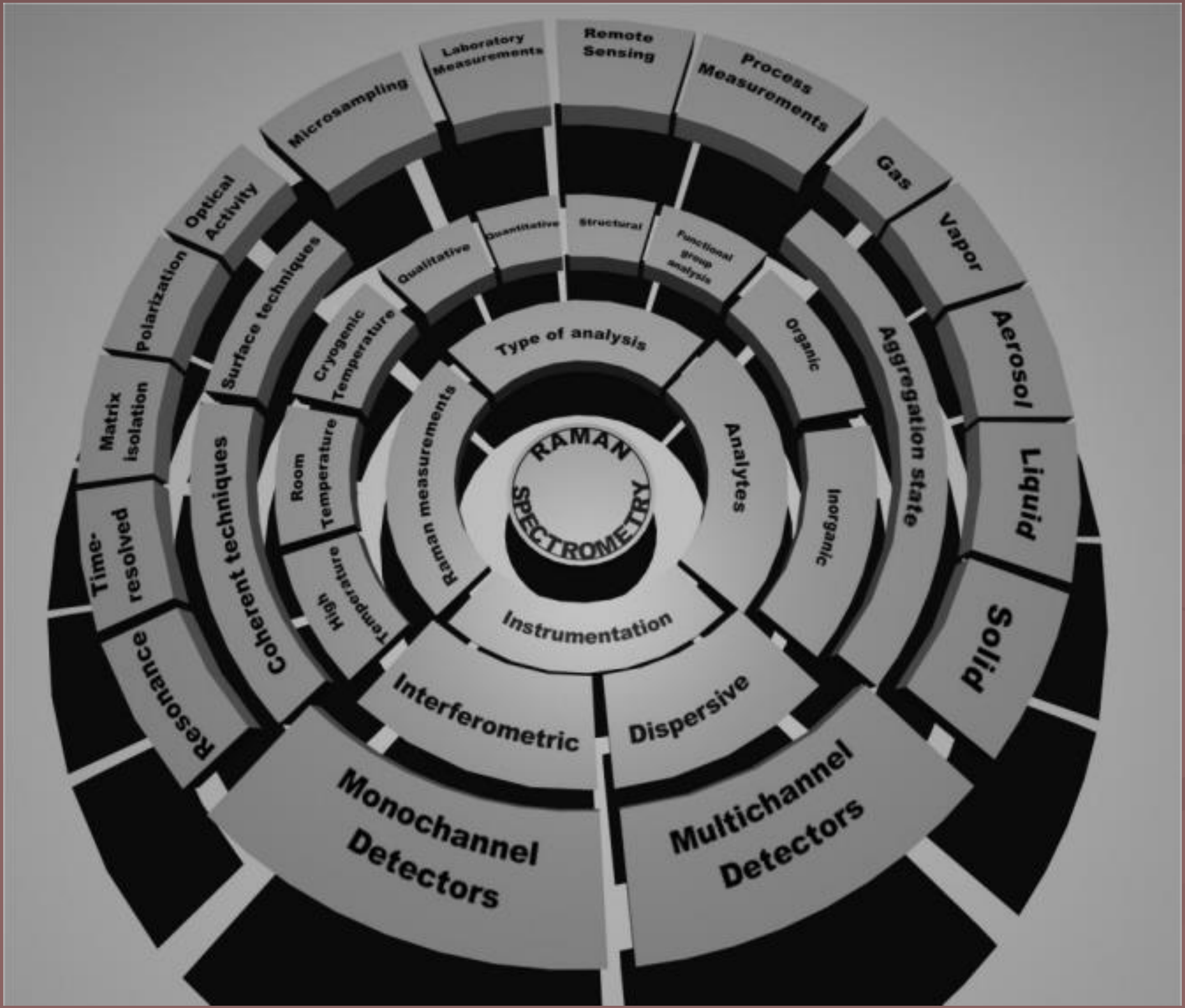
Basic of Raman spectrocopy

Vincenzo SPAGNOLO
Physics Department
Technical University Bari

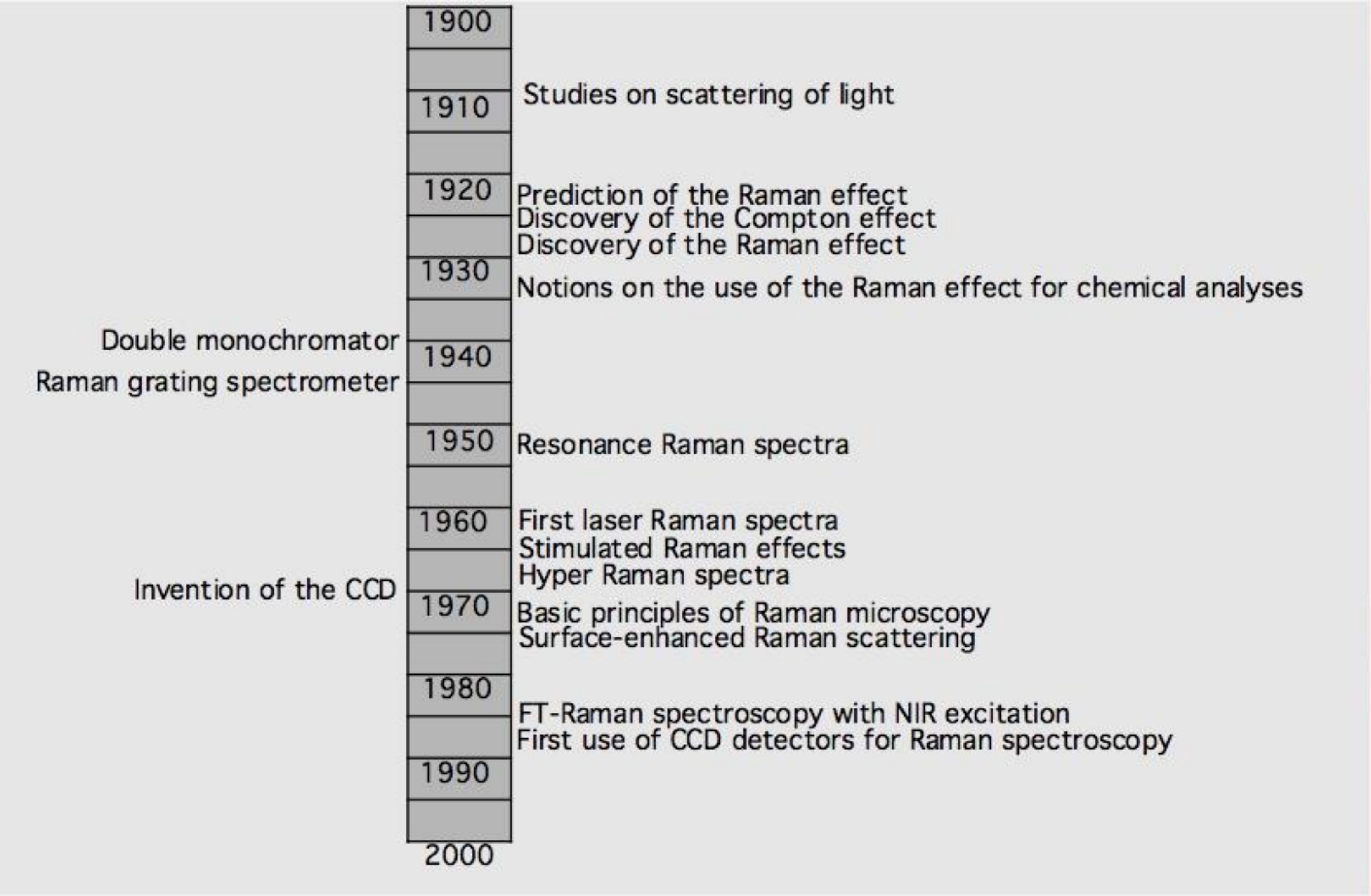
Introduction



The graph on the left shows a good summary of the capabilities and kinds of Raman spectrometry. Just follow each quadrant and the different topics it includes.

(From: www.spectroscopynow.com/coi/cda/detail.cda?page=3&id=1882&type=EducationFeature&chId=6)

History



	1900	
		Studies on scattering of light
	1910	
	1920	Prediction of the Raman effect
		Discovery of the Compton effect
		Discovery of the Raman effect
	1930	Notions on the use of the Raman effect for chemical analyses
Double monochromator		
	1940	
Raman grating spectrometer		
	1950	Resonance Raman spectra
	1960	First laser Raman spectra
		Stimulated Raman effects
		Hyper Raman spectra
Invention of the CCD		
	1970	Basic principles of Raman microscopy
		Surface-enhanced Raman scattering
	1980	
		FT-Raman spectroscopy with NIR excitation
		First use of CCD detectors for Raman spectroscopy
	1990	
	2000	

