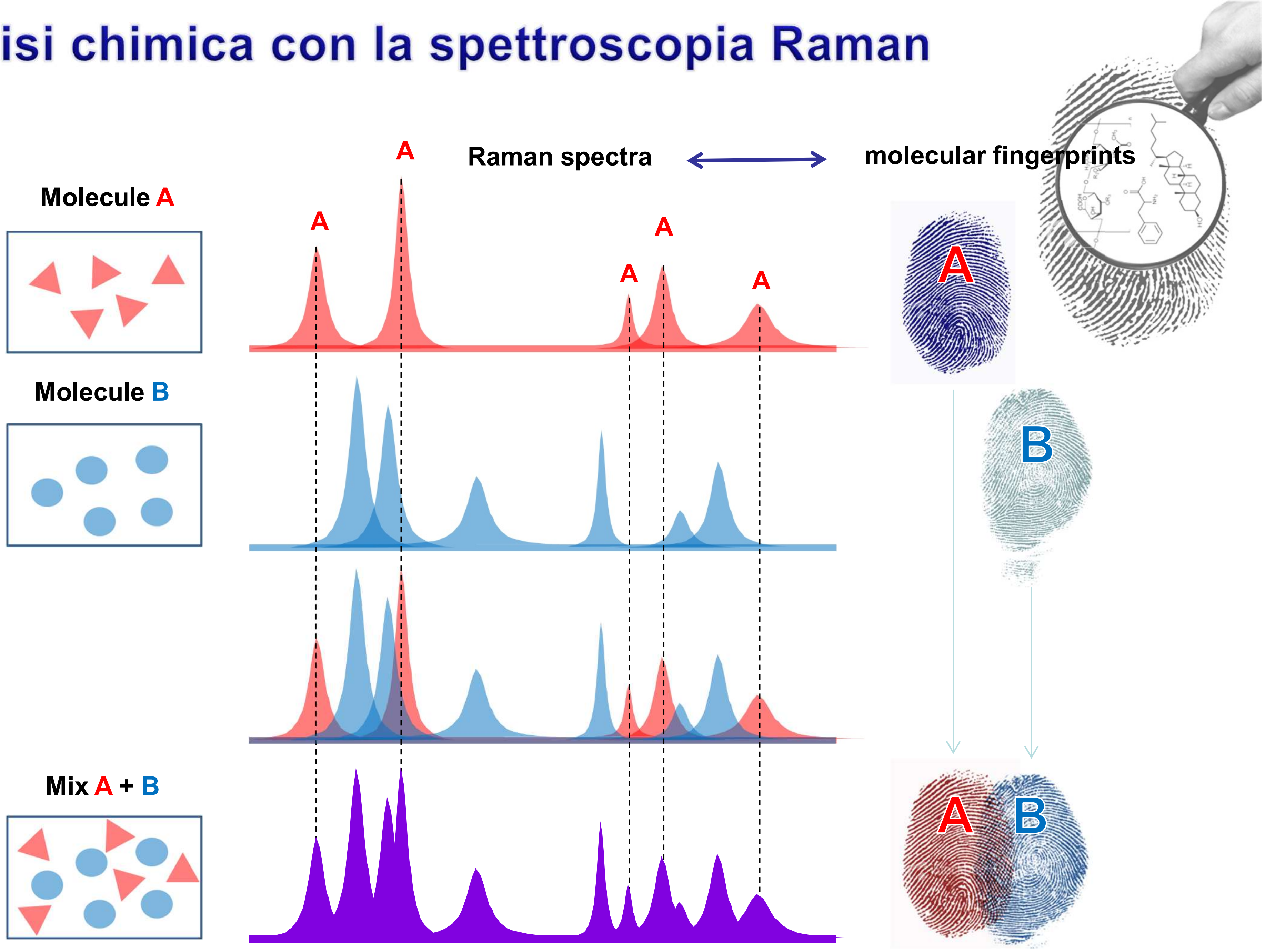


DIFFERENCES
each molecule has a unique Raman spectrum

spectrum ↔ structure direct correlation

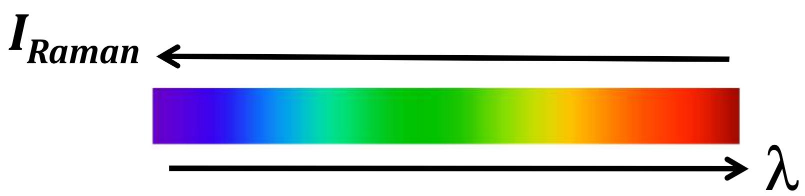
SIMILARITIES
characteristic “group” Raman shifts

nalisi chimica con la spettroscopia Raman

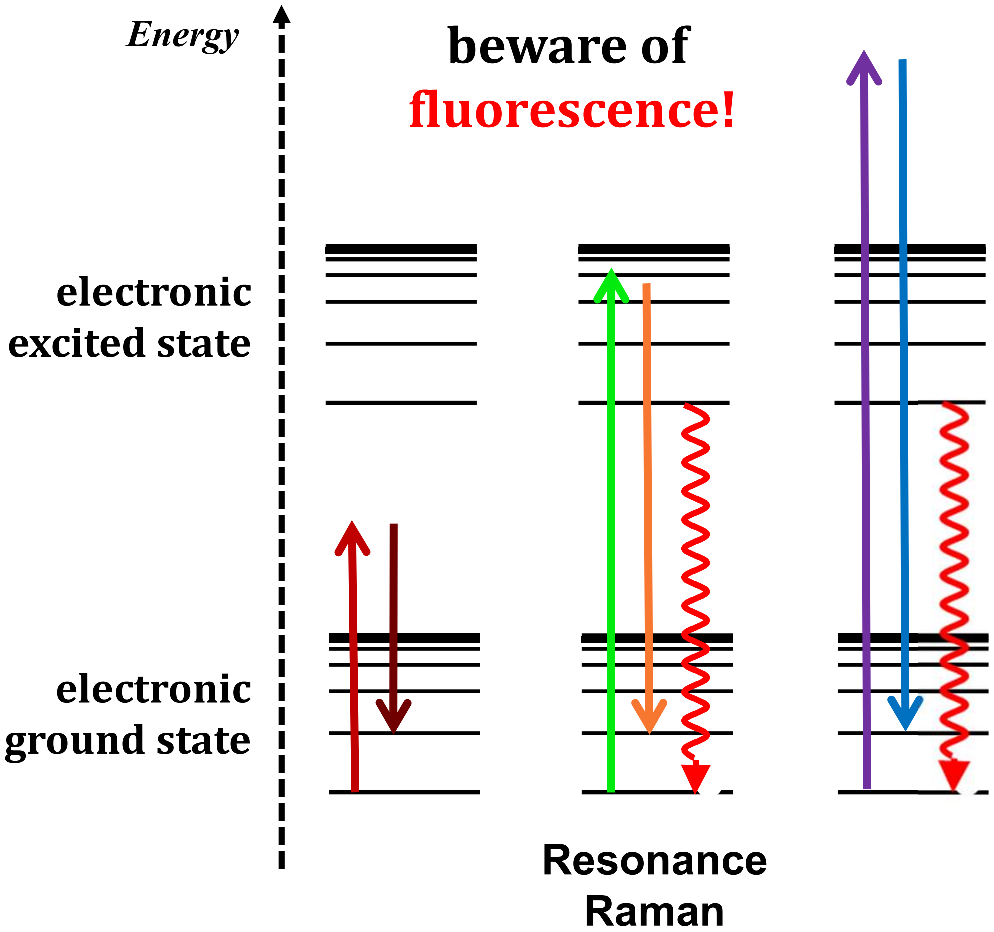


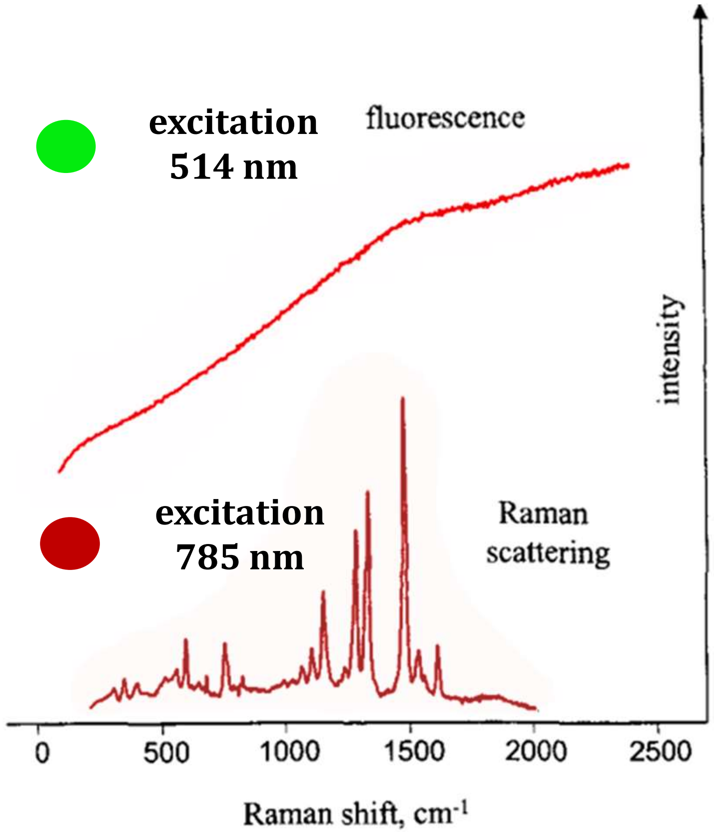
Excitation wavelength matters...

$I_{Raman} \propto (\nu_0)^4$



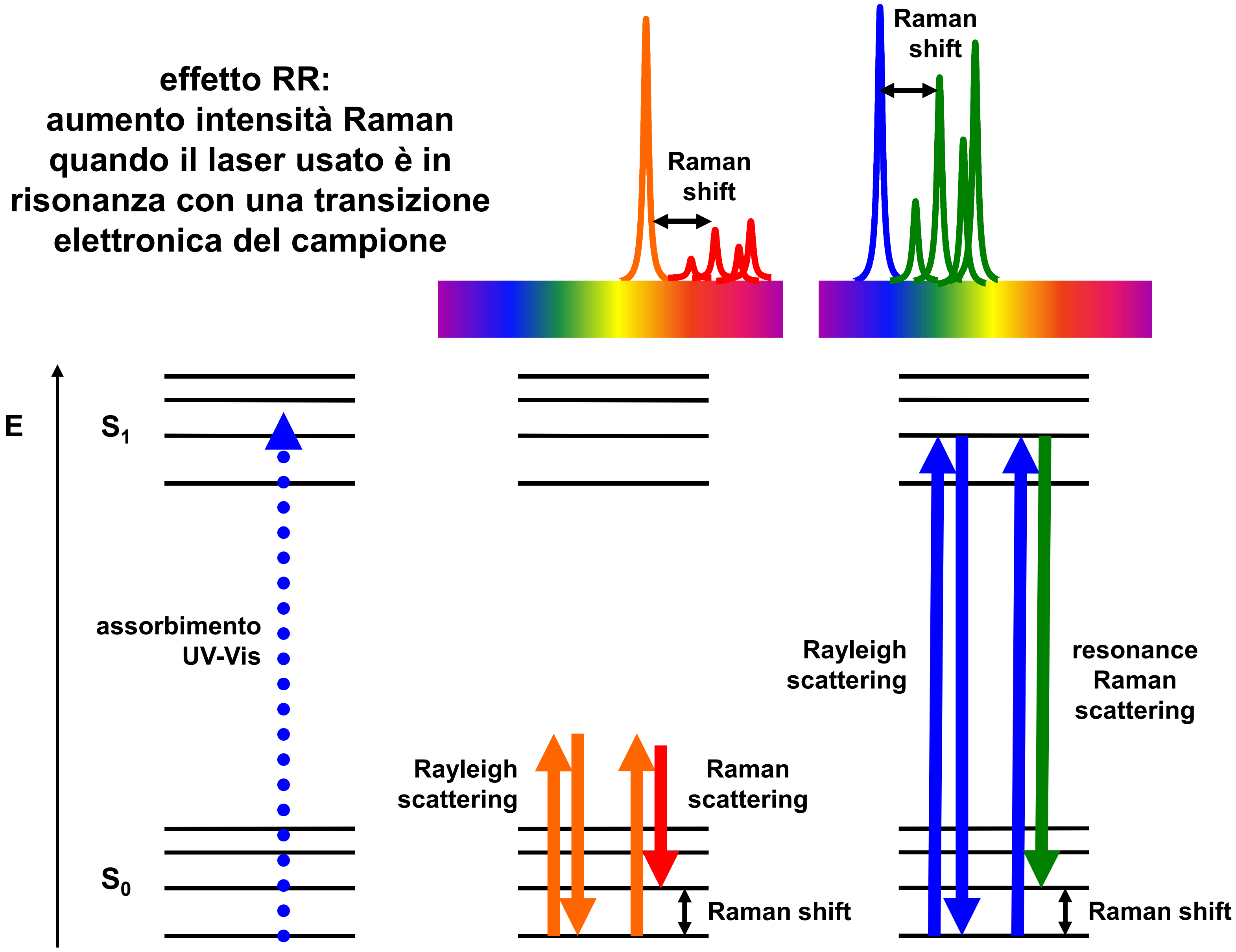
overall intensity depends on the laser "color"



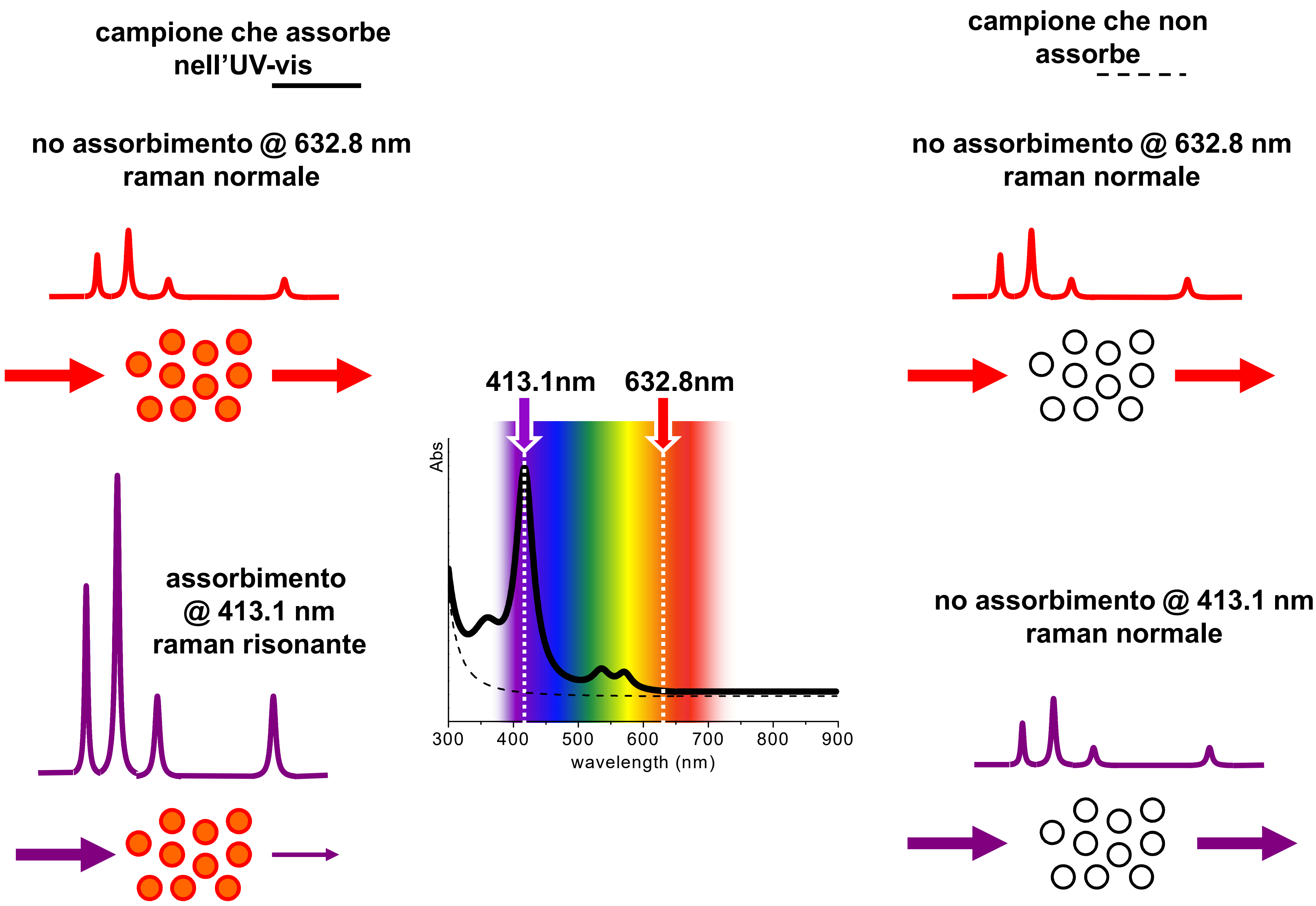


La Spettroscopia Raman Risonante (RR)

effetto RR:
aumento intensità Raman quando il laser usato è in risonanza con una transizione elettronica del campione