Light scattering

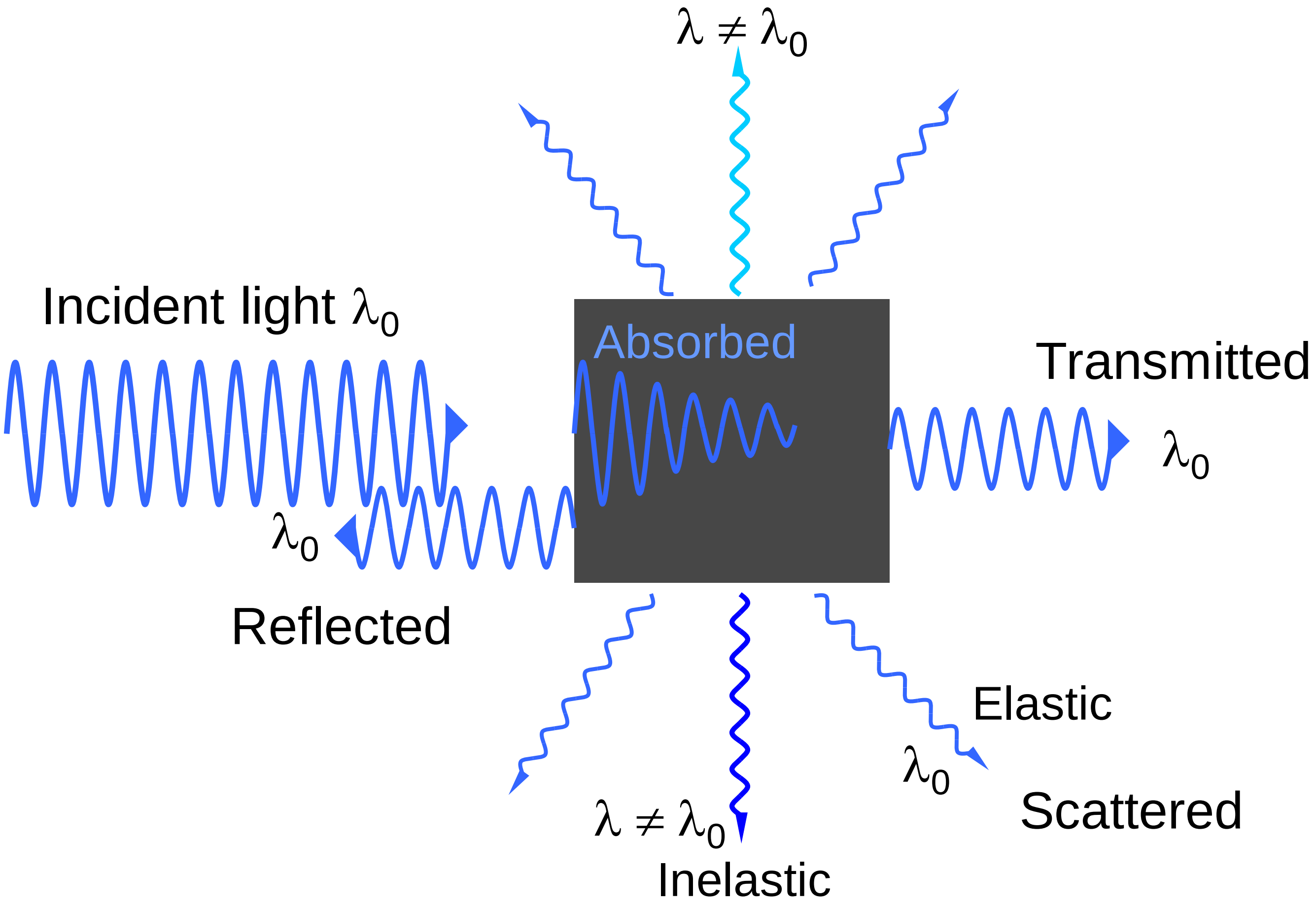
Rayleigh: Elastic scattering

www.phy.cam.ac.uk/history/historypictures/LordRayleigh.jpg

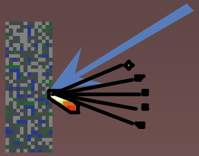
Raman: Inelastic scattering

www.iisc.ernet.in/images/CVRaman.gif

Optical options



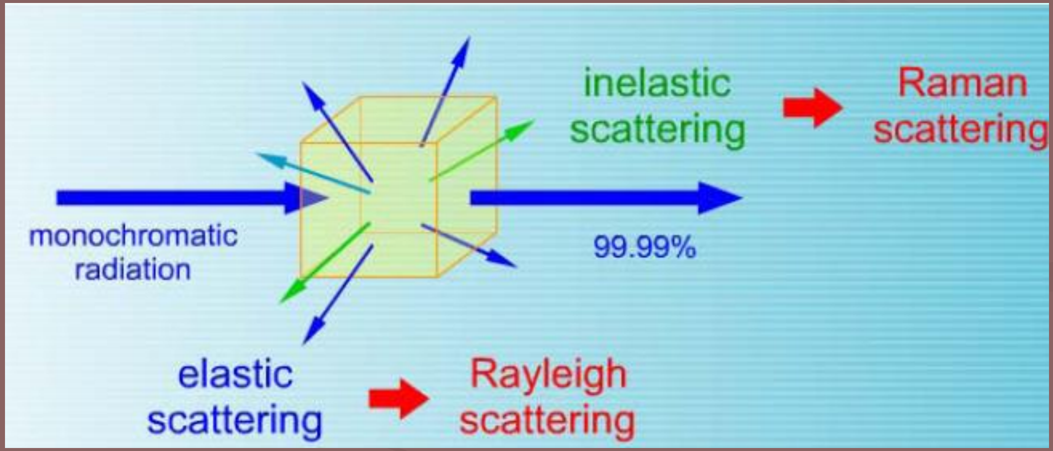
- Raman scattering: Inelastic light scattering



Introduction

- When light enters a medium it is part reflected part refracted part scattered and part absorbed.

Scattering is due to inhomogeneities inside the medium. When these inhomogeneities are not static (density fluctuations) the scattered light can have a change of frequency. This is called Raman scattering.

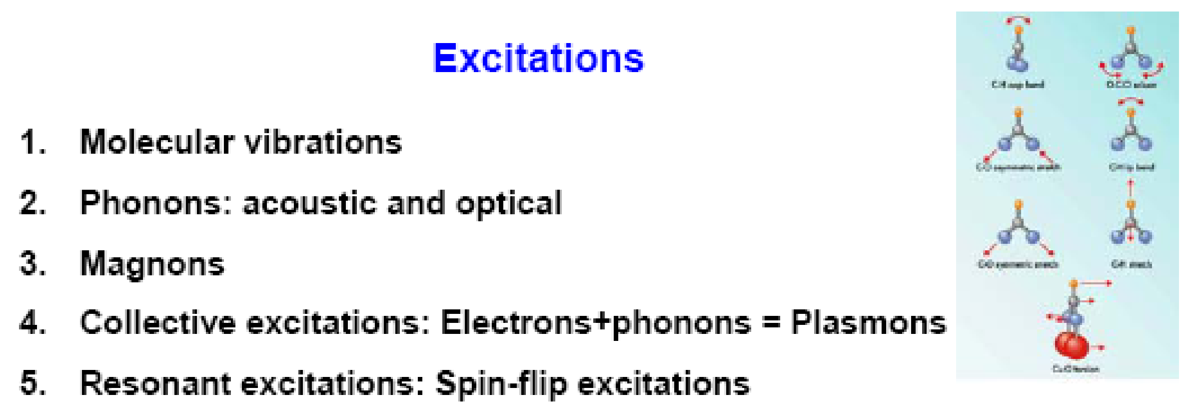


monochromatic radiation

inelastic scattering → Raman scattering

99.99%

elastic scattering → Rayleigh scattering



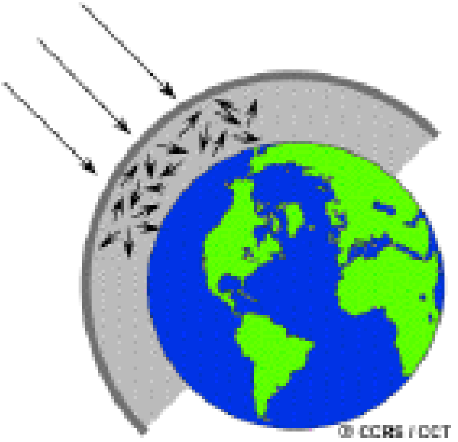
Excitations

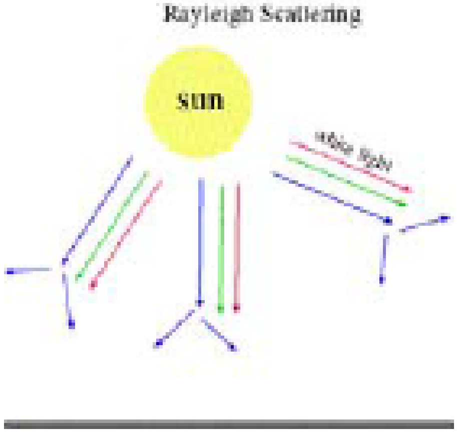
1. Molecular vibrations
2. Phonons: acoustic and optical
3. Magnons
4. Collective excitations: Electrons+phonons = Plasmons
5. Resonant excitations: Spin-flip excitations

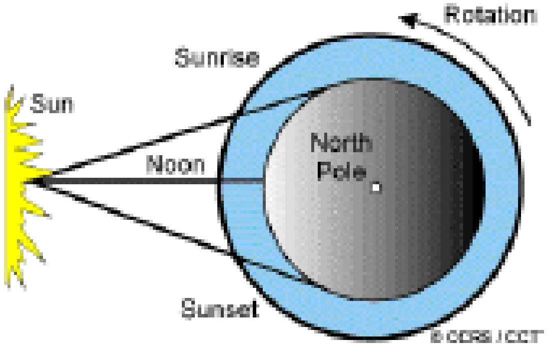
Introduction

Before Raman … : Rayleigh and Mie

$$\hbar\omega_i = \hbar\omega_s$$







Scattered intensity

$$I = I_0 \frac{1+\cos^2\theta}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

Cross section

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$

Introduction

Rayleigh scattering (named after Lord Rayleigh) is the scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the light. It can occur when light travels in transparent solids and liquids, but is most prominently seen in gases.

Why is the sky blue?

The amount of scattering is strongly dependent on the wavelength, being proportional to λ^{-4}:

$$I = I_0 \frac{1+\cos^2\theta}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6,$$

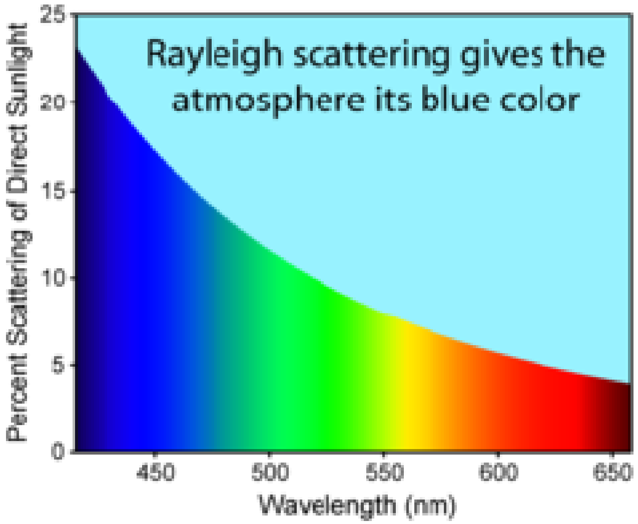
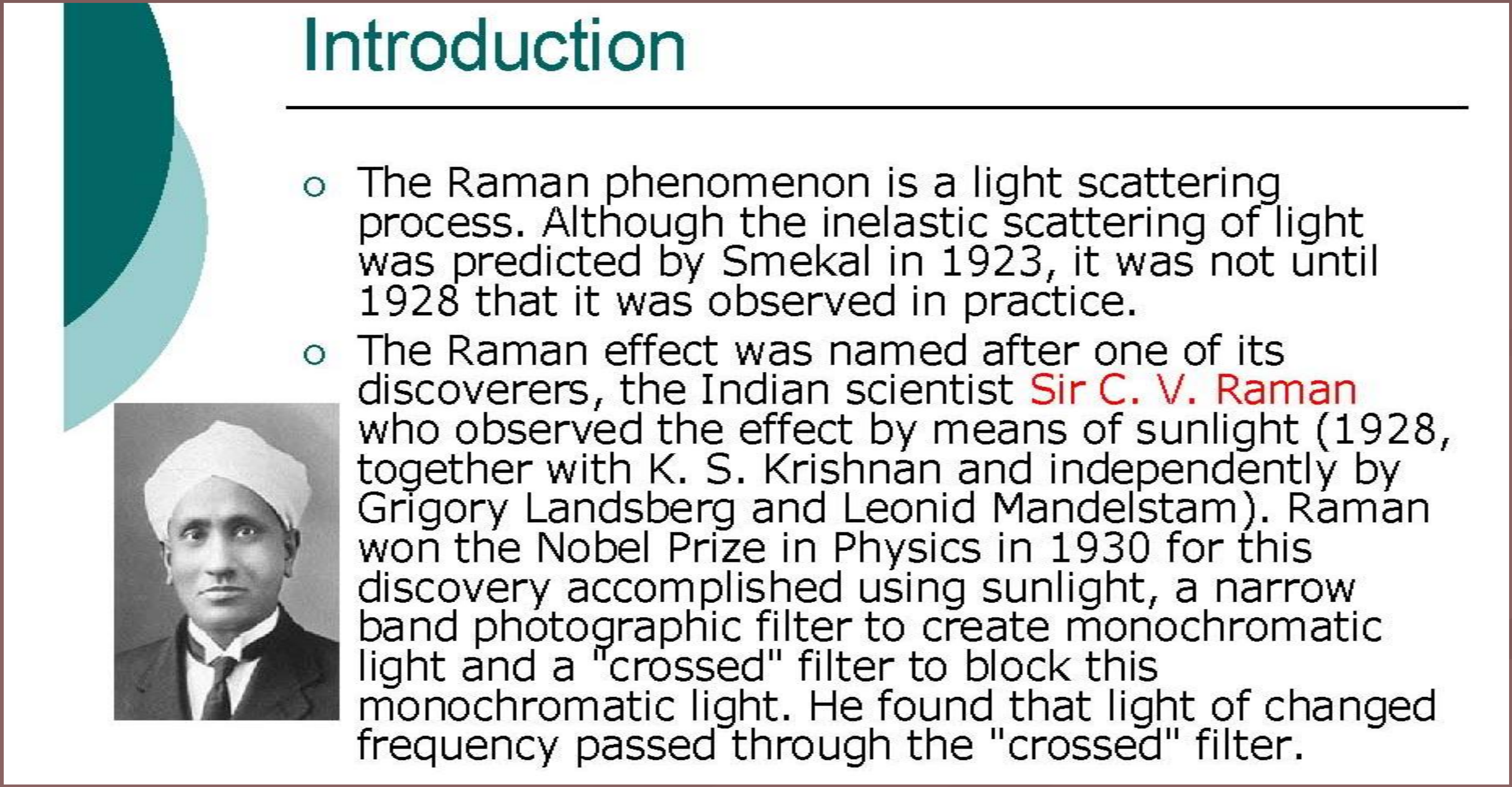