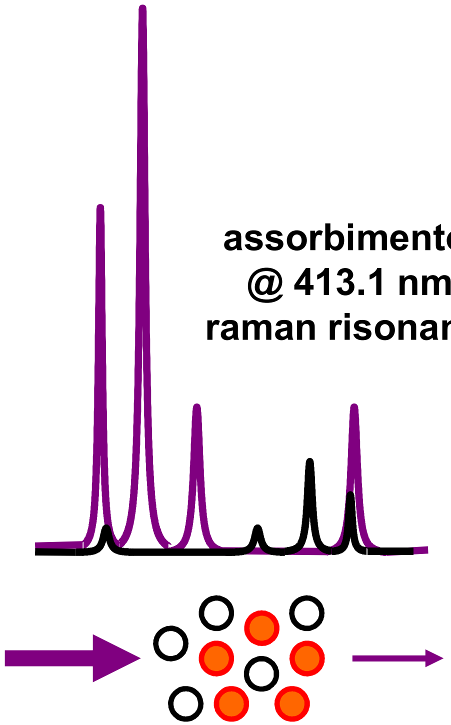


La Spettroscopia Raman Risonante (RR)

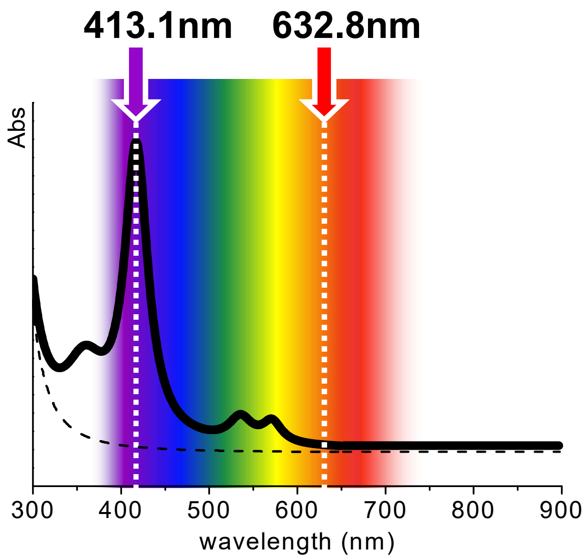


La Spettroscopia Raman Risonante (RR)

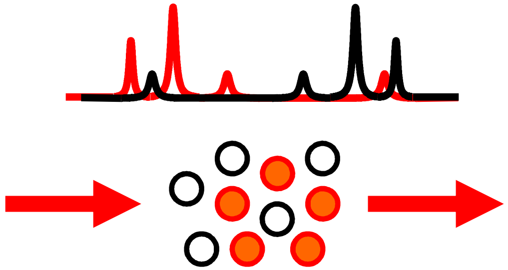
effetto RR introduce selettività in sistemi a più componenti dove essi si differenzino per le proprietà di assorbimento



assorbimento @ 413.1 nm raman risonante



no assorbimento @ 632.8 nm raman normale



IMPORTANZA DI SCEGLIERE IL LASER “GIUSTO”

[fluorescenza e Raman Risonante nei tessuti]

FL Fluorescenza

RR Raman risonante

(pro o contro?)

esempio:
tessuto bioptico

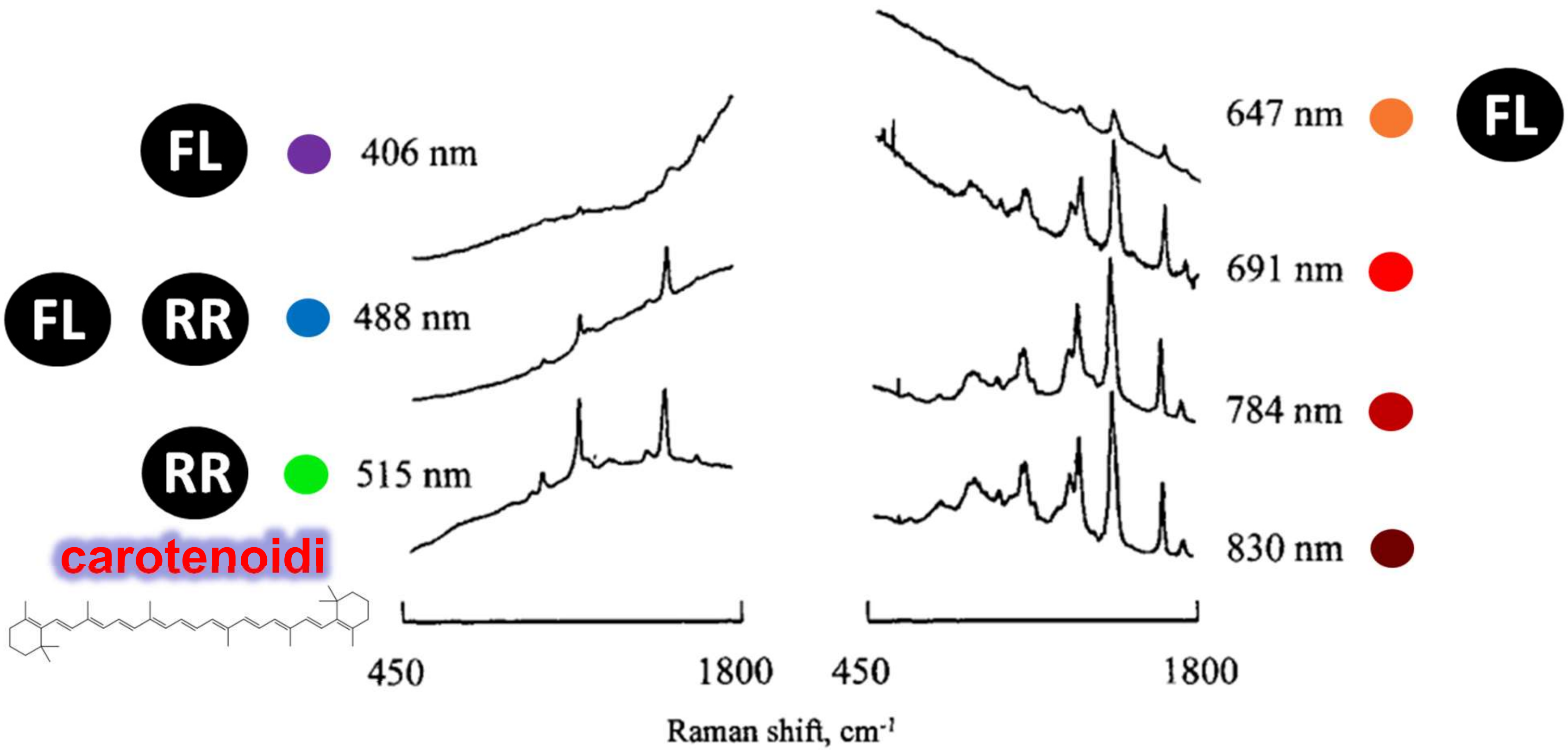
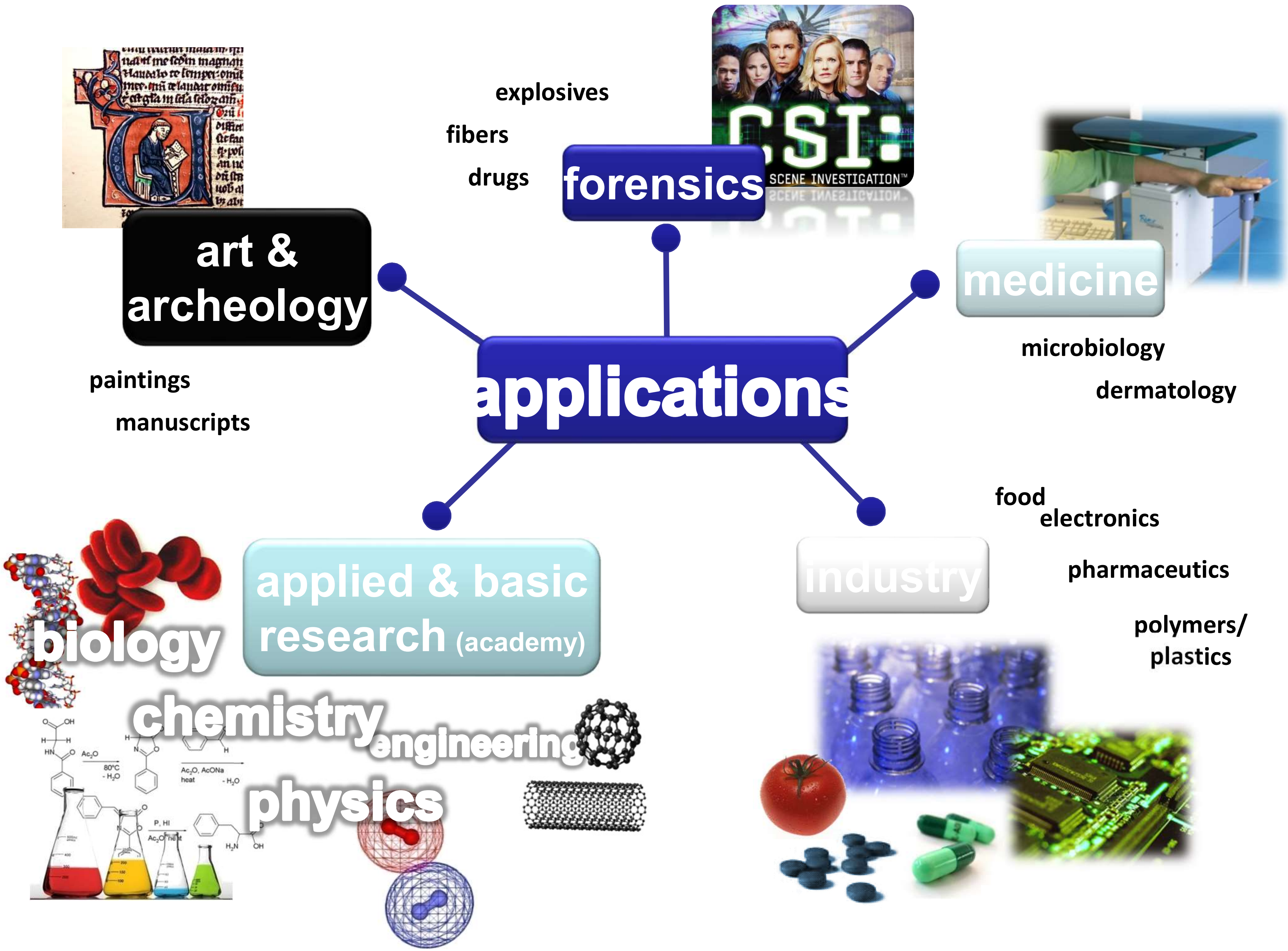


Immagine adattata da
McCreery R.L., “Raman Spectroscopy for Chemical Analysis”, Wiley, NY, 2000

Raman characteristics: a summary

- **flexibile** ***(liquid, solid, etc. samples, no preparation)***
- **non-destructive**
- **water "friendly"** ***(water poor scatterer)***


applications
art & archeology
paintings
manuscripts
forensics
explosives
fibers
drugs
CSI:
SCENE INVESTIGATION™
medicine
microbiology
dermatology
industry
food
electronics
pharmaceutics
polymers/ plastics
applied & basic research (academy)
biology
chemistry
engineering
physics

About Mars
· The Red Planet
· Methane on Mars
· Life on Mars?
· The Ages of Mars

ExoMars Programme
· Programme overview
· ExoMars mission team
· Meet the team

ExoMars 2016 Mission
· Mission overview
· Trace Gas Orbiter
· Schiaparelli (EDM)
· Trace Gas Orbiter instruments
· Schiaparelli science

· Mission overview
· ExoMars rover
· Rover instruments
· Rover drill
· Surface platform
· Landing site

Exploring Mars
· Missions to Mars
· European heritage
· Mars Sample Return

Resources
· Images & Videos

THE EXOMARS ROVER INSTRUMENT SUITE

RLS - RAMAN SPECTROMETER

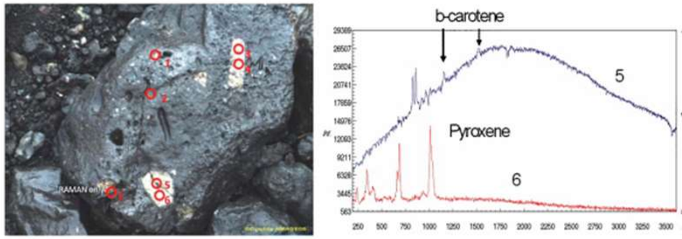
The Raman instrument provides a powerful tool for the definitive identification and characterisation of minerals and biomarkers. Raman spectroscopy is sensitive to the composition and structure of any mineral or organic compound. This capability provides direct information of potential organic compounds that can be related with present or past signatures of life on Mars as well as general mineralogical information for igneous, metamorphous, and sedimentary processes, especially water-related geo-processes.

The Raman spectrometer will be used:

1. to identify organic compounds and search for signatures of life;
2. to identify the mineral products and indicators of biological activities;
3. to characterise mineral phases produced by water-related processes; and
4. to characterise igneous minerals and their products resulting from alteration processes (e.g. oxidation).

Raman will also support the scientific measurements by correlating its spectral information with other

analysis by other instruments.



In-situ analysis of basalt rocks using a Raman spectrometer.
Credit: ESA-Raman team / AMASE

Search here

17-May-2016 09:08 UT

Shortcut URL
http://exploration.esa.int/jump.cfm?oid=45103

Related Articles
· Looking for signatures of life on Mars
· PanCam - the Panoramic Camera
· ISEM - Infrared Spectrometer for ExoMars
· CLUPI - Close-UP Imager
· WISDOM - Water Ice and Subsurface Deposit Observation on Mars

LA STRUMENTAZIONE RAMAN

dimensioni sempre più contenute: il Raman esce fuori dai laboratori

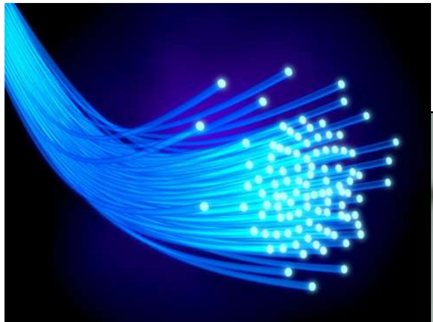
in una stanza

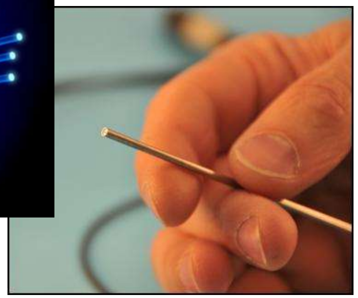
su un tavolo

in una valigia

in mano

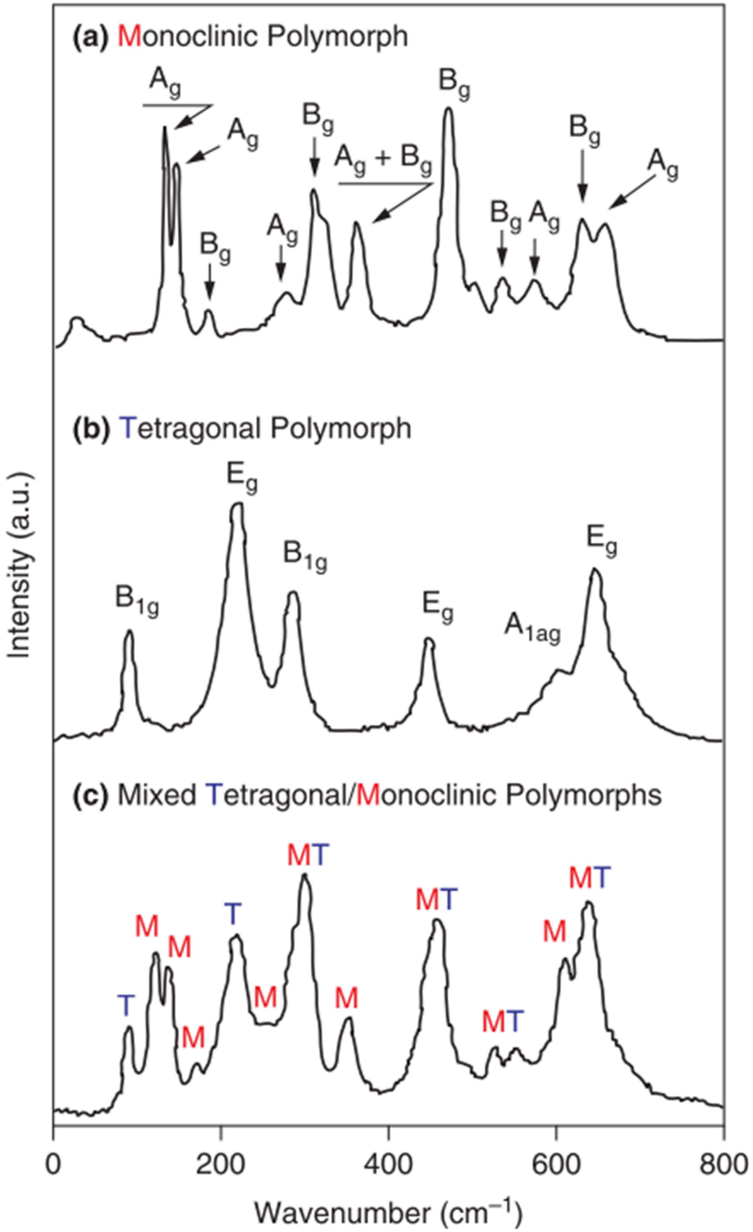
1980 **1990** **2000** **2010**

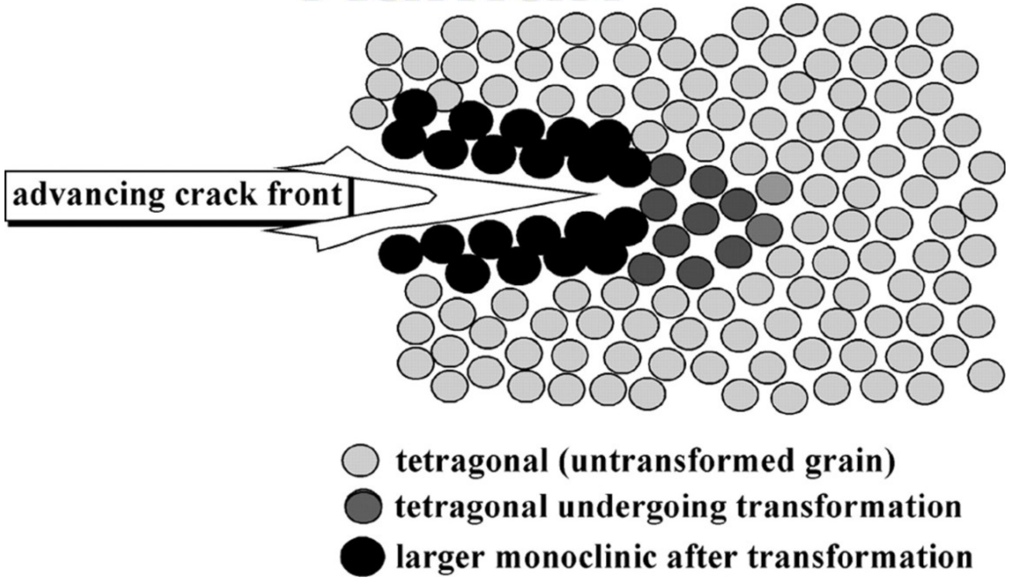




illuminazione e raccolta luce in fibra ottica

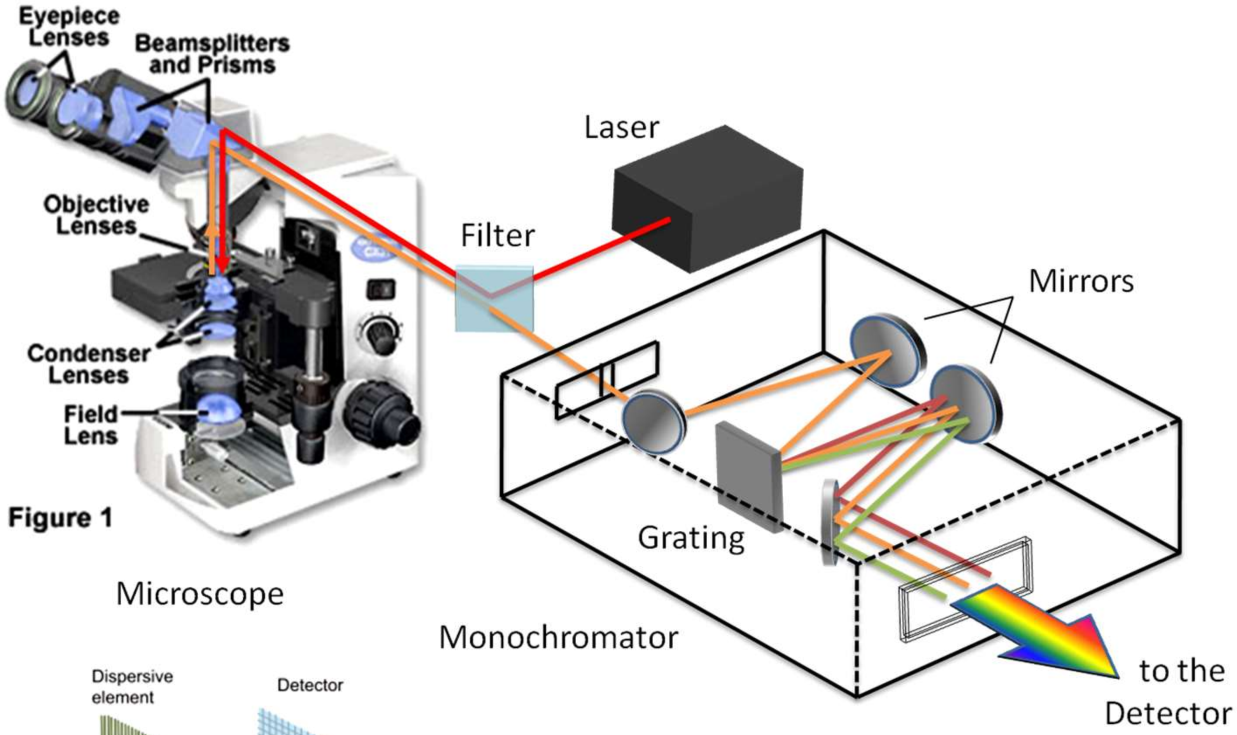
Applicazioni spettroscopia Raman



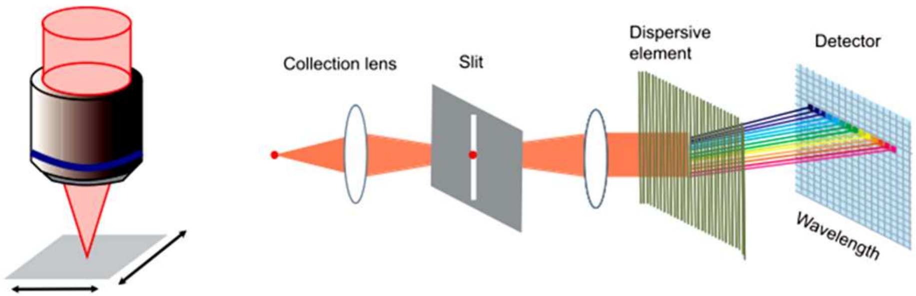


diffraction limited spatial resolution

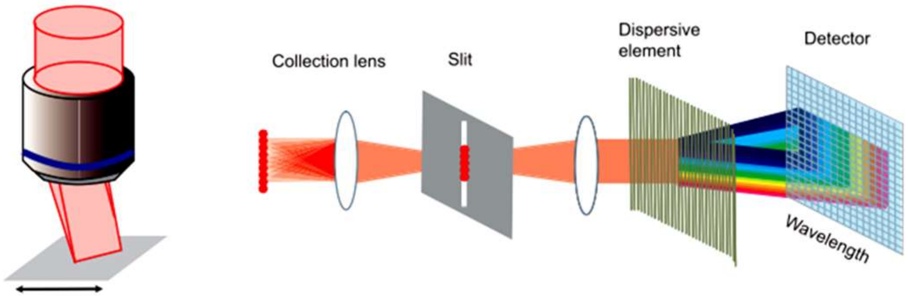
$$R = \frac{0.61 \cdot \lambda}{N.A.}$$



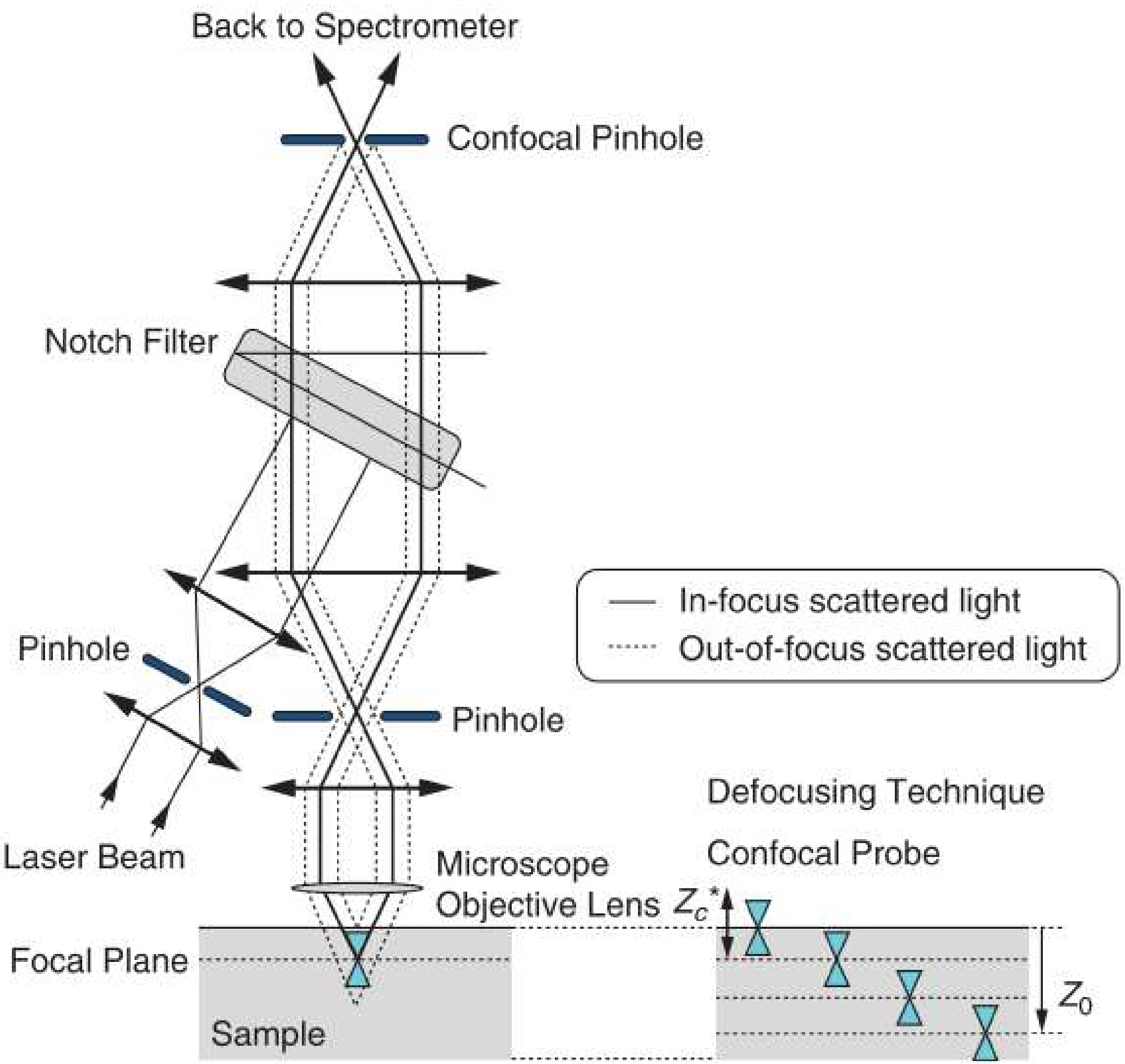
Point scanning

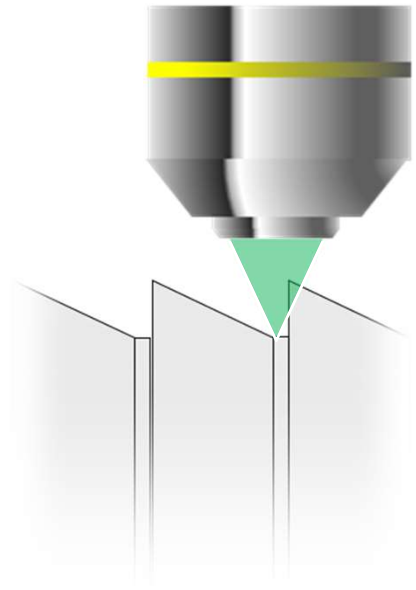


Line scanning



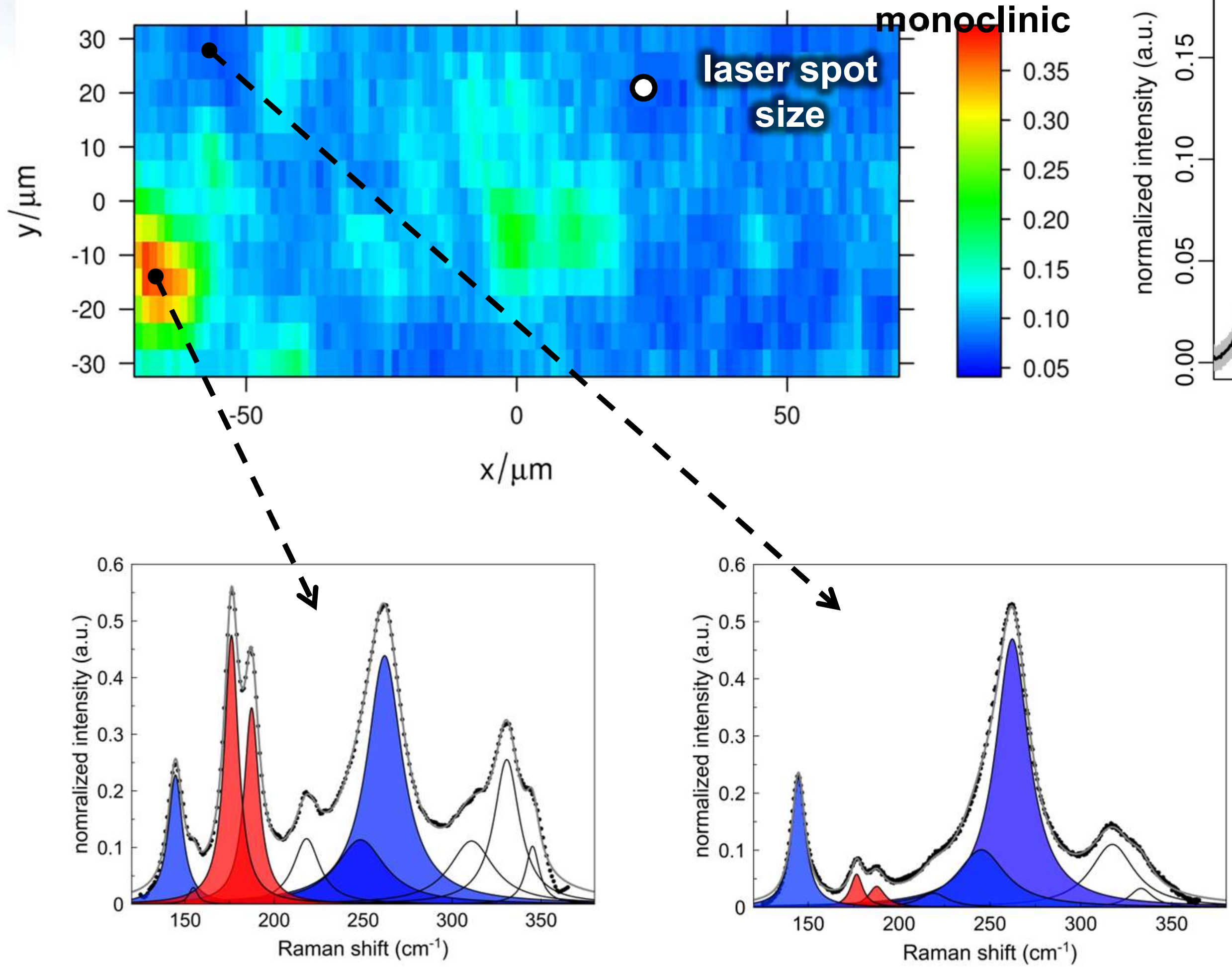
Raman microscopy (microspectroscopy)