Figure showing the more intense scattering of blue light by the atmosphere relative to red light



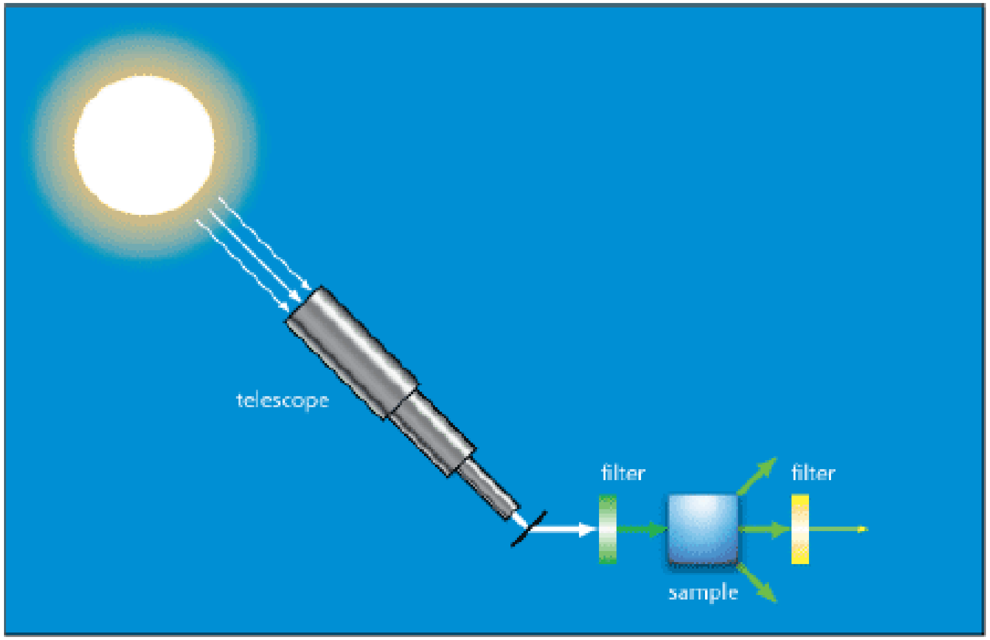
Introduction

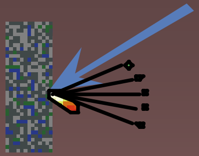
- The Raman phenomenon is a light scattering process. Although the inelastic scattering of light was predicted by Smekal in 1923, it was not until 1928 that it was observed in practice.
- The Raman effect was named after one of its discoverers, the Indian scientist Sir C. V. Raman who observed the effect by means of sunlight (1928, together with K. S. Krishnan and independently by Grigory Landsberg and Leonid Mandelstam). Raman won the Nobel Prize in Physics in 1930 for this discovery accomplished using sunlight, a narrow band photographic filter to create monochromatic light and a "crossed" filter to block this monochromatic light. He found that light of changed frequency passed through the "crossed" filter.

In one of Raman's experiments demonstrating inelastic scattering he used light from the Sun focused using **a telescope** to obtain a high intensity light.

This was passed through a monochromatic filter, and then through a variety of liquids where it underwent scattering.

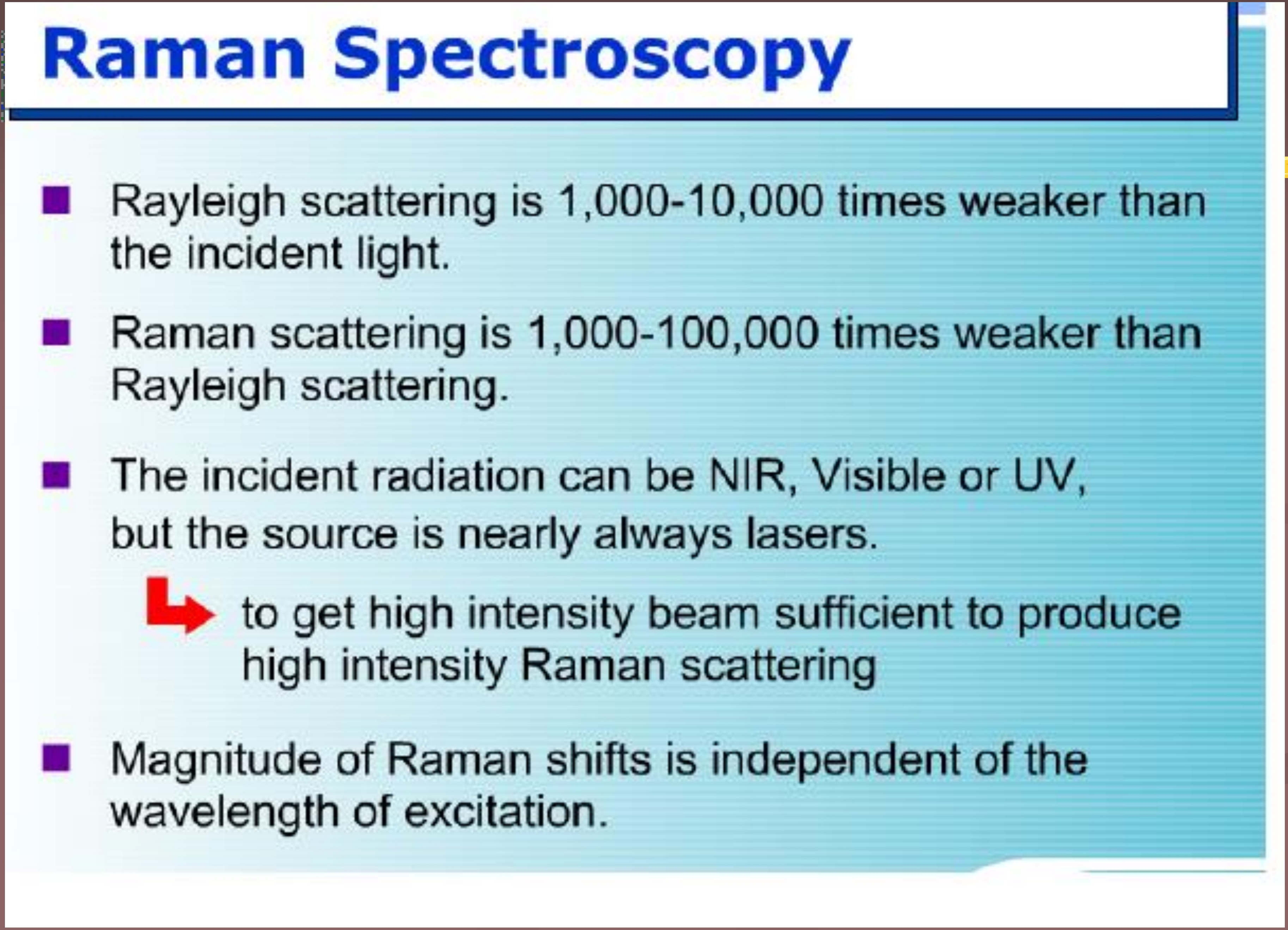
After passing through these he observed it with a crossed filter that blocked the monochromatic light. Some light was seen passing through this filter, which showed that its wavelength had been changed.





Classical Theory

- Rayleigh scattering
  - The induced oscillations of electric charge due to the applied field emit light mostly at the same frequency as the applied field
- Raman scattering
  - About 1 out of 10^8 photons is scattered inelastically (i.e., energy changed)
  - Increase in energy: anti-Stokes shift
  - Decrease in energy: Stokes shift



Raman Spectroscopy

- Rayleigh scattering is 1,000-10,000 times weaker than the incident light.
- Raman scattering is 1,000-100,000 times weaker than Rayleigh scattering.
- The incident radiation can be NIR, Visible or UV, but the source is nearly always lasers.

  ↳ to get high intensity beam sufficient to produce high intensity Raman scattering
- Magnitude of Raman shifts is independent of the wavelength of excitation.

Light-Scattering Spectroscopy

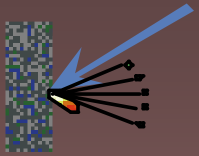
La propagazione della radiazione avviene in maniera rettilinea solo in mezzi omogenei.

Nel caso in cui il mezzo sia disomogeneo, ed in particolare se le disomogeneità hanno dimensioni confrontabili alla lunghezza d'onda della radiazione, si avrà diffusione in direzioni arbitrarie oppure ben definite.

Per **disomogeneità puramente geometriche o locali indipendenti dal tempo la diffusione è elastica.** A seconda della natura e della dimensione della disomogeneità ottica il processo è detto Tyndall scattering, Mie scattering, o Rayleigh scattering.

Per **disomogeneità dipendenti dal tempo la diffusione è anelastica** e per disomogeneità periodiche nel tempo si ha la comparsa di bande laterali (rispetto alla linea di eccitazione). Questo è il caso delle varie forme di scattering Brillouin e scattering Raman.