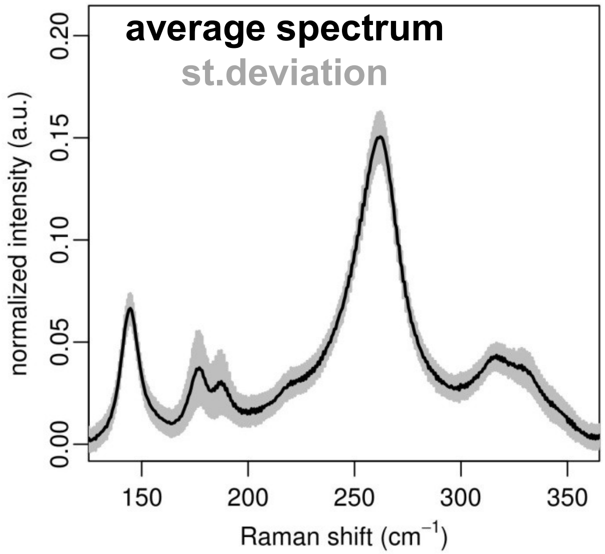

Back to Spectrometer
Confocal Pinhole
Notch Filter
In-focus scattered light
Out-of-focus scattered light
Pinhole
Pinhole
Laser Beam
Microscope
Objective Lens
Defocusing Technique
Confocal Probe
Z_c^*
Focal Plane
Sample
Z_0



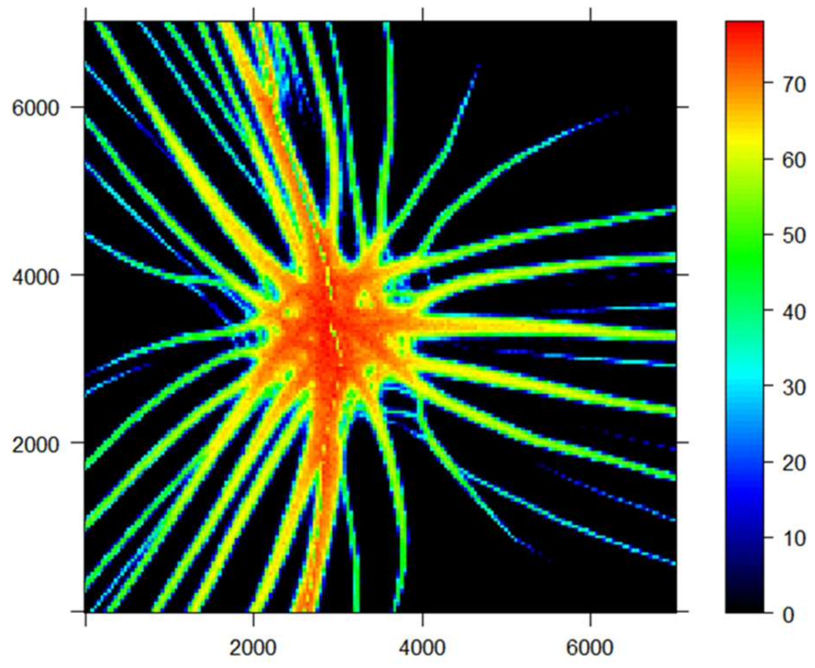
SAMPL

Raman map (1400 spectra)

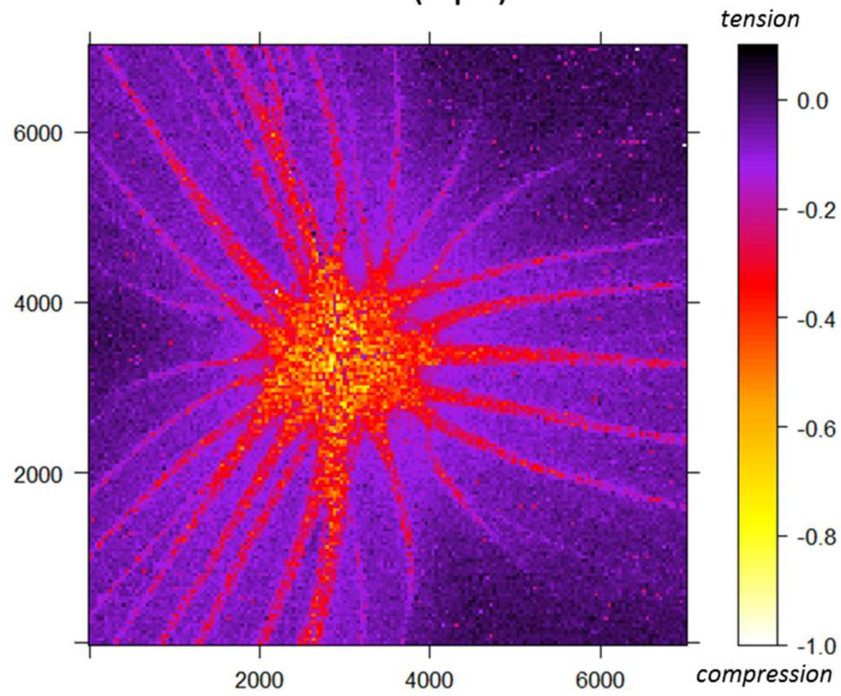




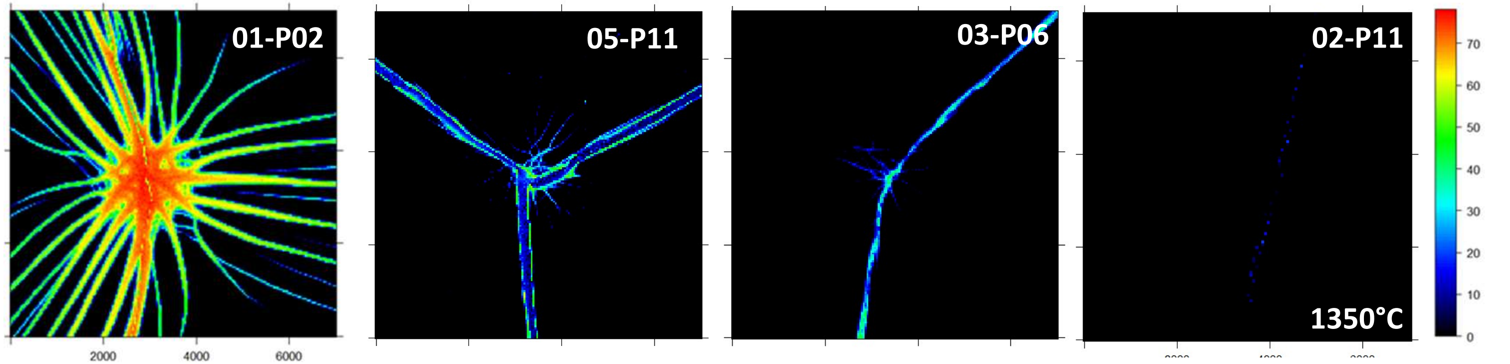
monoclinic %



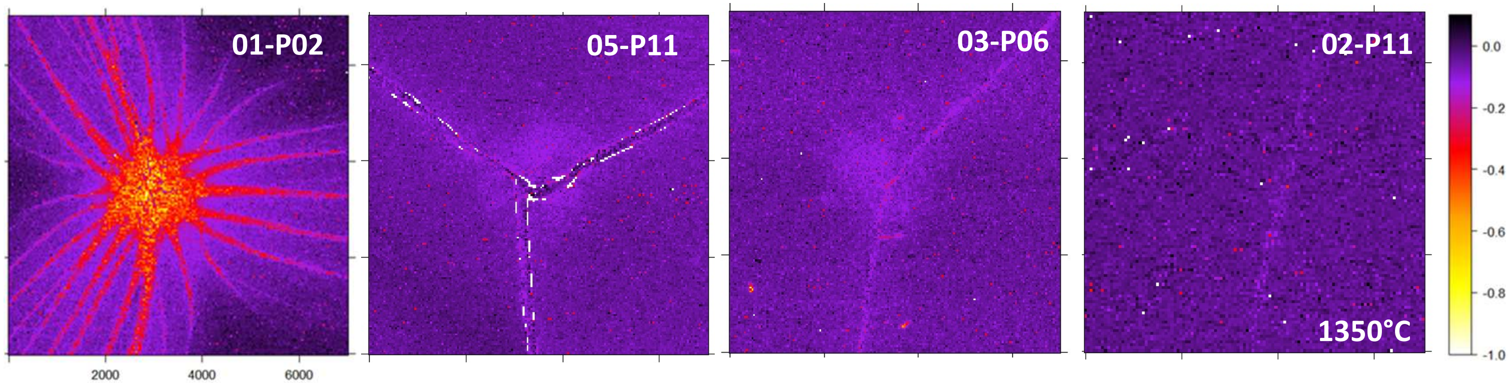
stress (Gpa)



monoclinic (% vol)



stress (GPa)



ZA_8Sr_8-Ce10.5	**ZA_8Sr_8-Ce11**	**ZA_8Sr_8-Ce11.5**	**ZA_8Mg_8**
(10.5Ce-TZP/ 8vol%Al_2O_3/ 8vol%$SrAl_{12}O_{19}$)	**(11Ce-TZP/ 8vol%Al_2O_3/ 8vol%$SrAl_{12}O_{19}$)**	**(11.5Ce-TZP/ 8vol%Al_2O_3/ 8vol%$SrAl_{12}O_{19}$)**	**(10Ce-TZP/ 8vol% Al_2O_3/ 8vol%$CeMgAl_{11}O_{19}$)**

Applicazioni microscopia Raman

Fig. 1: I) Orange rectangle indicates scan position on polished rock section.

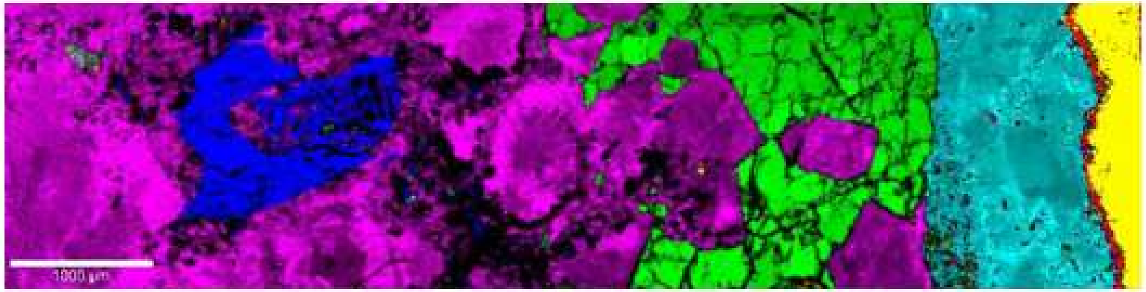


Fig. 2: I) Combined false color image and the corresponding color-coded spectra.

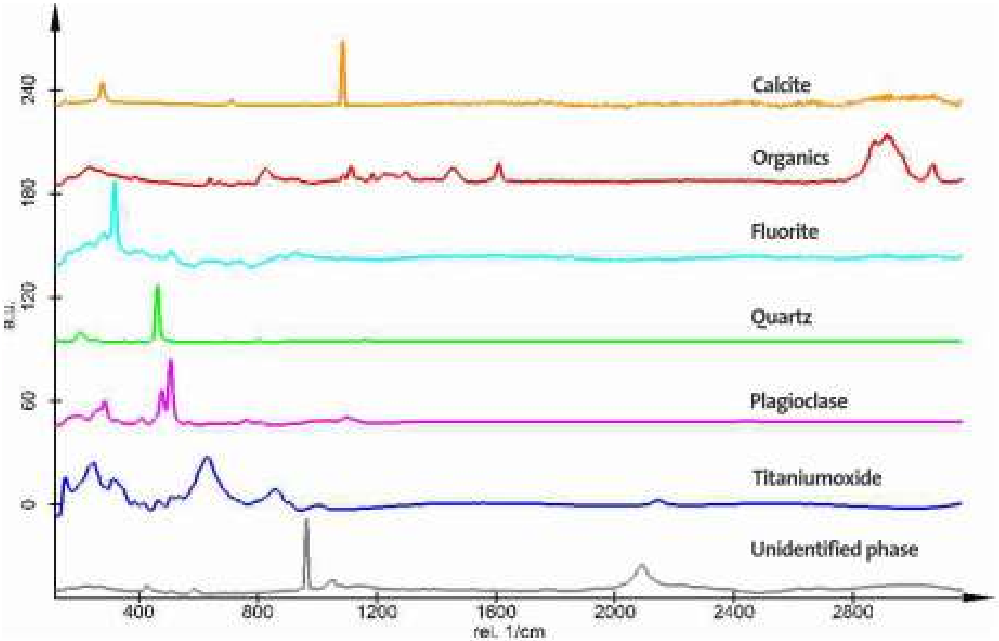


Fig. 2: II) Corresponding Raman spectra.

Applicazioni microscopia Raman

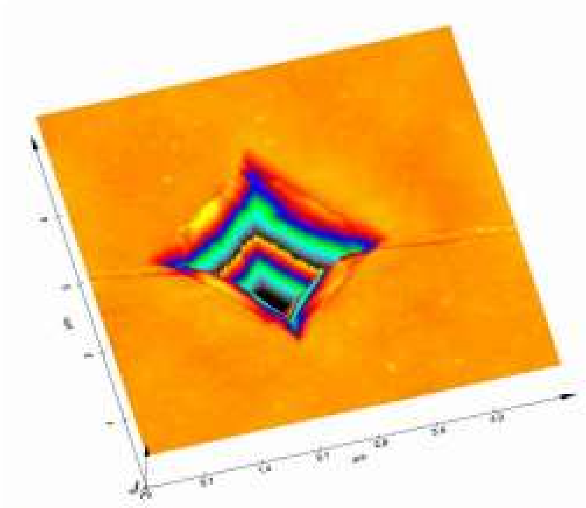


Fig. 1: AFM image, 5 x 5 µm scale.

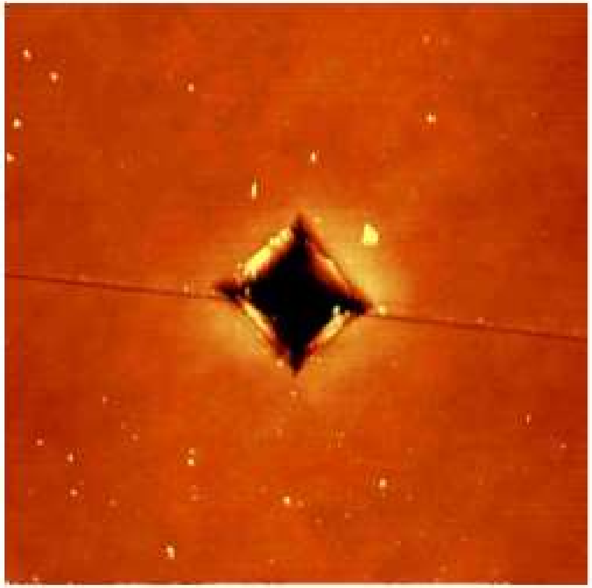


Fig. 2: AFM image: Topography around a Vickers indent, 10 x 10 µm scale

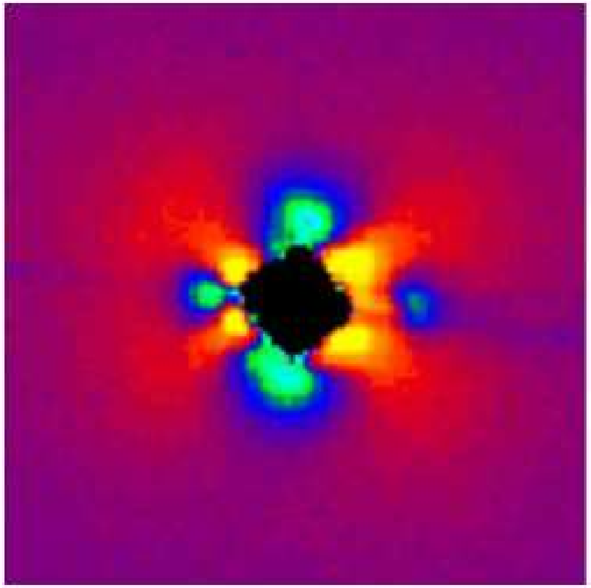
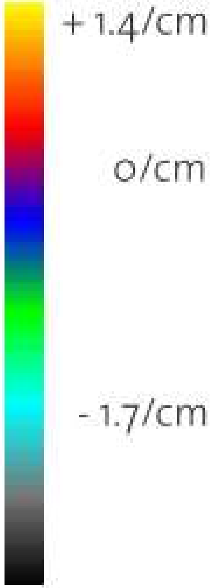
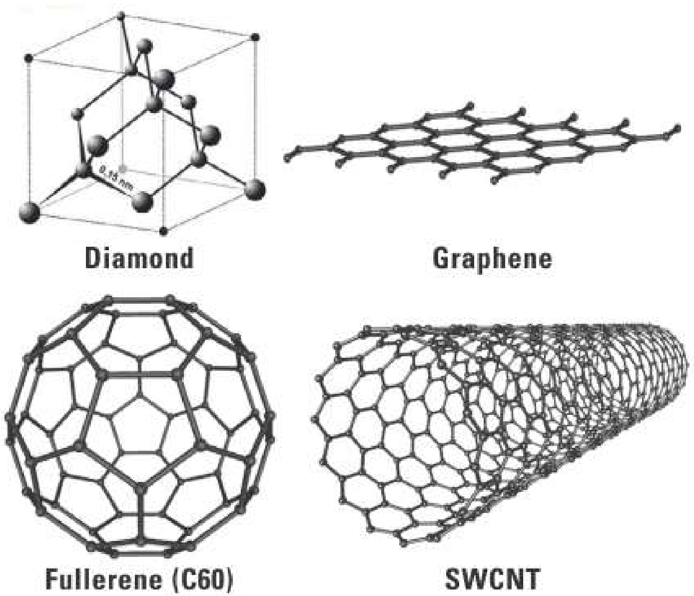


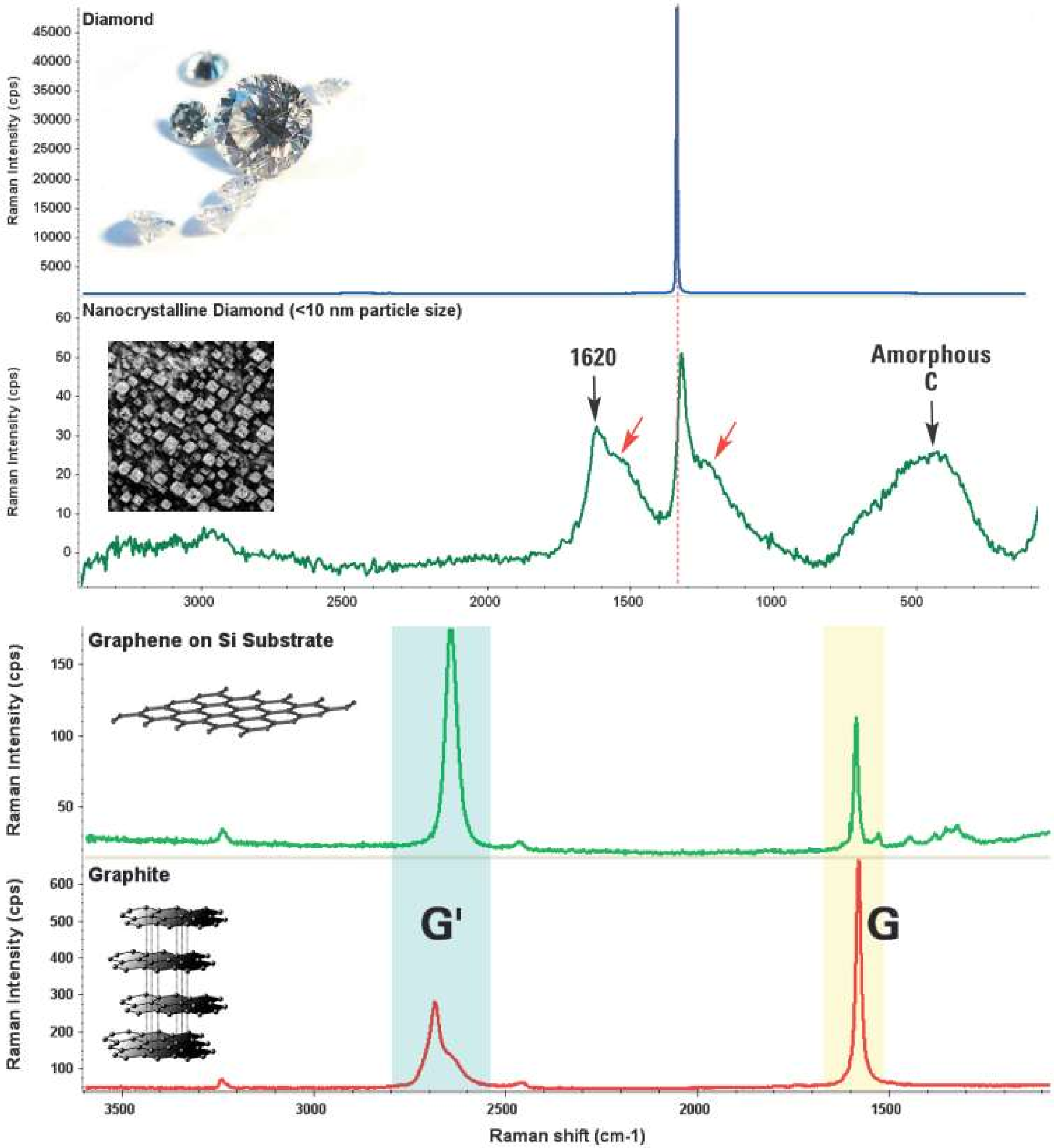
Fig. 3: Stress image of the same area as in fig. 2, obtained in the Raman Imaging Mode, 10 x 10 µm scale

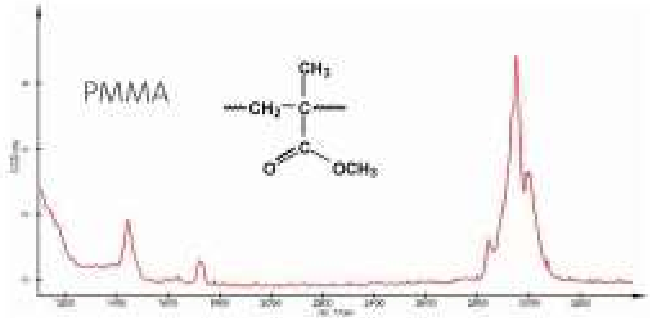


Scale bar

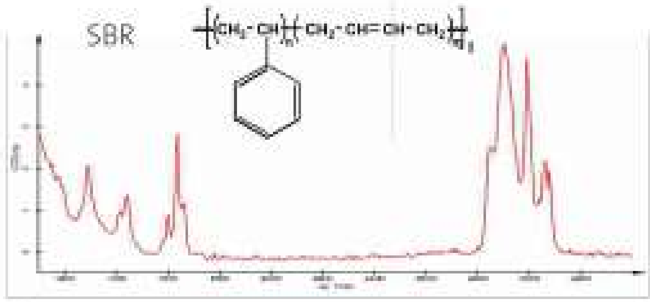
Caratterizzazione materiali a base di C







3

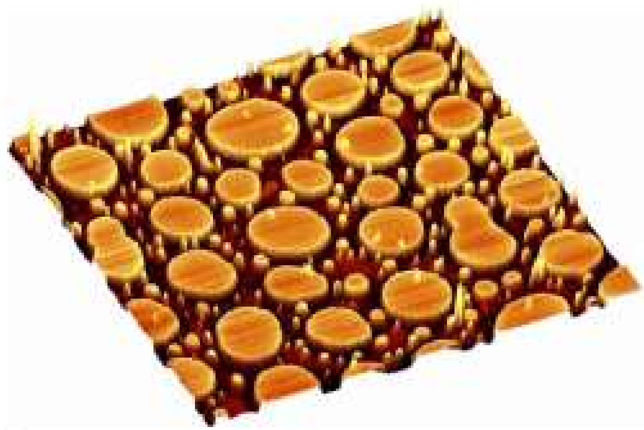


4

Fig. 3: Raman spectrum of PMMA

Fig. 4: Raman spectrum of SBR

Fig. 5: Overview AFM image of a PMMA-SBR blend.



5

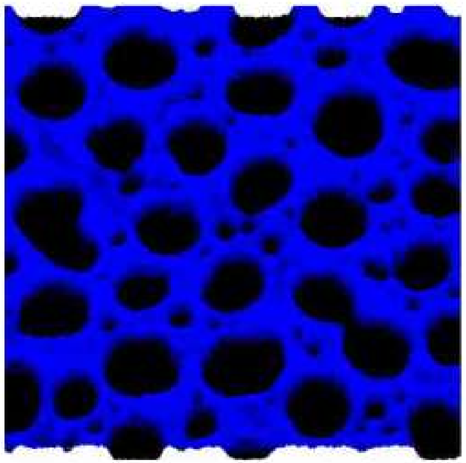


Fig. 9: Color coded Raman image of SBR resulting from the integral intensity of each spectrum.

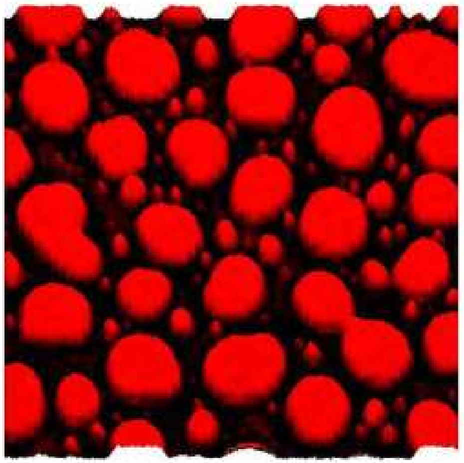


Fig. 10: Color coded Raman image of PMMA resulting from the integral intensity of each spectrum.

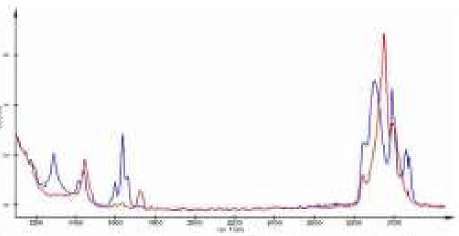


Fig. 11: Corresponding spectra: SBR (blue) and PMMA (red).

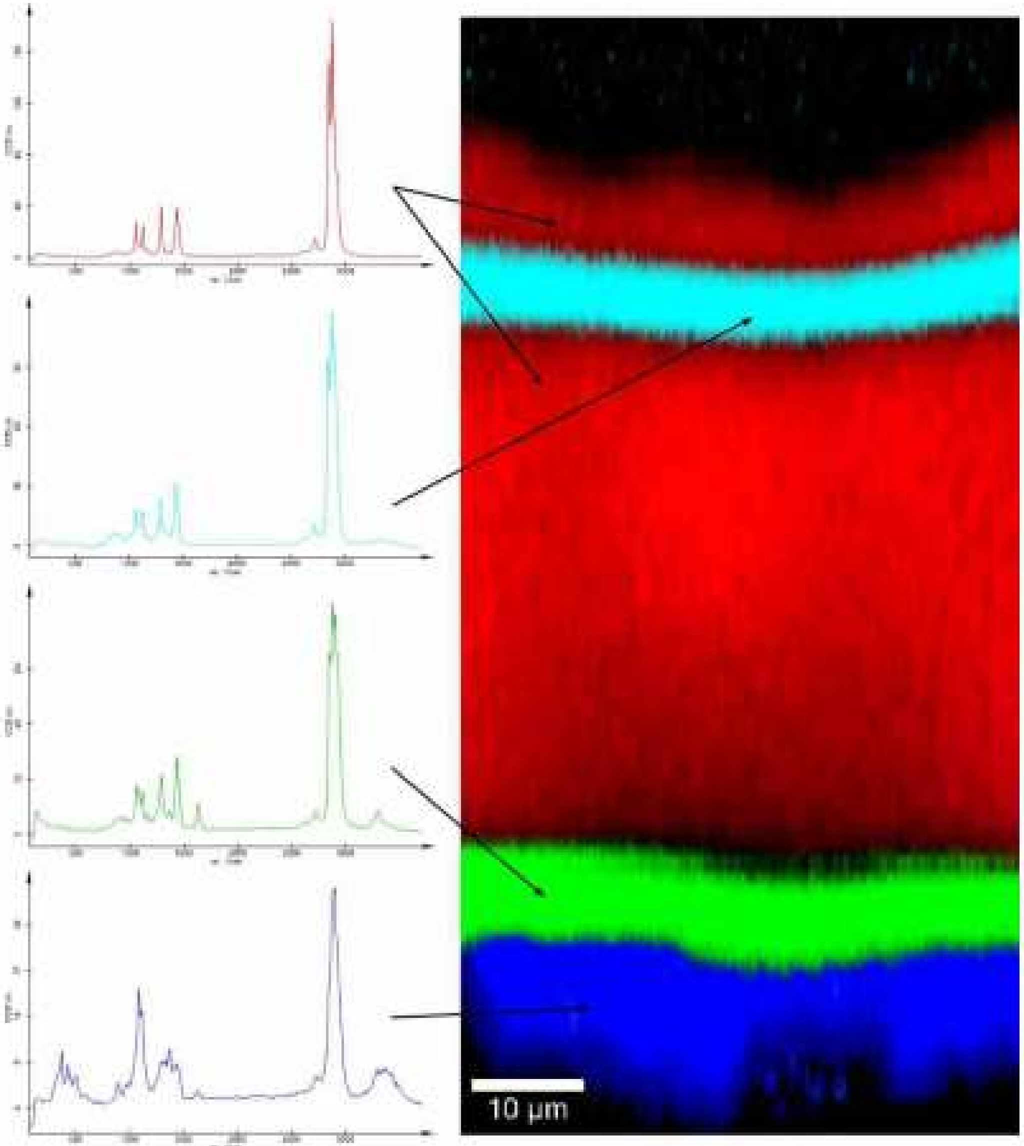


Fig. 1: Raman spectra (left) and Raman image (right) of the inner coating of an orange juice container