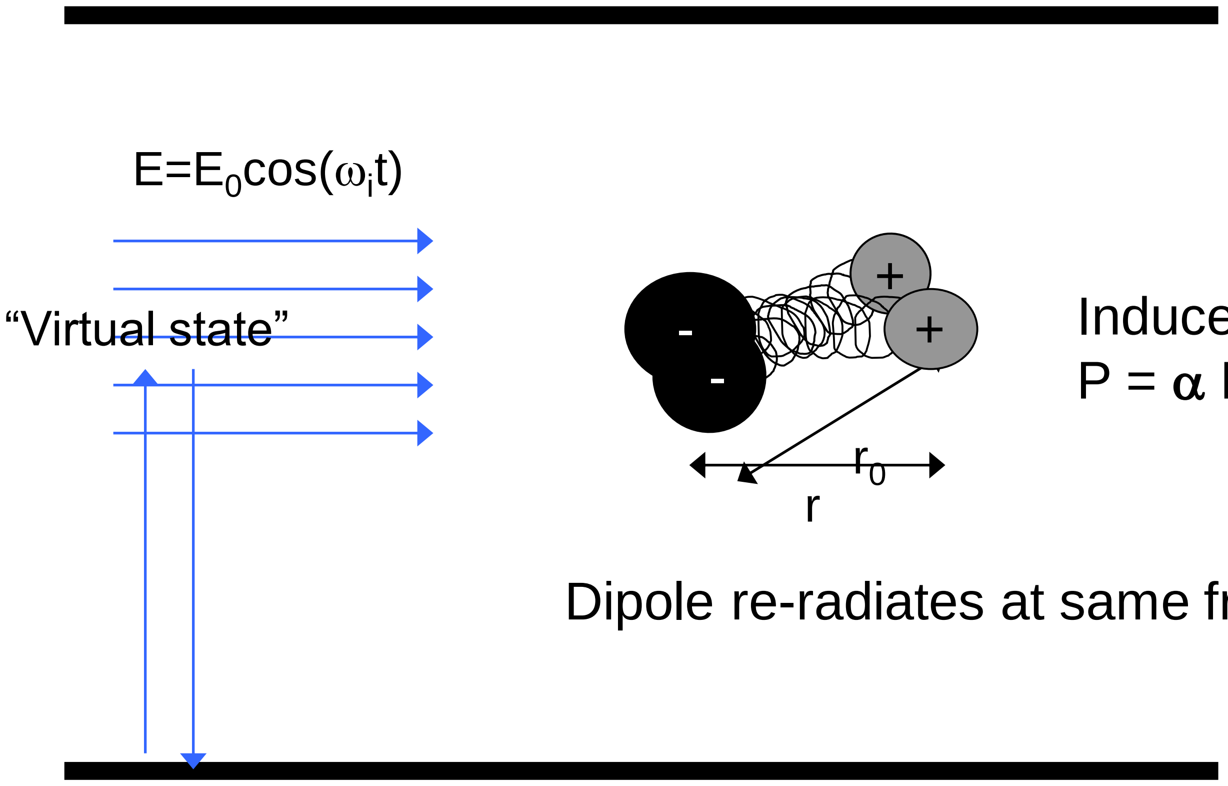
Dall'analisi degli esperimenti di scattering si ottengono informazioni relative agli stati elettronici e vibrazionali dei materiali.



Polarization

- ○ Induced movement of charge in response to an electric field (light)
  $\mu_{in} = \alpha \mathbf{E}$
- ○ The frequency and intensity of the scattered radiation is determined by the frequency and magnitude of the oscillating dipole moment induced by the incident light.

Elastic scattering



Electronic excited state

$E = E_0 \cos(\omega_i t)$

“Virtual state”

Induced polarization
$P = \alpha E$ (α: polarizability)

Dipole re-radiates at same frequency ω_i

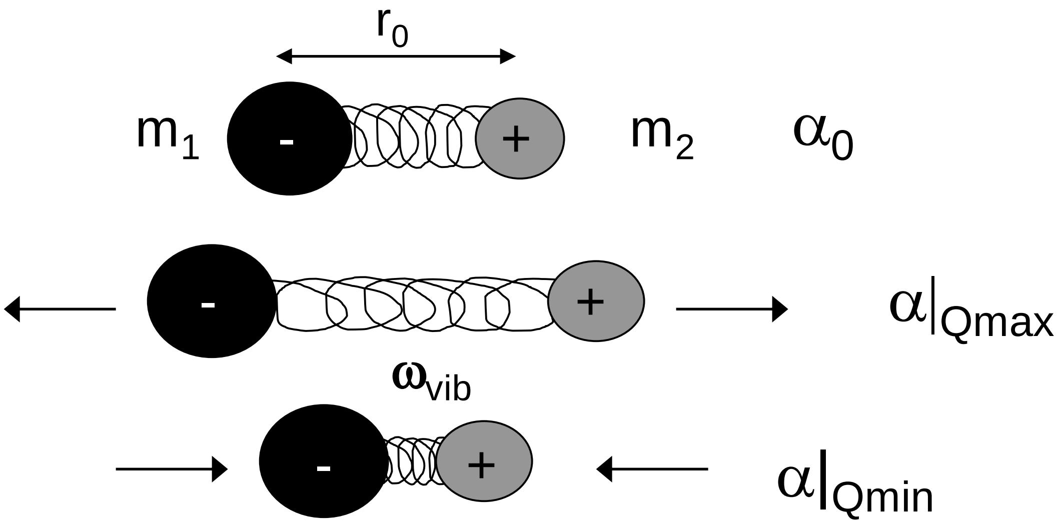
Electronic ground state

Inelastic scattering

Vibration changes polarizability:

$$Q = Q_0 \cos\left(\omega_{vib} t\right)$$

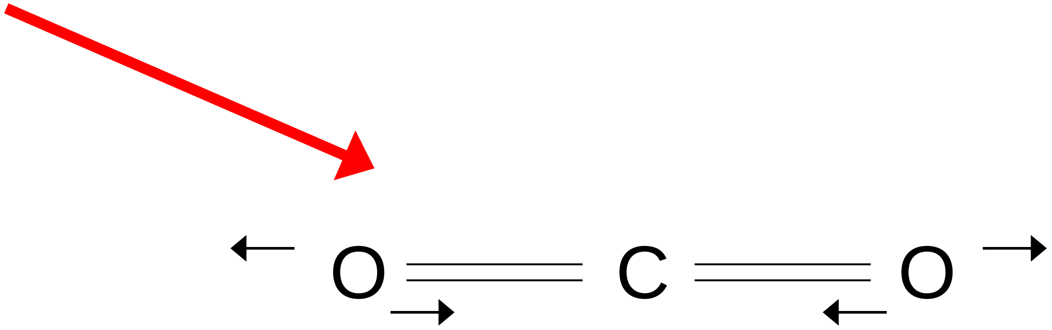
Periodic displacement



Frequency of scattered light differs from the incident light by an amount corresponding to a normal mode of the mechanical oscillator $\omega_s = \omega_i \pm \omega_{vib}$

Energy scales

- Visible light (red), 620 nm ↔ 2 eV ↔ 484 THz ↔ 16130 cm^{-1}



- CO_2 symmetric mode, 1335 cm^{-1} ↔ 41 THz ↔ 0.165 eV ↔ 7.5 μm

Vibrational energies << Optical energies

… Raman scattering

Descrizione classica dell'effetto Raman vibrazionale

Detto **p** il momento di dipolo di una molecola ed **E**=**E**$_0$ cosω_L t il campo elettrico di un'onda e.m. incidente si ha

$$p_i = \mu_{0i} + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \dots$$

dove μ_{oi} è l'eventuale momento di dipolo permanente, α_{ij} è la polarizzabilità e β_{ijk} , γ_{ijkl} , … sono le iperpolarizzabilità.

I termini di ordine superiore al primo nel campo elettrico danno luogo a processi nonlineari come lo scattering iper-Raman. Supponendo di poter trascurare tali termini:

$$p_i \cong \mu_{0i} + \alpha_{ij} E_j$$

Quando la molecola vibra possono cambiare sia l'eventuale momento di dipolo permanente che la polarizzabilità.

Entrambi possono essere espansi in serie di Taylor in termini di coordinate generalizzate q_n che descrivono gli n modi normali di vibrazione:

$$\mu_i(q) = \mu_i(0) + \sum_n \left(\frac{\partial \mu_i}{\partial q_n}\right)_0 q_n + \dots$$

$$\alpha_{ij}(q) = \alpha_{ij}(0) + \sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n}\right)_0 q_n + \dots$$

… Raman scattering

Essendo $\mu_i(0)=\mu_{0i}$ ed $\alpha_{ij}(0)$ il momento di dipolo e la polarizzabilità nella configurazione di equilibrio $q_n=0$.

Per vibrazioni di piccola ampiezza le coordinate $q_n(t)$ degli spostamenti nucleari possono essere approssimate da

$$q_n(t) = q_{0n}\cos(\omega_n t)$$

dove q_{on} ed ω_n rappresentano rispettivamente l'ampiezza e la frequenza dell'n-esimo modo di vibrazione.

Di conseguenza:

$$p_i = \mu_{0i} + \sum_n \left(\frac{\partial \mu_i}{\partial q_n}\right)_0 q_{0n}\cos(\omega_n t) + \alpha_{ij}(0)E_{0j}\cos(\omega_L t)$$
$$+ \sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n}\right)_0 q_{0n}\cos(\omega_n t)E_{0j}\cos(\omega_L t)$$

$$= \mu_{0i} + \sum_n \left(\frac{\partial \mu_i}{\partial q_n}\right)_0 q_{0n}\cos(\omega_n t) + \alpha_{ij}(0)E_{0j}\cos(\omega_L t)$$
$$+ \frac{1}{2} q_{0n}E_{0j}\sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n}\right)_0 \left\{\cos[(\omega_L+\omega_n)t] + \cos[(\omega_L-\omega_n)t]\right\}$$

… Raman scattering

$$\sum_n \left(\frac{\partial \mu_i}{\partial q_n}\right)_0 q_{0\,n} \cos(\omega_n t)$$

⟷ IR absorption

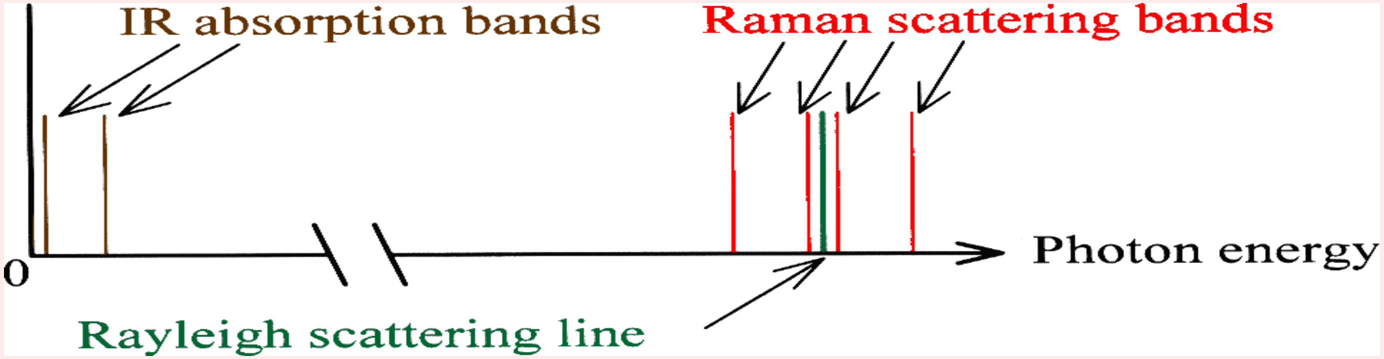
$$\alpha_{ij}(0) E_{0\,j} \cos(\omega_L t)$$

⟷ Rayleigh scattering

$$\frac{1}{2} q_{0\,n} E_{0\,j} \sum_n \left(\frac{\partial \alpha_{ij}}{\partial q_n}\right)_0 \{\cos[(\omega_L + \omega_n)t] + \cos[(\omega_L - \omega_n)t]\}$$

⇕

Raman scattering



I contributi microscopici di ogni molecola si sommano per dare onde macroscopiche con intensità che dipendono dalla popolazione $N(E_i)$ delle molecole nel livello iniziale E_i , dall’intensità della radiazione incidente e dall’espressione

$$(\partial\alpha_{ij}/\partial q_n)q_n .$$

… Raman scattering

In classical terms, the interaction can be viewed as a perturbation of the molecule’s electric field. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10^{-14} seconds or less. The virtual state description of scattering is shown in Figure 1.1a.