Applicazioni microscopia Raman

Depth Profiling

Applicazioni microscopia Raman

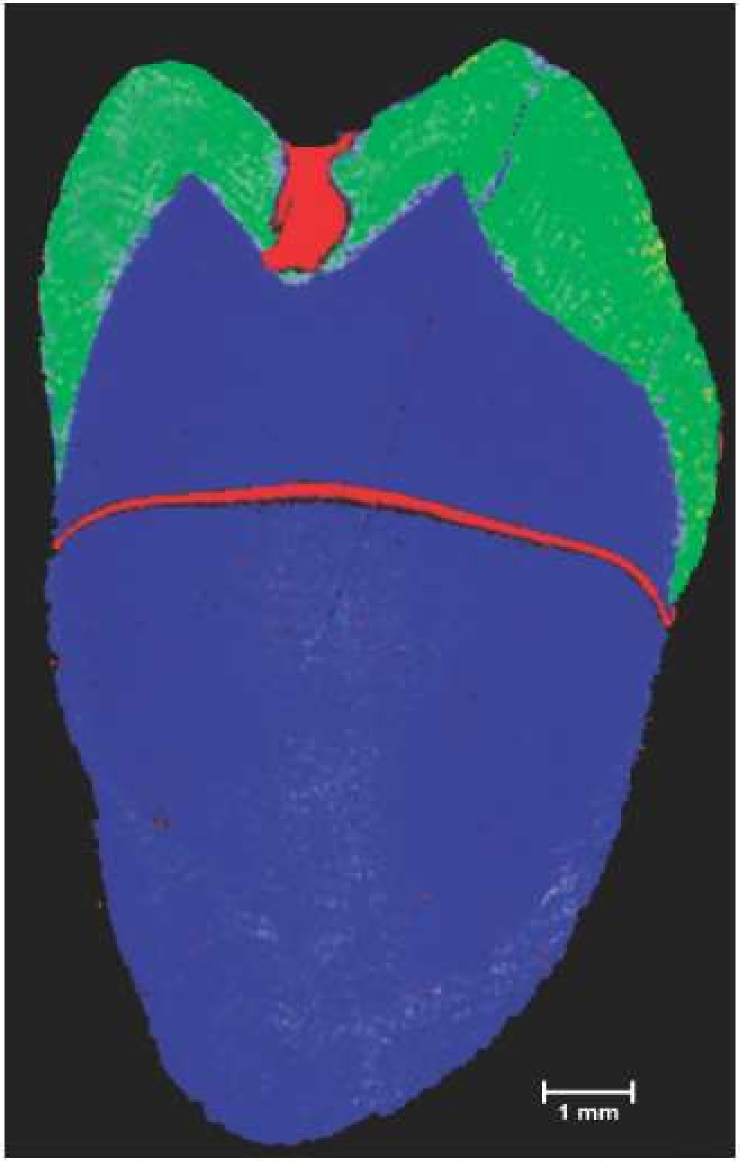


Figure 1 – StreamLine™ image of tooth. The dentine is coloured blue, enamel green, and areas of high fluorescence in red

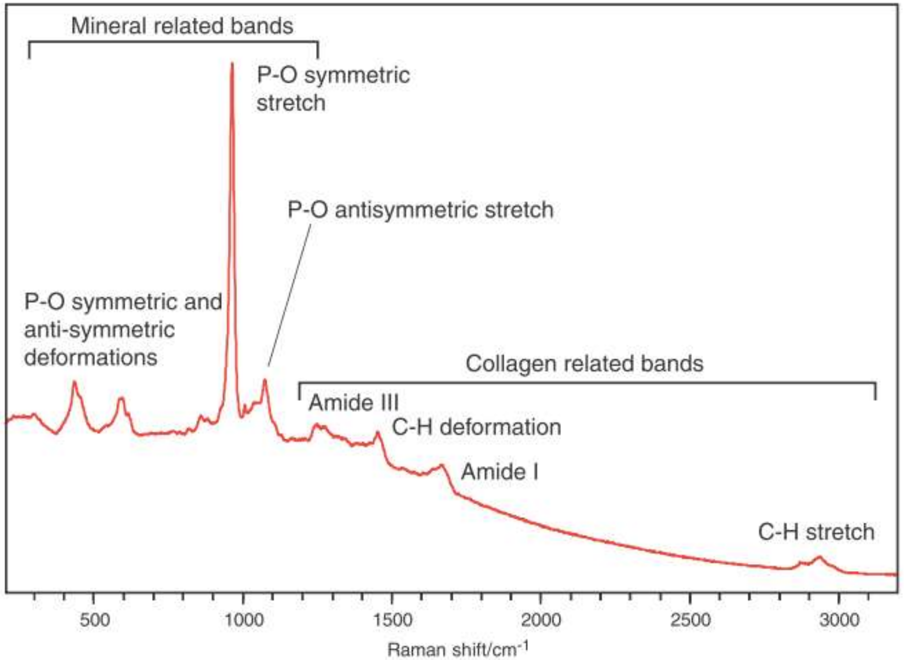
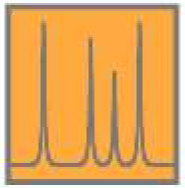
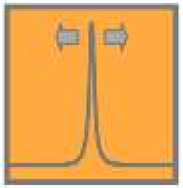


Figure 2 – Typical spectrum measured from the dentine region. Bands associated with both the mineral and collagen content are assigned and labelled

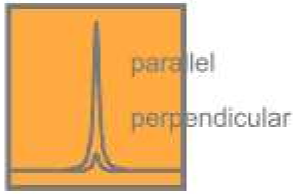
Information from Raman Spectroscopy



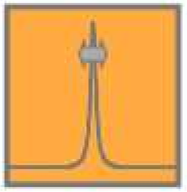
characteristic Raman frequencies → composition of material — e.g. MoS_2, MoO_3



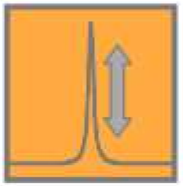
changes in frequency of Raman peak → stress/strai n state — e.g. Si 10 cm^{-1} shift per % strain



polarisation of Raman peak → crystal symmetry and orientation — e.g. orientation of CVD diamond grains



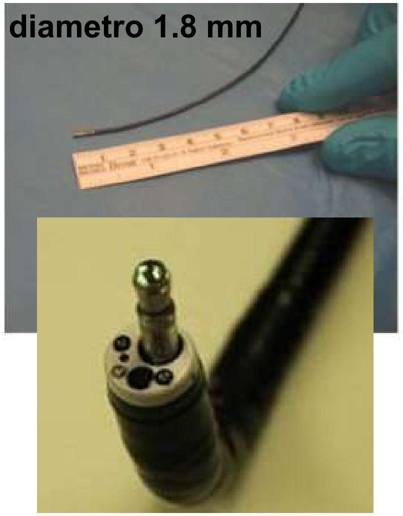
width of Raman peak → quality of crystal — e.g. amount of plastic deformation

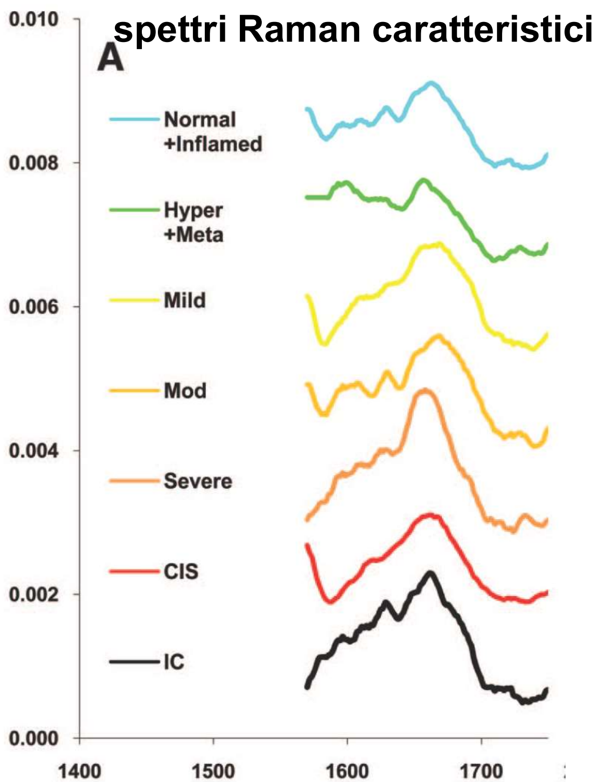


intensity of Raman peak → amount of material — e.g. thickness of transparent coating

ENDOSCOPIA RAMAN
verso la "biopsia ottica"

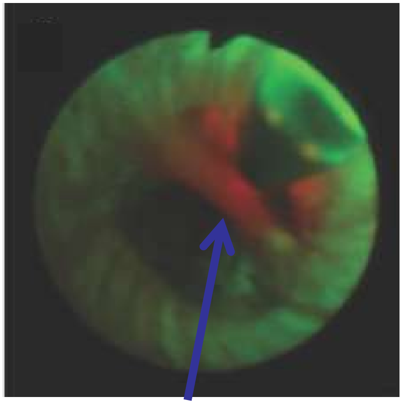
esempio broncoscopia *(da Short et al. <u>J. Thoracic Oncol</u>. 2011)*





invasive squamous cell carcinoma

immagine ottica



zona illuminata dal laser

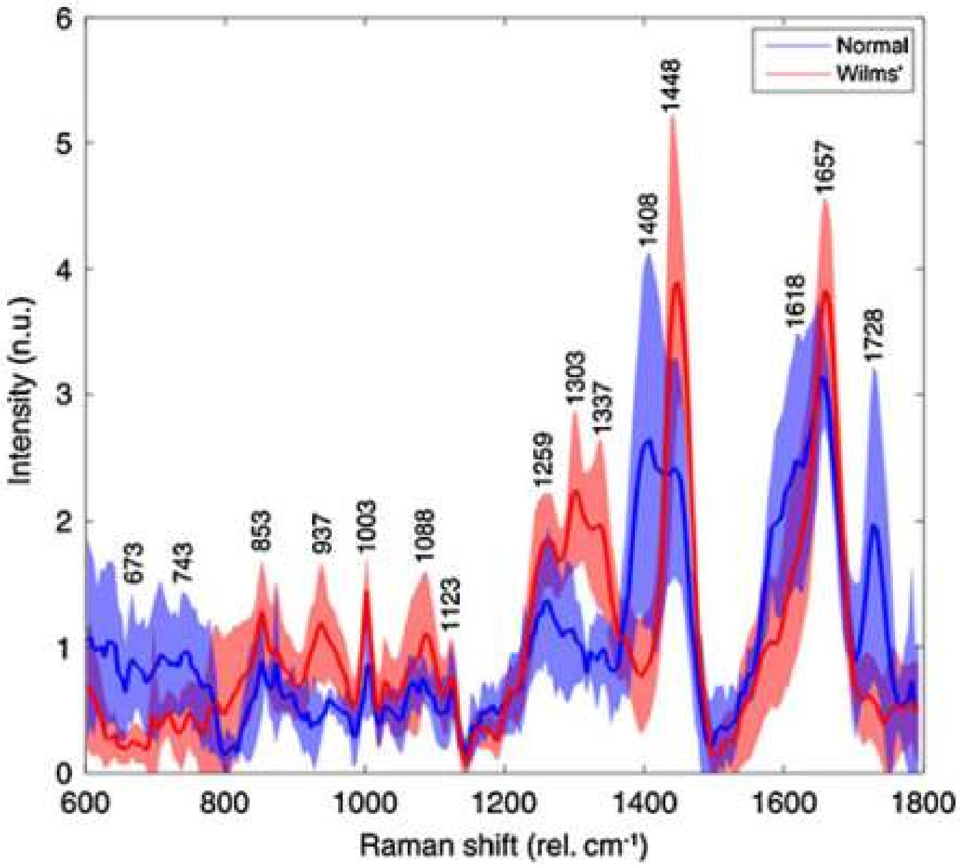
SENSIBILITA' 96%
SPECIFICITA' 91%
(lesioni pre-neoplastiche)

DIAGNOSI RAMAN INTRAOPERATORIA

una guida per il chirurgo

esempio Raman intraoperatoria ***(da Lieber and Kaber*** ***J. Pediatric Surg*** ***. 2010)***

diagnosi tumore di Wilms in età pediatrica



SENSIBILITA' 93% SPECIFICITA' 100%

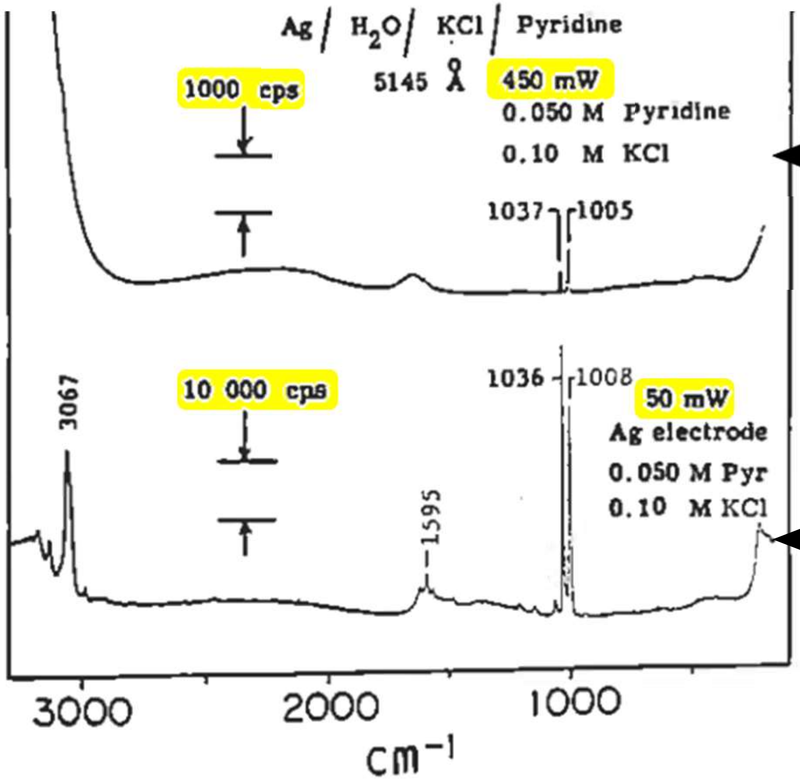
SERS

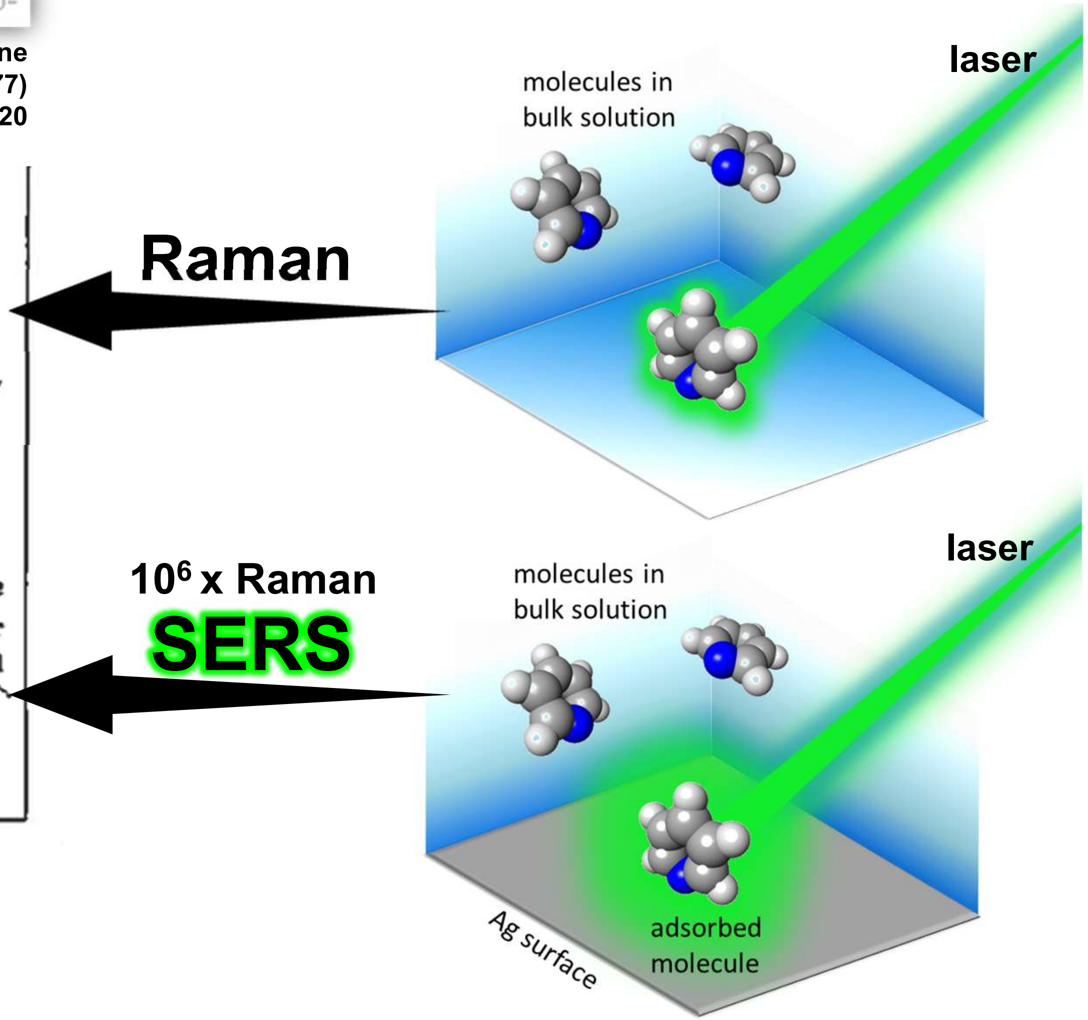
urface enhanced **Raman scattering** (SERS)

1977

is required to produce a solution signal of 700 Hz, one concludes that a monolayer surface signal is 10^6 times more intense than the solution signal and if 10 mono-

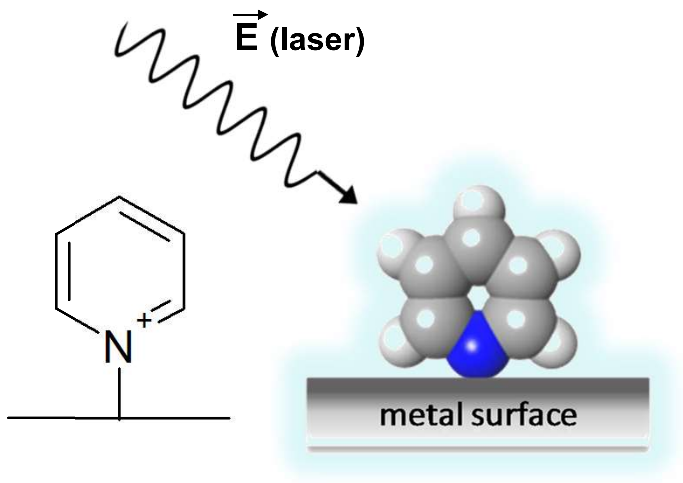
Jeanmarie and Van Duyne
(1977)
J.Electroanal.Chem. 84: 1-20





Surface-enhanced Raman scattering (SERS)

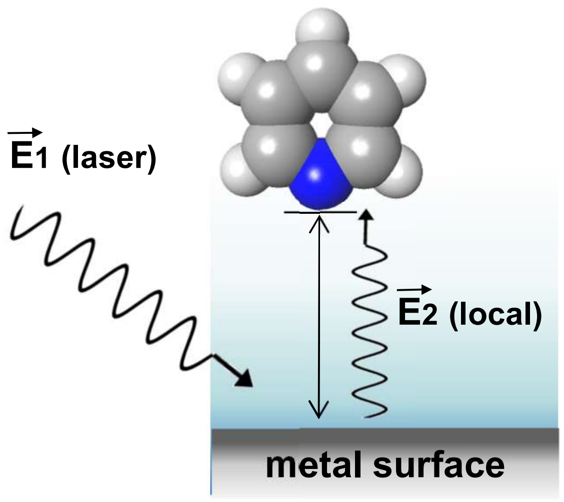
I "chemical mechanism" for enhancement

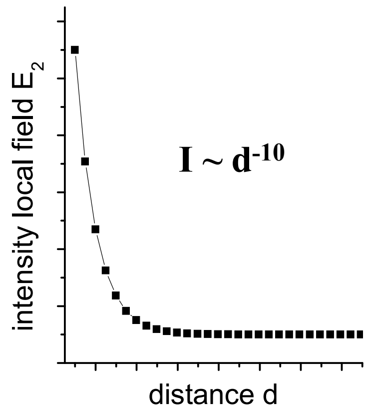


- requires the formation of a <u>chemical bond</u>
  between the adsorbate and the metal (chemisorption)

- formation of a new electronic state

II "electromagnetic" mechanism for enhancement

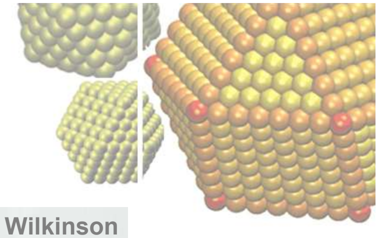




- does not require the direct adsorption of
  the molecule on the metal surface

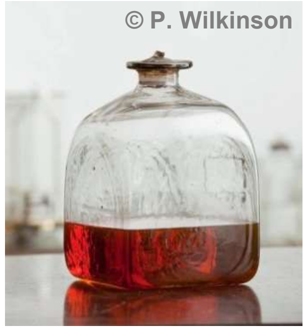
- rapidly decays with distance from surface

metal nanoparticles



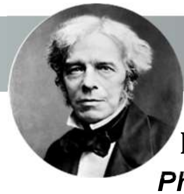
The Lycurgus Cup (British Museum)

Stained glass (Chartres cathedral)



"Ruby gold" (Faraday Museum)

4th century — 12th century — 19th century



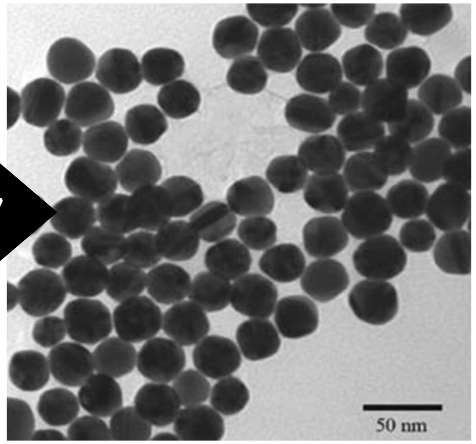
M. Faraday (1791-1869)

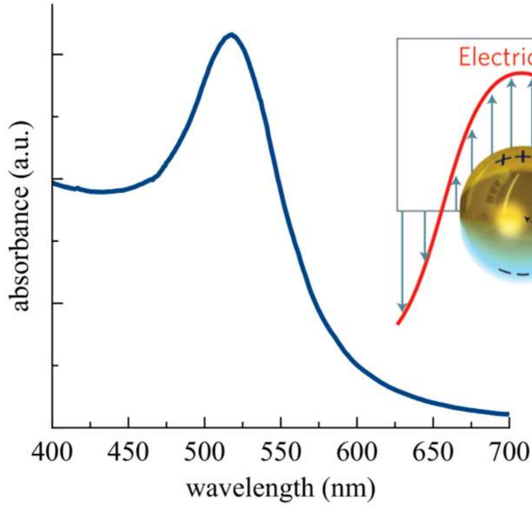
Phil. Trans. R. Soc. 147 (1857), 145-181

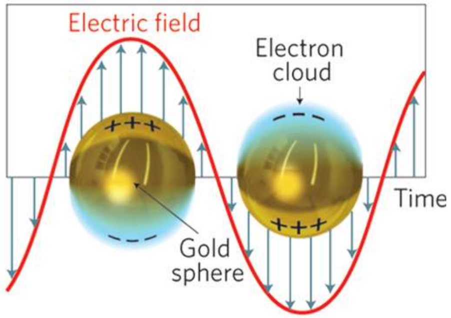
nanotechnology

plasmonics

21st century



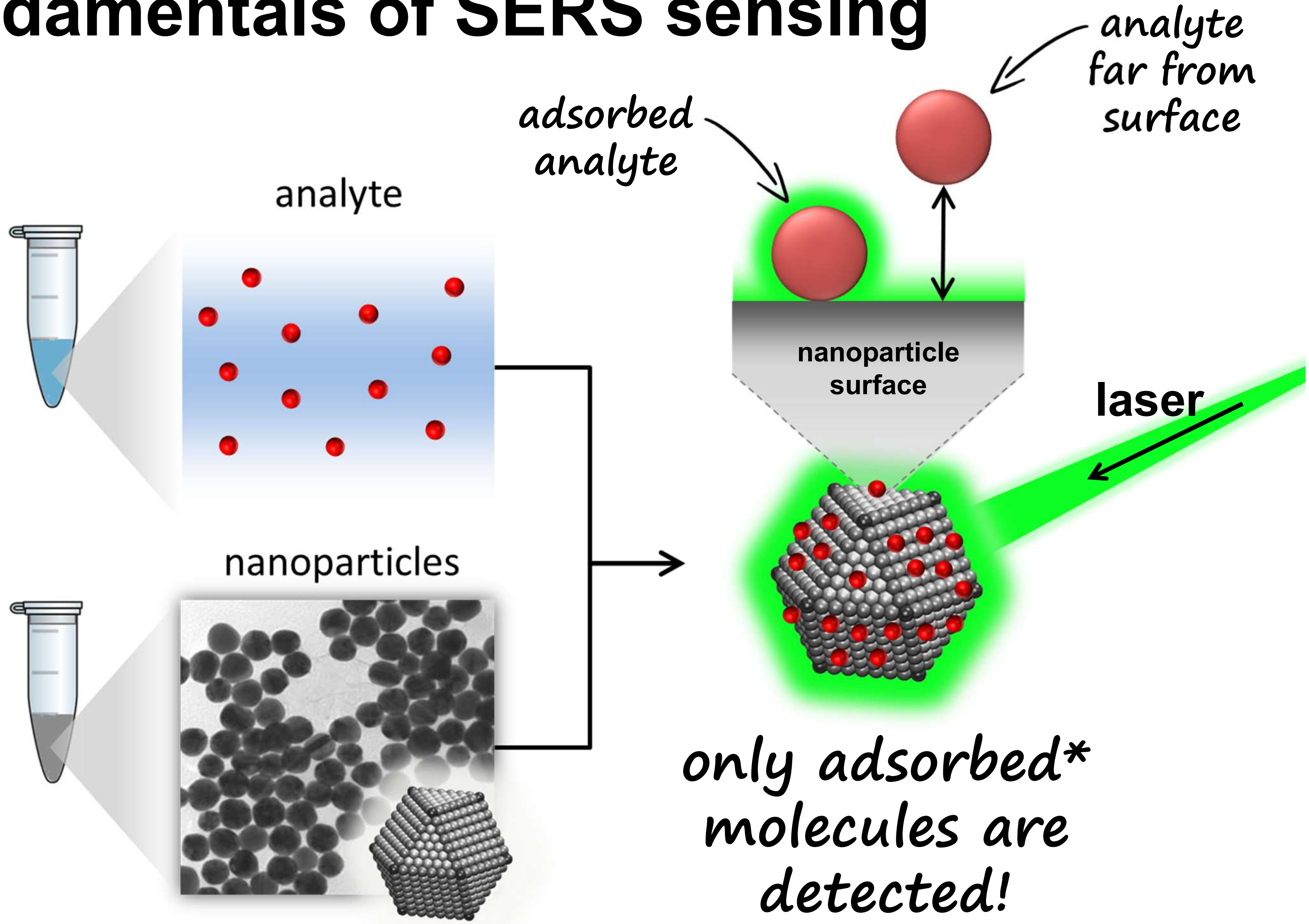




ML Juan et al. Nat. Photon. 5, 349–356 (2011)

Willets and RP Van Duyne Annu. Rev. Phys. Chem 58, 267–97 (2007)

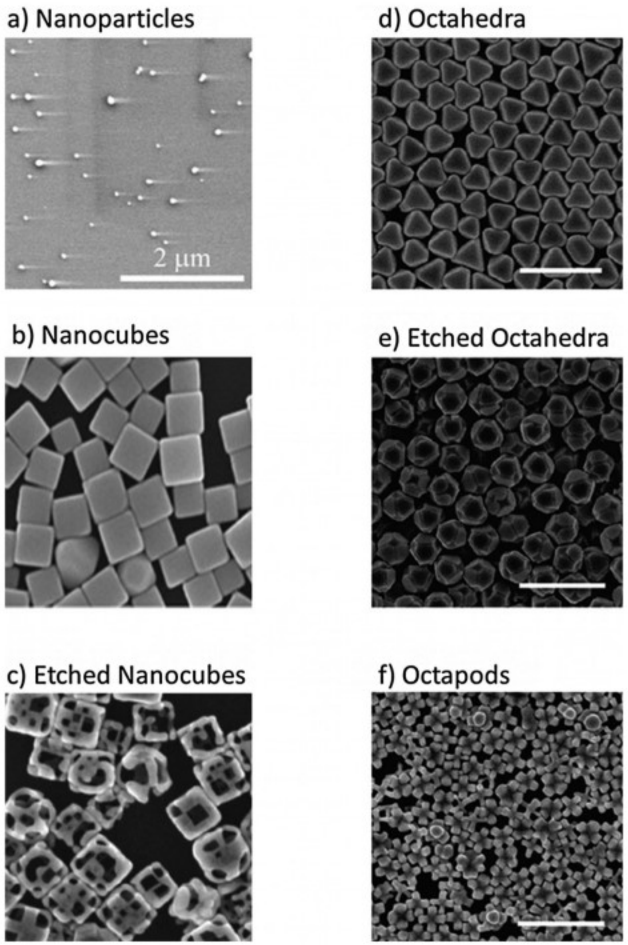
fundamentals of SERS sensing



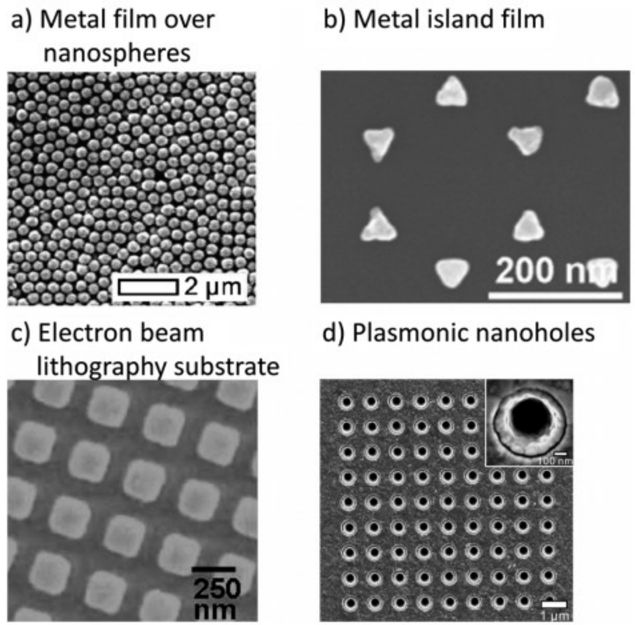
*or VERY close to the surface

SUBSTRATI SERS

Colloidali (nanoparticelle metalliche in sospensione in una fase liquida)