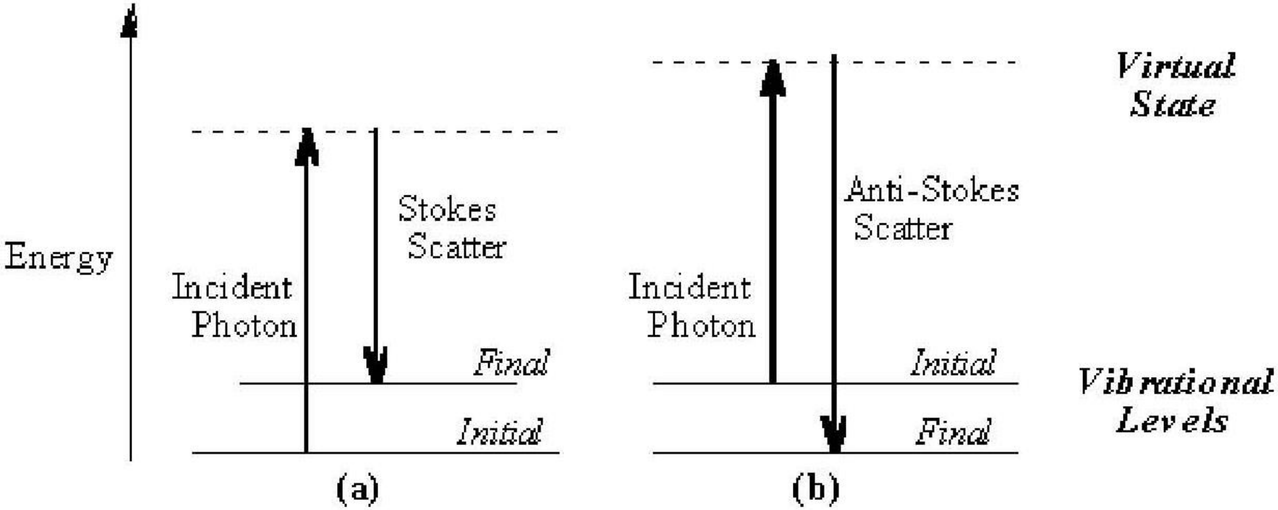
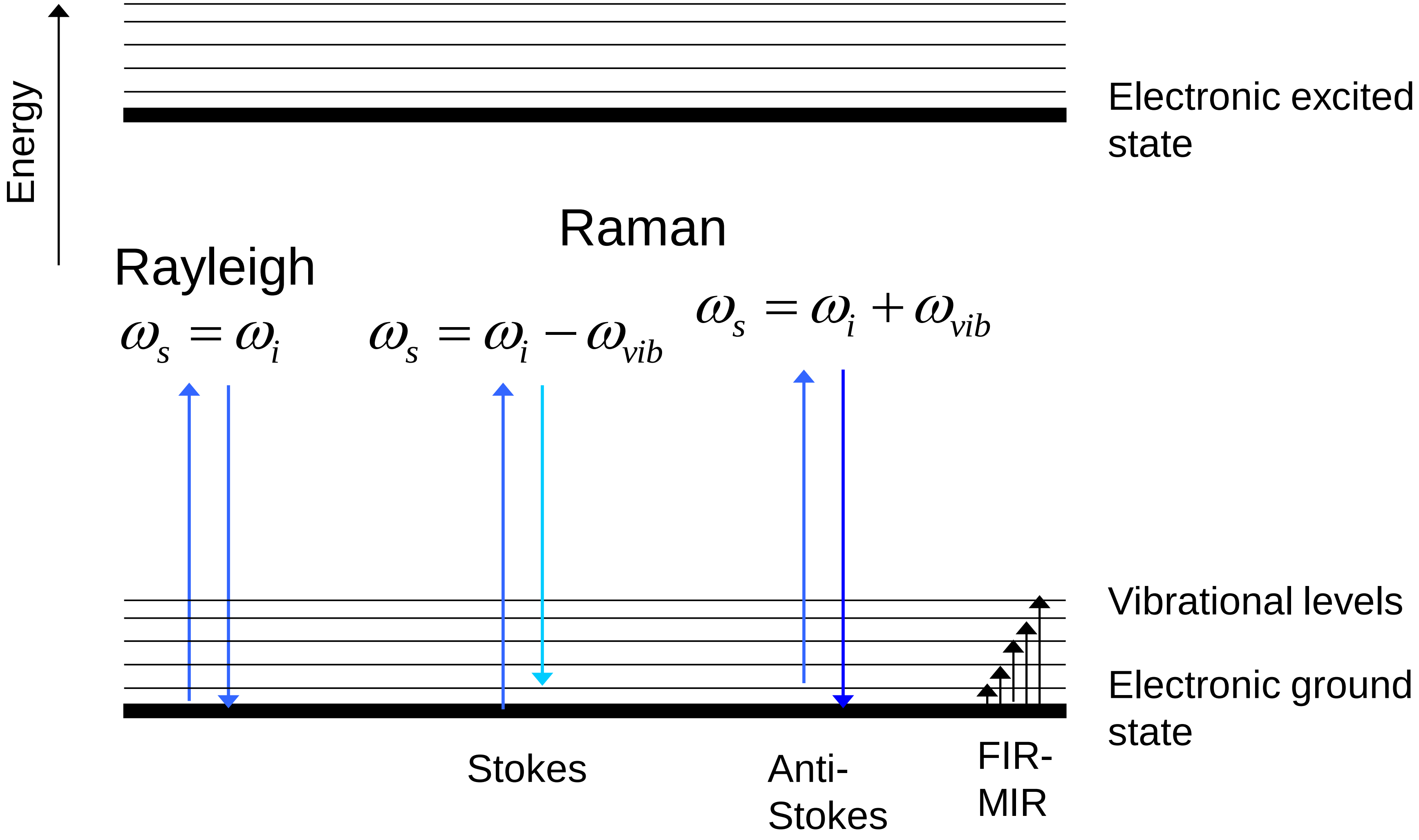


Figure 1.1. Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

Scattering processes



Energy

Electronic excited state

Raman

Rayleigh

$\omega_s = \omega_i$

$\omega_s = \omega_i - \omega_{vib}$

$\omega_s = \omega_i + \omega_{vib}$

Vibrational levels

Electronic ground state

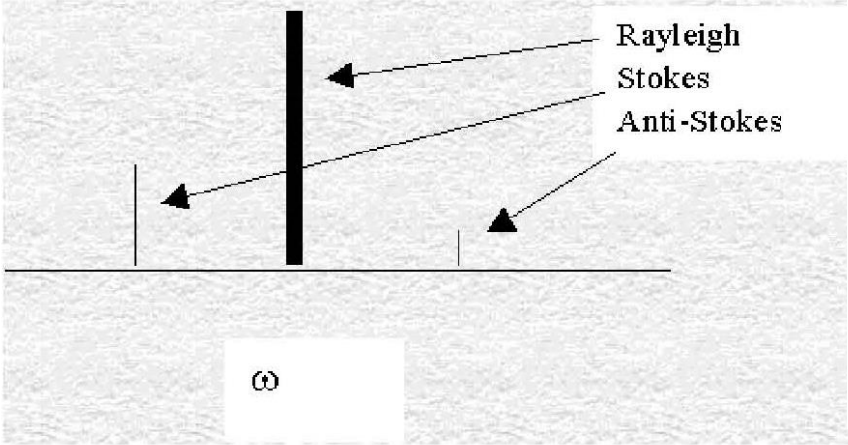
Stokes

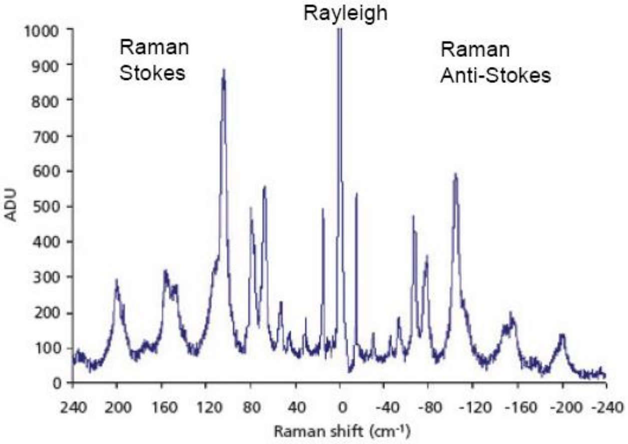
Anti-Stokes

FIR-MIR

… Raman spectrum

The energy of the scattered radiation is less than the incident radiation for the Stokes line and the energy of the scattered radiation is more than the incident radiation for the anti-Stokes line. The energy increase or decrease from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule and therefore the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule.





Raman spectrum of L-cystine

In the example spectrum, notice that the Stokes and anti-Stokes lines are equally displaced from the Rayleigh line. This occurs because in either case one vibrational quantum of energy is gained or lost. Also, note that the anti-Stokes line is much less intense than the Stokes line. This occurs because only molecules that are vibrationally excited prior to irradiation can give rise to the anti-Stokes line. Hence, in Raman spectroscopy, only the more intense Stokes line is normally measured.

… Raman shift

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 1.1a. Numerically, the energy difference between the initial and final vibrational levels, or **Raman shift** in wave numbers (cm^{-1}), is calculated through the equation below

$$\bar{\nu} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

in which $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature rise in a material.

Raman Active

- In order for a particular mode of vibration to be Raman active its polarizability has to change (must be non-zero) with respect to its normal mode coordinate q_i.

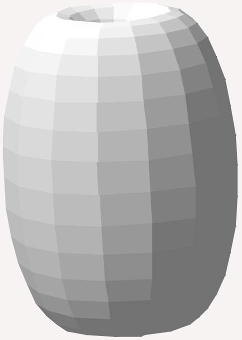
$$\alpha_1 = \frac{\partial \alpha}{\partial q_i} q_i$$

More math

In actual molecules, the nice linear relationship does not hold since both P and E are vectors. Then the equation must be written as

$$\begin{bmatrix} \mathrm{P_x} \\ \mathrm{P_y} \\ \mathrm{P_z} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

The matrix is called the *polarizability tensor*. We can plot α_i (α in the i direction) in all directions we get a 3D surface. Conventionally we plot $1/\sqrt{\alpha_i}$ instead, and get a *polarizability ellipsoid*.