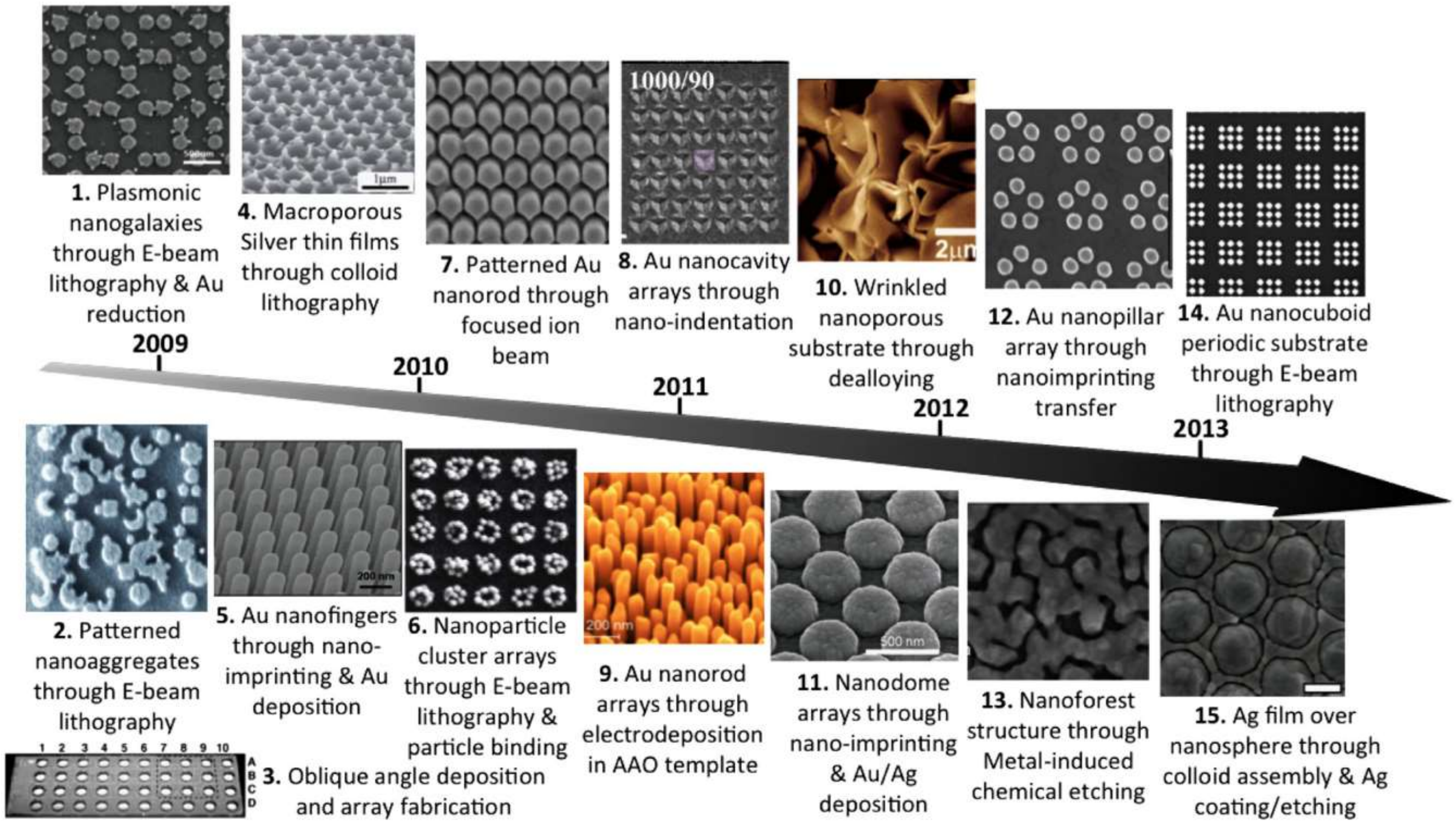


Non Colloidali (superfici metalliche nanostrutturate)



Top-down

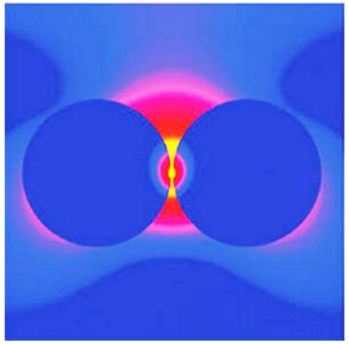
Bottom-up



Approach	Nanofabrication technology	Average enhancement factors, metals
Top-down fabrication	E-beam lithography	5×10^8, Au
	Focus ion beam	10^7, Au
	Nano-indentation	5.85×10^7, Au
	Metal-induced chemical etching	10^7, Au
	Ar ion sputtering	10^{10}, Ag
Button-up assembly	Nanoparticle Immobilization	10^6, Au
	Oblique angle deposition (OAD)	10^8–10^{10}, Ag
	Galvanic displacement reaction	10^7–10^8, Au

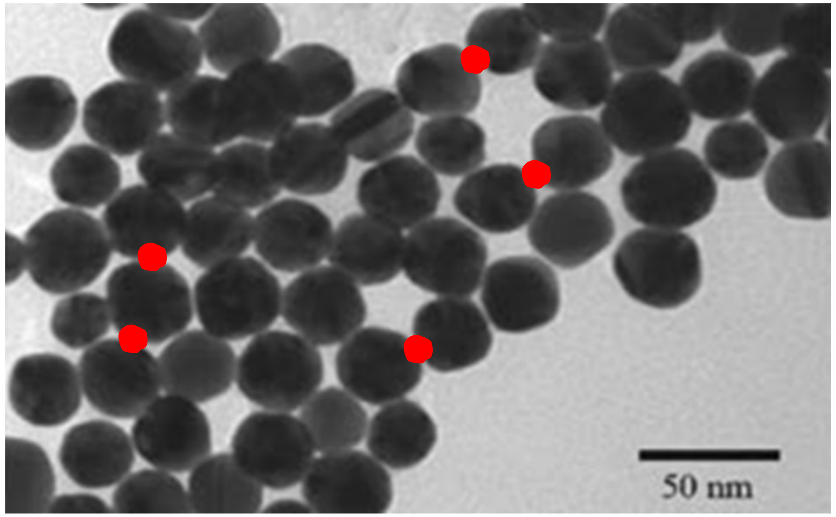
quantitative SERS

$$SERS\ intensity \propto \textcolor{red}{hot\ spots}\ density$$



a junction or close interaction of two or more plasmonic objects […] with the ability to concentrate an incident electromagnetic field

(R.P. Van Duyne, PCCP 2013, 15, 21-36)



quantitative SERS

an example

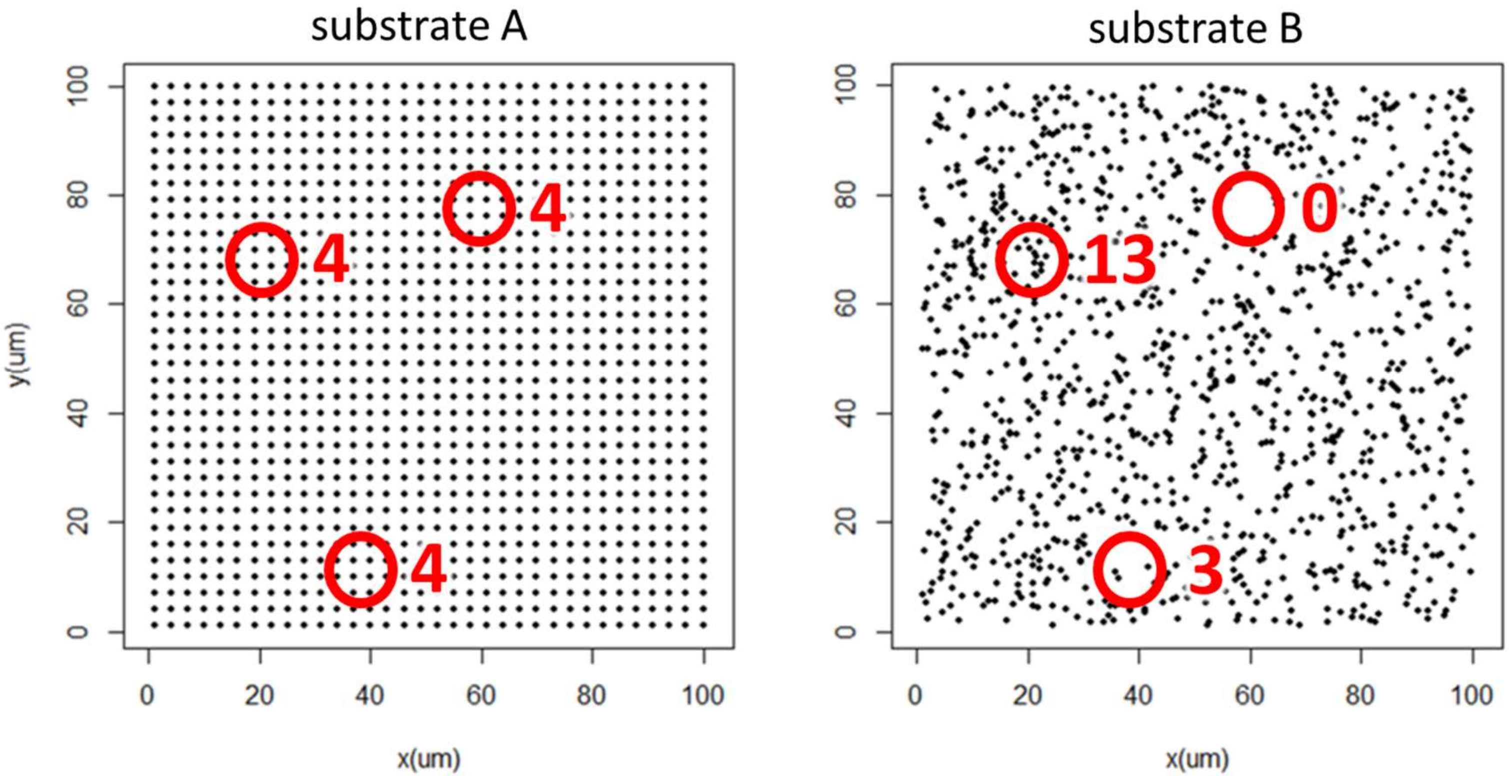
repeatability ⟷ hot spots distribution

(same operator, apparatus, laboratory, short time intervals)

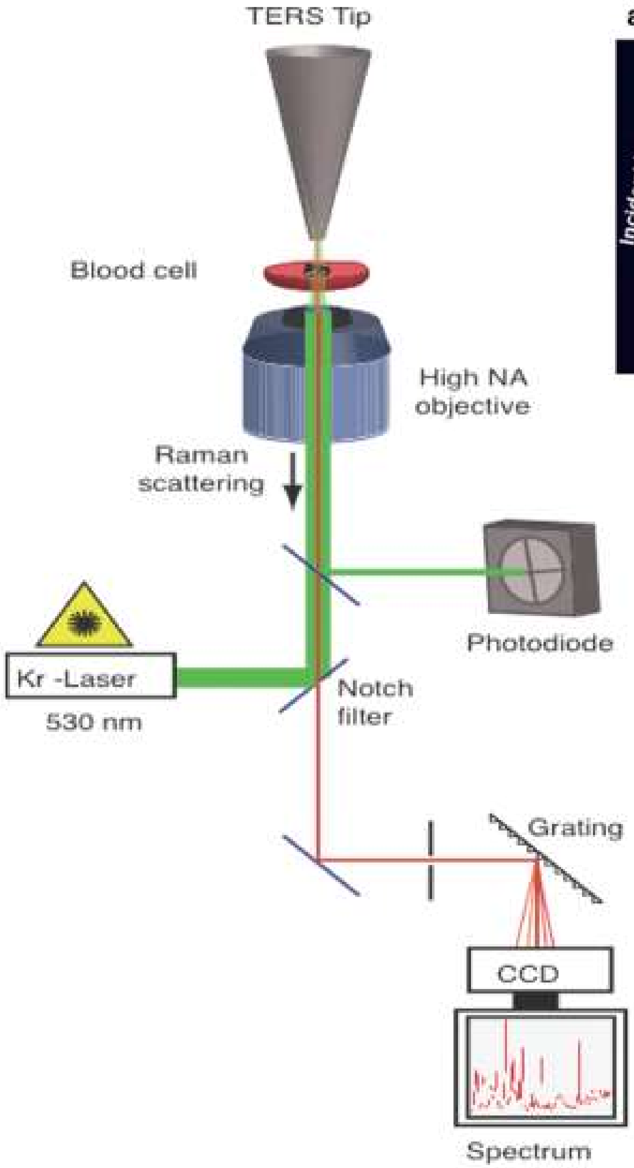
(in both time and space)

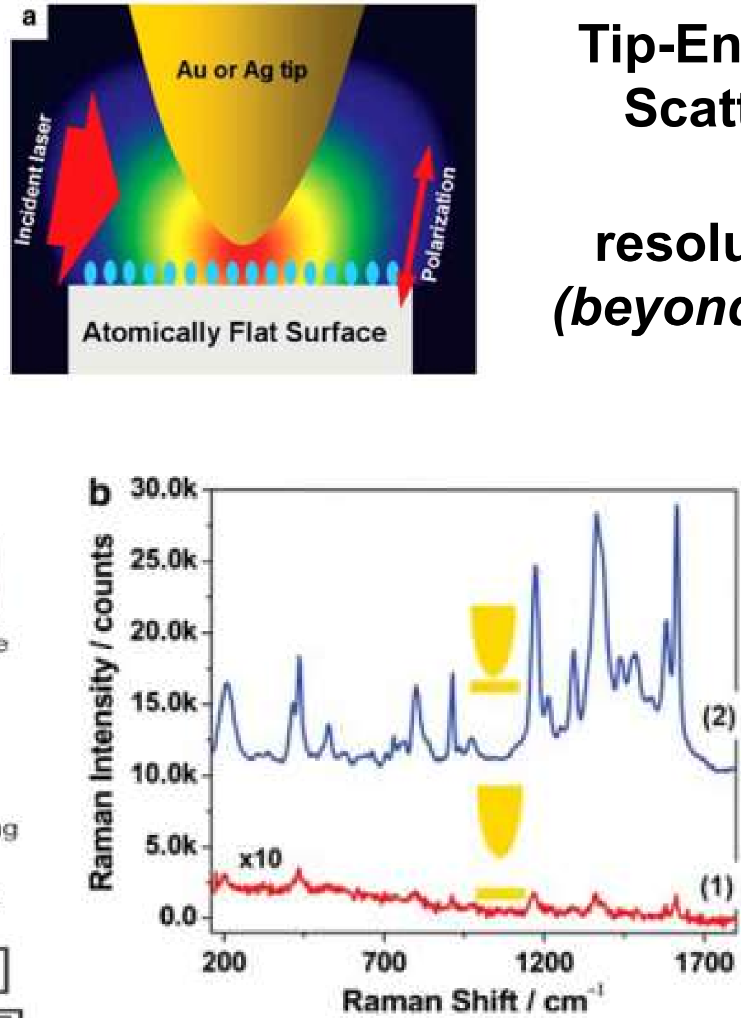
point (·) = hot-spot

circle (○) = laser spot (probe)



SERS using an AFM tip





Tip-Enhanced Raman Scattering (TERS)

resolution = tip width
(beyond diffraction limit)

tip down

tip up

Microfluid Nanofluid (2009) 6:285–297
Nano Lett. 2011, 11, 1868–1873