… Raman selection rules and intensity

- A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, **P**, induced in a molecule by an external electric field, **E**, is proportional to the field as shown in equation 2.

  $$\mathbf{P} = \alpha\, \mathbf{E} \qquad (2)$$

  The proportionality constant α is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave.

  Raman scattering occurs because a molecular vibration can change the polarizability. The change is described by the polarizability derivative,

  $$\frac{\delta\alpha}{\delta Q}$$

  where **Q** is the normal coordinate of the vibration. The selection rule for a Raman-active vibration, that there be a change in polarizability during the vibration, is given in the equation:

  $$\frac{\delta\alpha}{\delta Q} \neq 0$$

… Raman selection rules

- The Raman selection rule is analogous to the more familiar selection rule for an infrared-active vibration, which states that there must be a net change in permanent dipole moment during the vibration. From group theory it is straightforward to show that if a molecule has a center of symmetry, vibrations which are Raman-active will be silent in the infrared, and vice versa.

- Scattering intensity is proportional to the square of the induced dipole moment, that is to the square of the polarizability derivative,

$$\left(\frac{\delta\alpha}{\delta Q}\right)^2$$

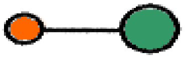
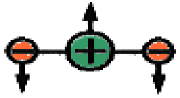
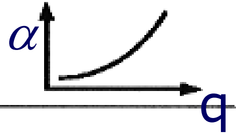
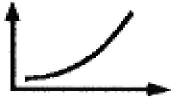
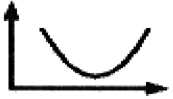
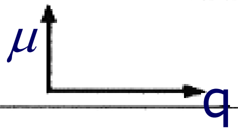
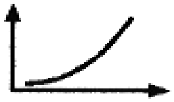
- If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. **The vibrations of a highly polar moiety, such as the O-H bond, are usually weak.** WHY? Because an external electric field can not induce a large change in the dipole moment and stretching or bending the bond does not change this.

- Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The pi-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the distribution of electron density substantially, and causes a large change in induced dipole moment.

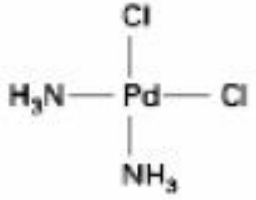
… Raman selection rules

Regole di selezione Una vibrazione può contribuire al processo Raman se essa induce una variazione nella polarizzabilità.

Una vibrazione è invece "IR-active" se induce una variazione nel momento di dipolo.

Molecule vibration					
					
Change of α with q					
$\frac{d\alpha}{dq}$	$\neq 0$	$\neq 0$	$\neq 0$	$=0$	$=0$
Raman active	yes	yes	yes	no	no
Change of μ with q					
$\frac{d\mu}{dq}$	$=0$	$\neq 0$	$=0$	$\neq 0$	$\neq 0$
Infrared active	no	yes	no	yes	yes

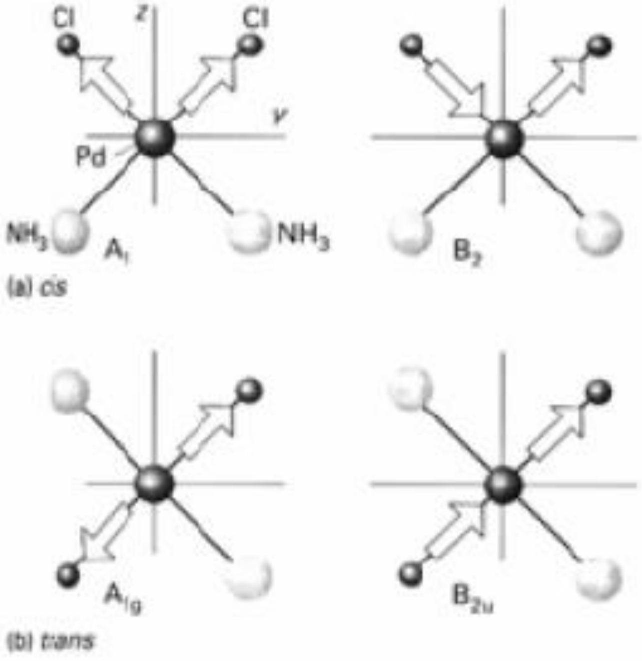
Simmetry / Group Theory



$$H_3N-\overset{Cl}{\underset{NH_3}{Pd}}-Cl$$

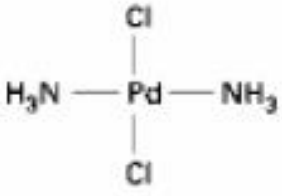
16 *cis*-$[PdCl_2(NH_3)_2]$

C_{2v}



4.26 Some of the Pd–Cl stretching modes of a $[PdCl_2(NH_3)_2]$ square-planar complex. The motion of the Pd atom (which preserves the center of mass of the molecule) is not shown.

Both IR and Raman active



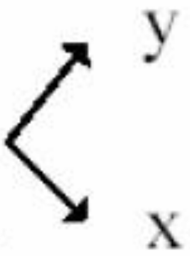
$$H_3N-\overset{Cl}{\underset{Cl}{Pd}}-NH_3$$

17 *trans*-$[PdCl_2(NH_3)_2]$

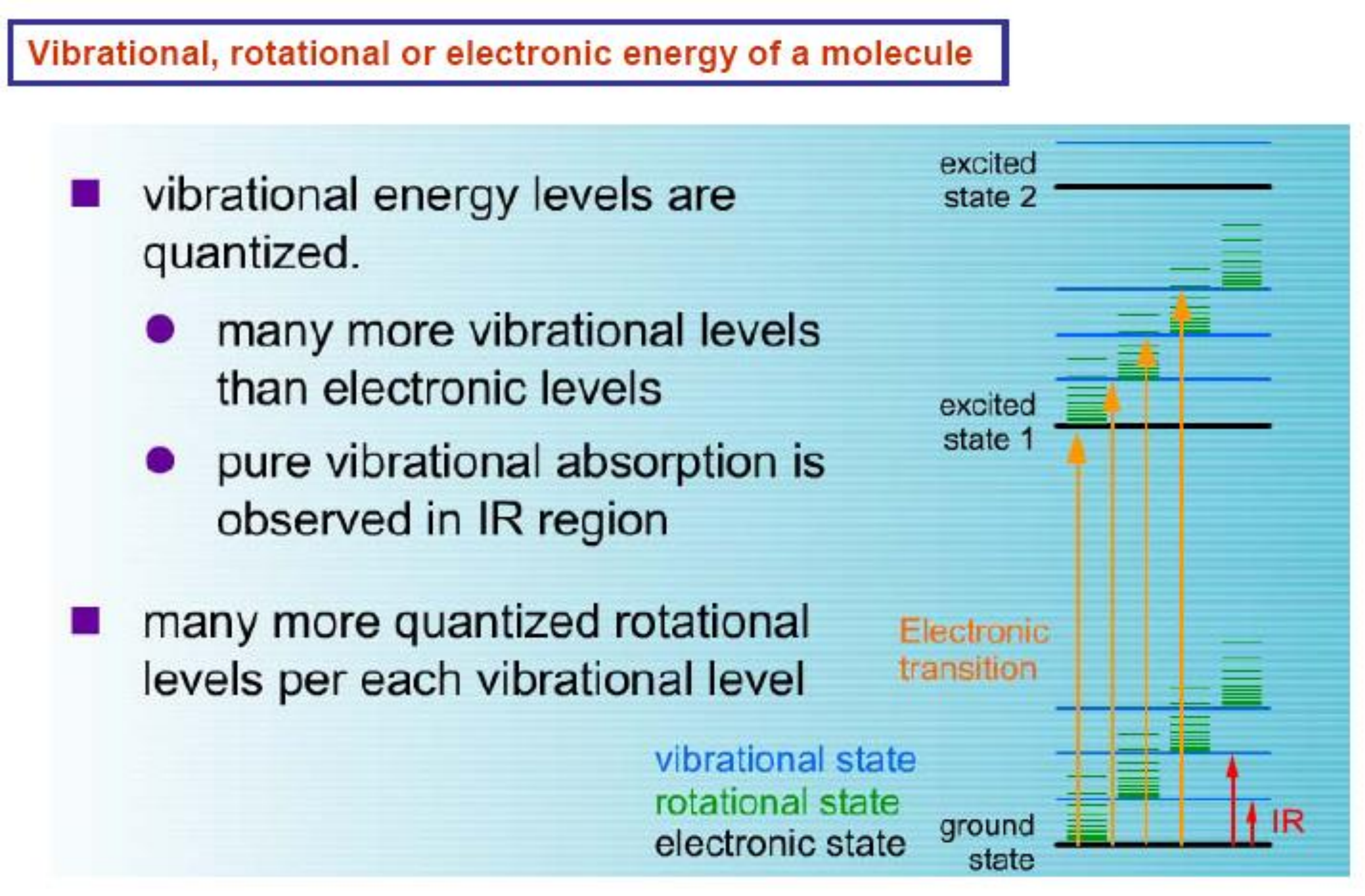
D_{2h}

Only B_{2u} IR active

A_{1g} is Raman active



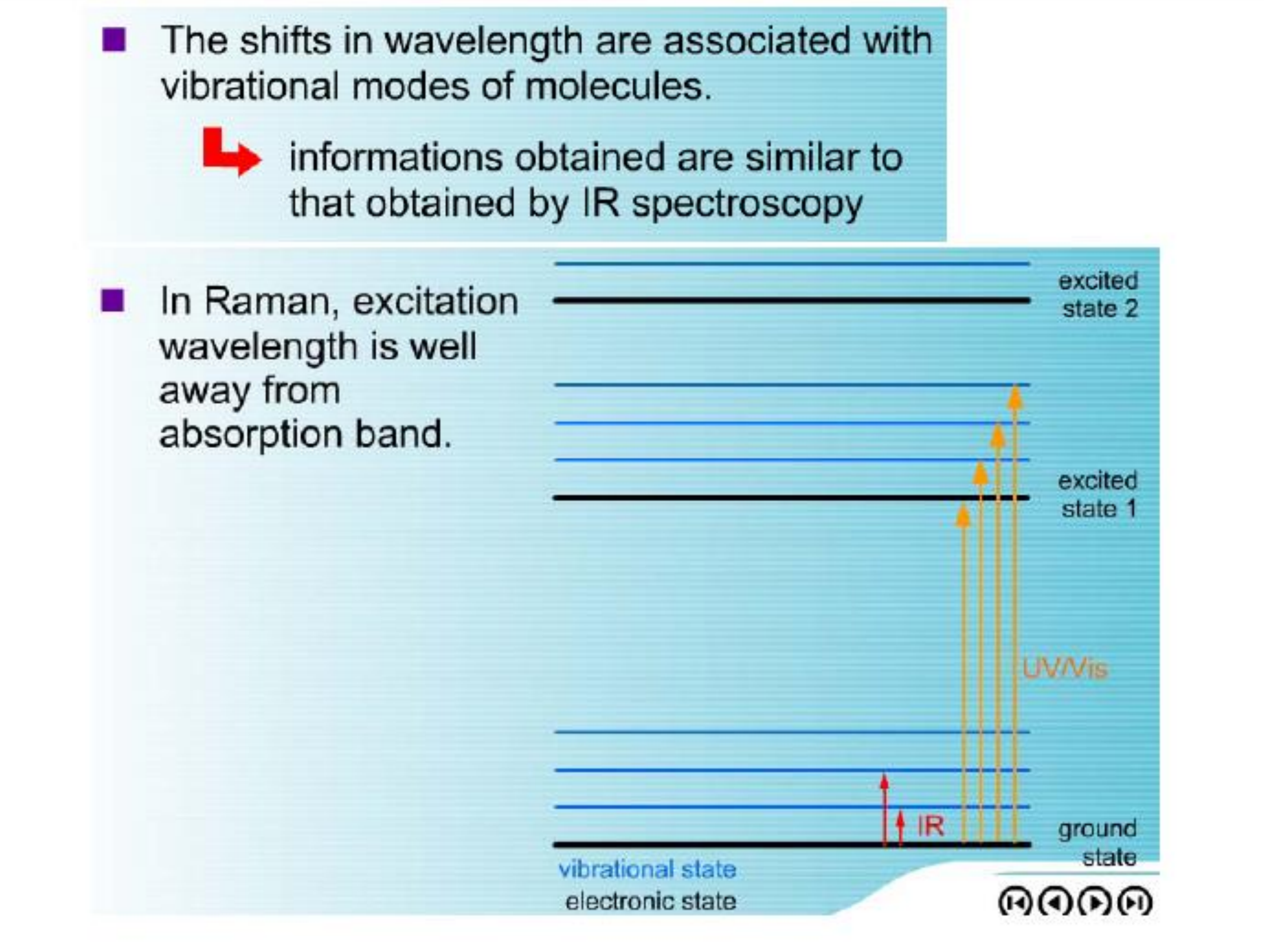
Energy levels



Vibrational, rotational or electronic energy of a molecule

- vibrational energy levels are quantized.
  - many more vibrational levels than electronic levels
  - pure vibrational absorption is observed in IR region
- many more quantized rotational levels per each vibrational level

….Energy levels

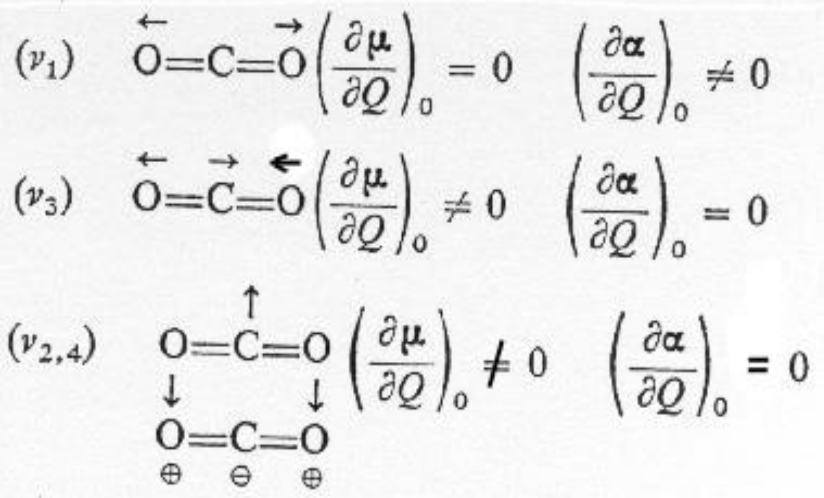


- The shifts in wavelength are associated with vibrational modes of molecules.

  ↳ informations obtained are similar to that obtained by IR spectroscopy

- In Raman, excitation wavelength is well away from absorption band.

Example: There are 4 normal modes of CO_2. Only ν_1 is Raman active



$$(\nu_1)\quad \overset{\leftarrow}{O}{=}C{=}\vec{O}\quad \left(\frac{\partial \mu}{\partial Q}\right)_0 = 0 \qquad \left(\frac{\partial \alpha}{\partial Q}\right)_0 \neq 0$$

$$(\nu_3)\quad \overset{\leftarrow}{O}{=}\vec{C}{=}\overset{\leftarrow}{O}\quad \left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0 \qquad \left(\frac{\partial \alpha}{\partial Q}\right)_0 = 0$$

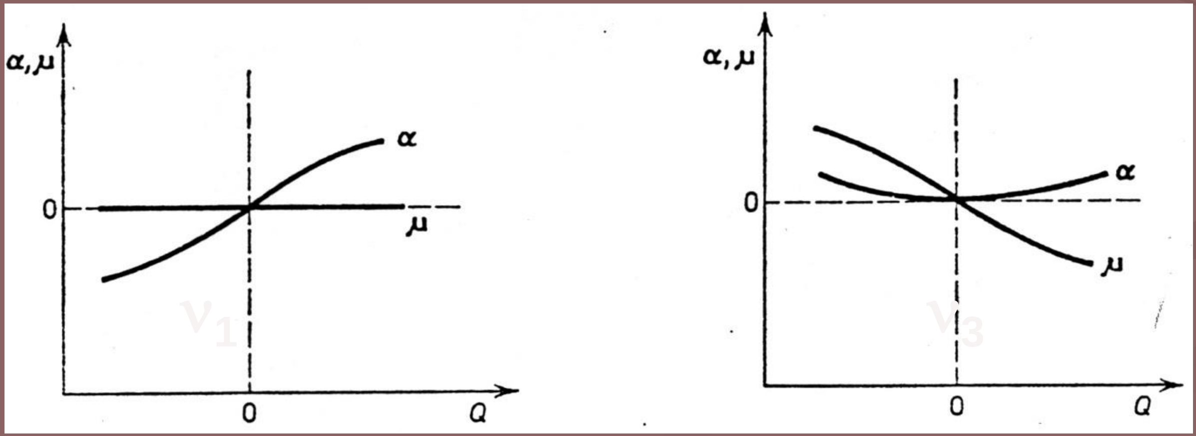
$$(\nu_{2,4})\quad \underset{\downarrow}{O}{=}\overset{\uparrow}{C}{=}\underset{\downarrow}{O}\quad \left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0 \qquad \left(\frac{\partial \alpha}{\partial Q}\right)_0 = 0$$

$$\underset{\oplus}{O}{=}\underset{\ominus}{C}{=}\underset{\oplus}{O}$$

μ is dipole moment;

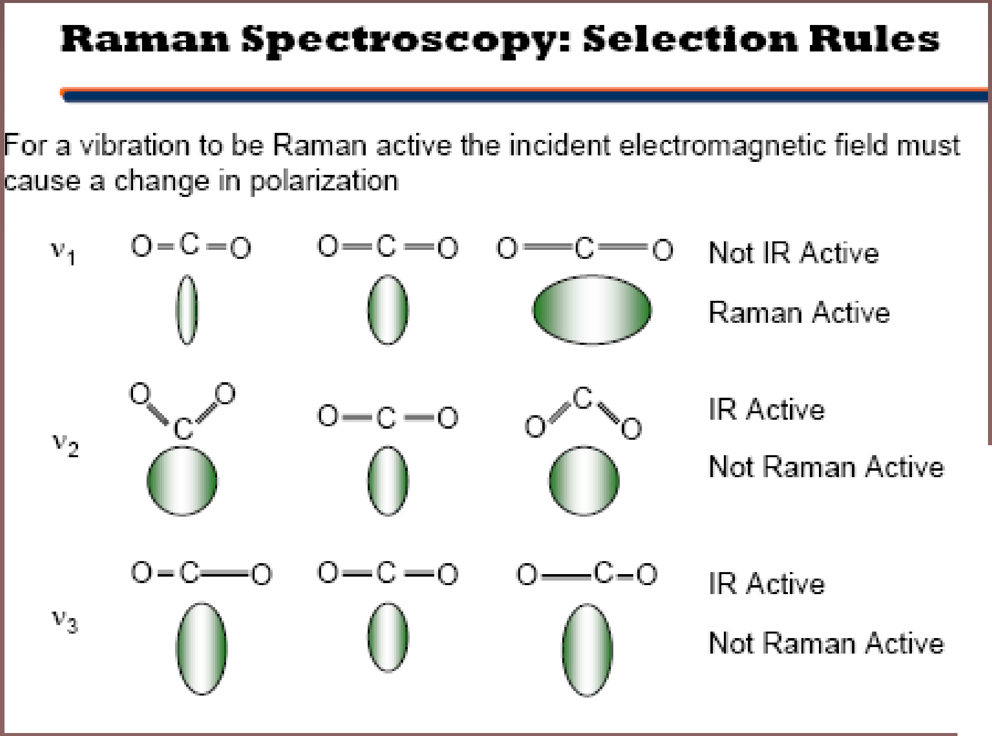
α is polarizability;

Q is vibration coordinate, The slopes are measured at Q = 0 (I.e. at the equilibrium position).



Change in dipole moment, μ, and polarizability, α, during CO_2 vibrations

CO_2



Raman Spectroscopy: Selection Rules

For a vibration to be Raman active the incident electromagnetic field must cause a change in polarization

ν_1: Not IR Active

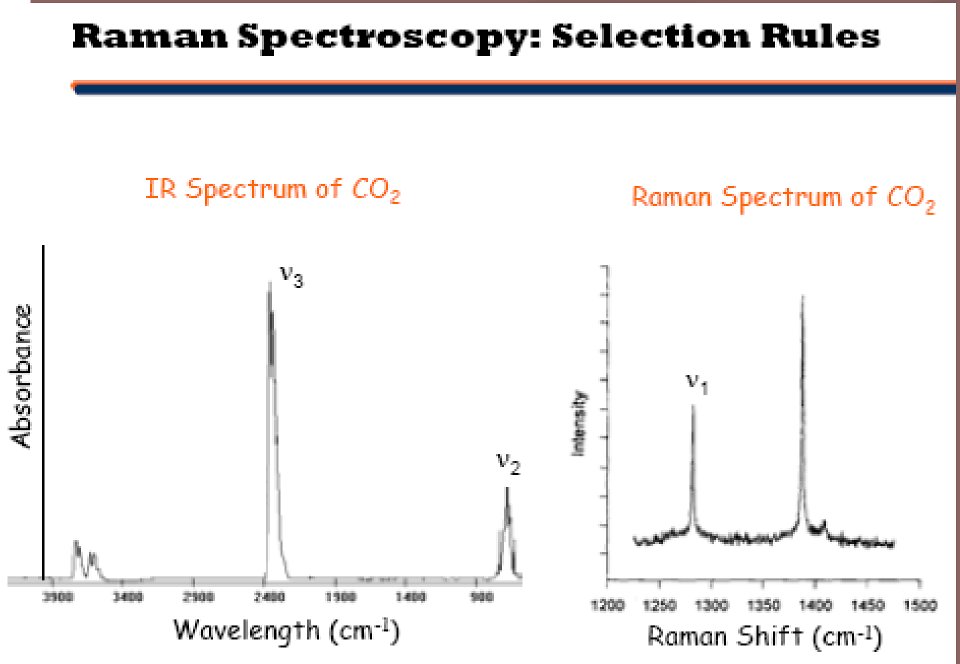
Raman Active

ν_2: IR Active

Not Raman Active

ν_3: IR Active

Not Raman Active

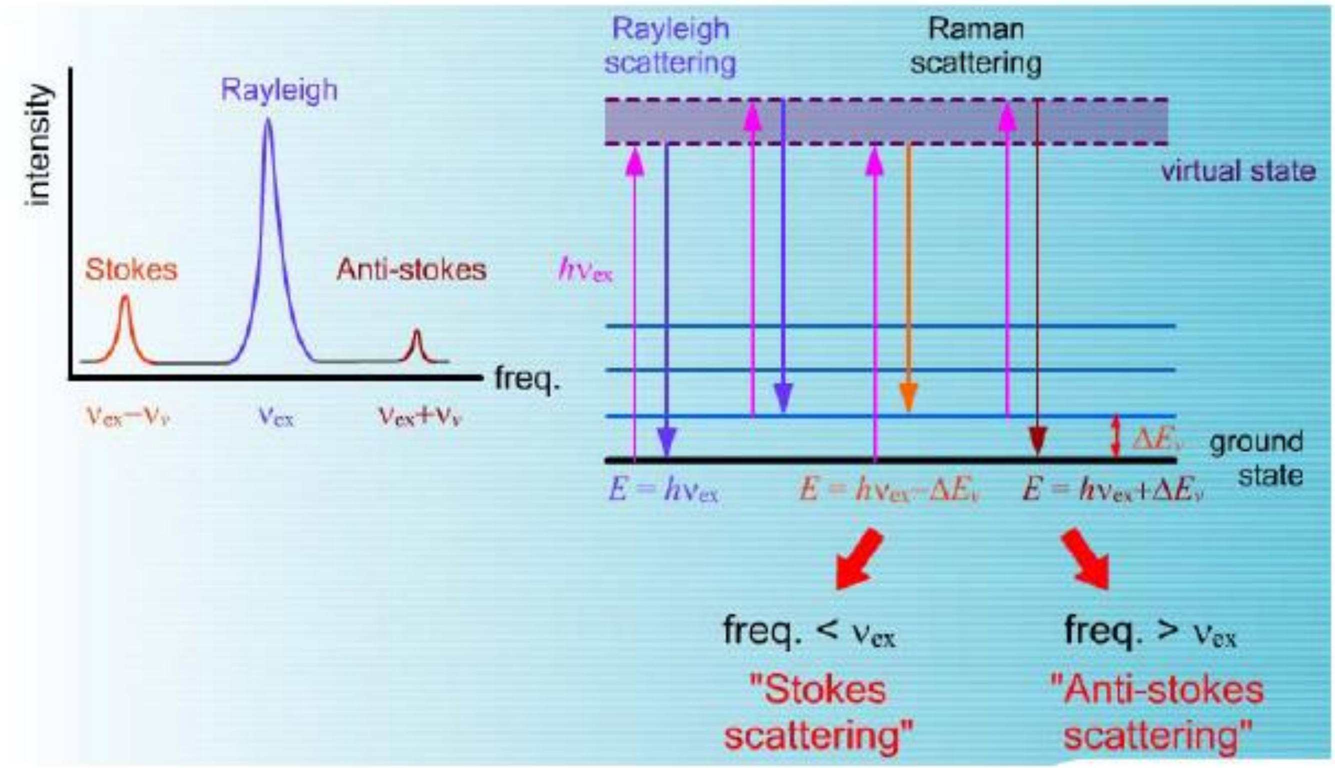


Raman Spectroscopy: Selection Rules

IR Spectrum of CO_2

Raman Spectrum of CO_2

Stokes and anti-Stokes



Normally in Raman spectroscopy only the Stokes half of the spectrum is used, due to its greater intensity.

Stokes and anti-Stokes

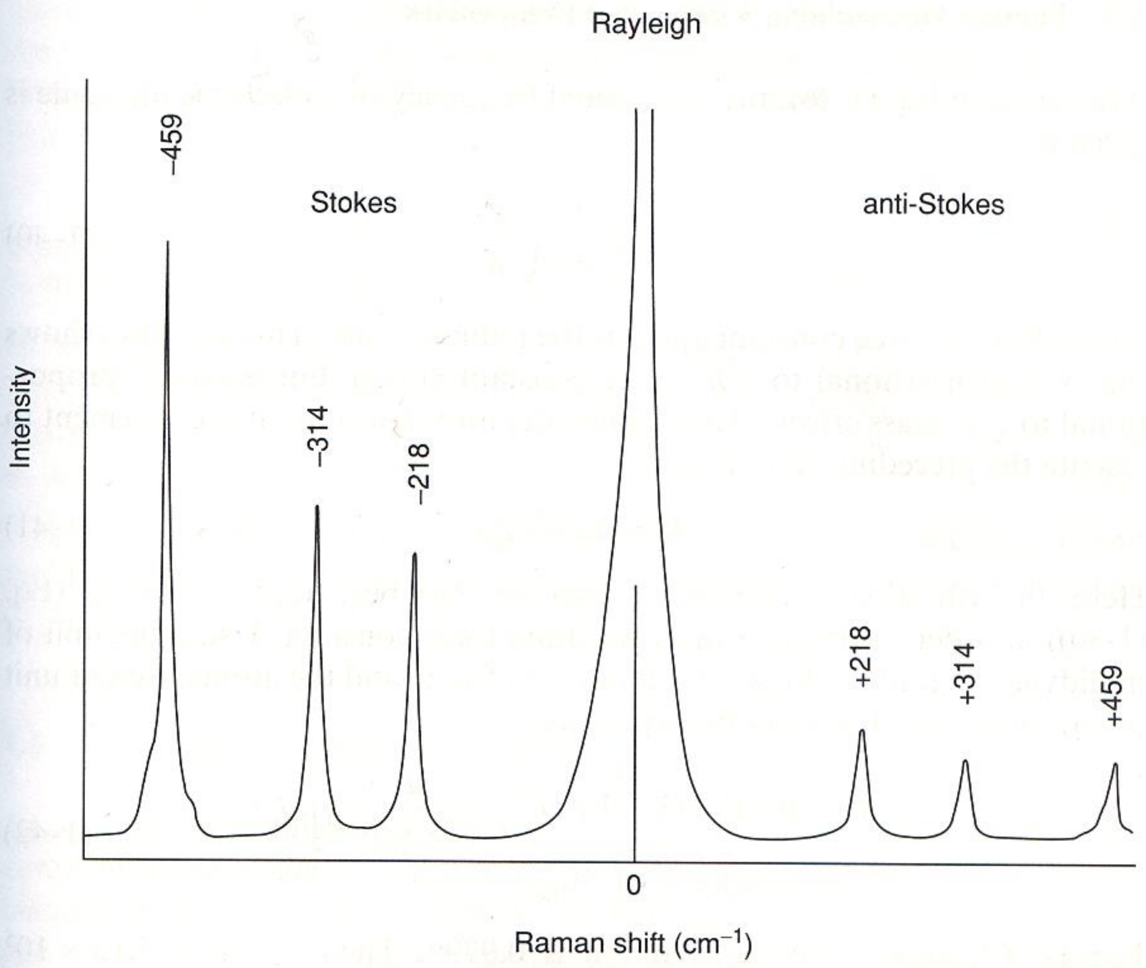
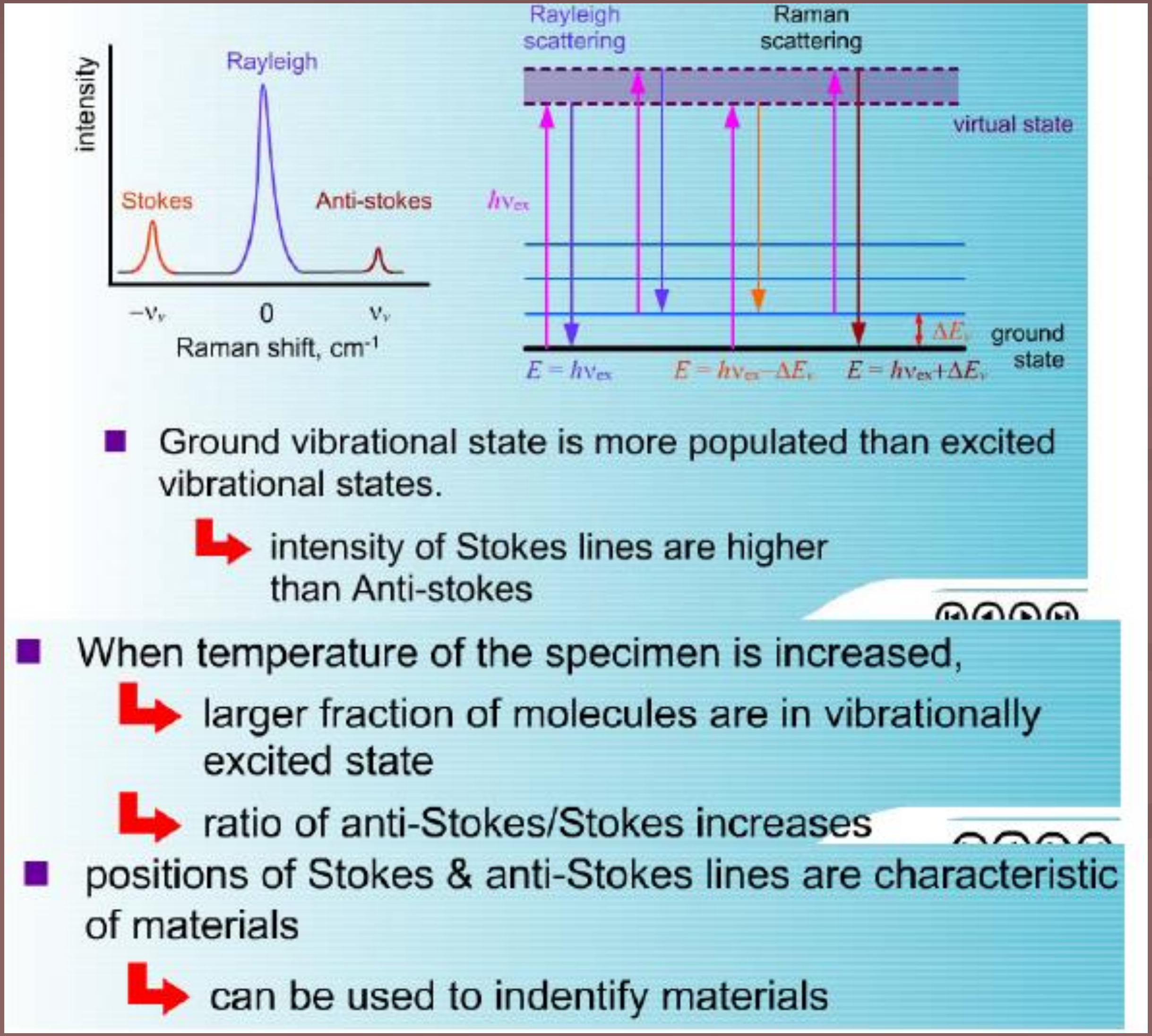


Figure 1-9 Raman spectrum of CCl_4 (488.0 nm excitation).

As you can see, the Stokes peaks correspond to lower photon frequencies and lower energies. The anti-Stokes side is symmetric but corresponds to higher frequencies and energies. The Stokes lines are stronger because the population of molecules at ν=0 is much larger than at ν=1 by the Maxwell-Boltzmann distribution law.

Stokes and anti-Stokes

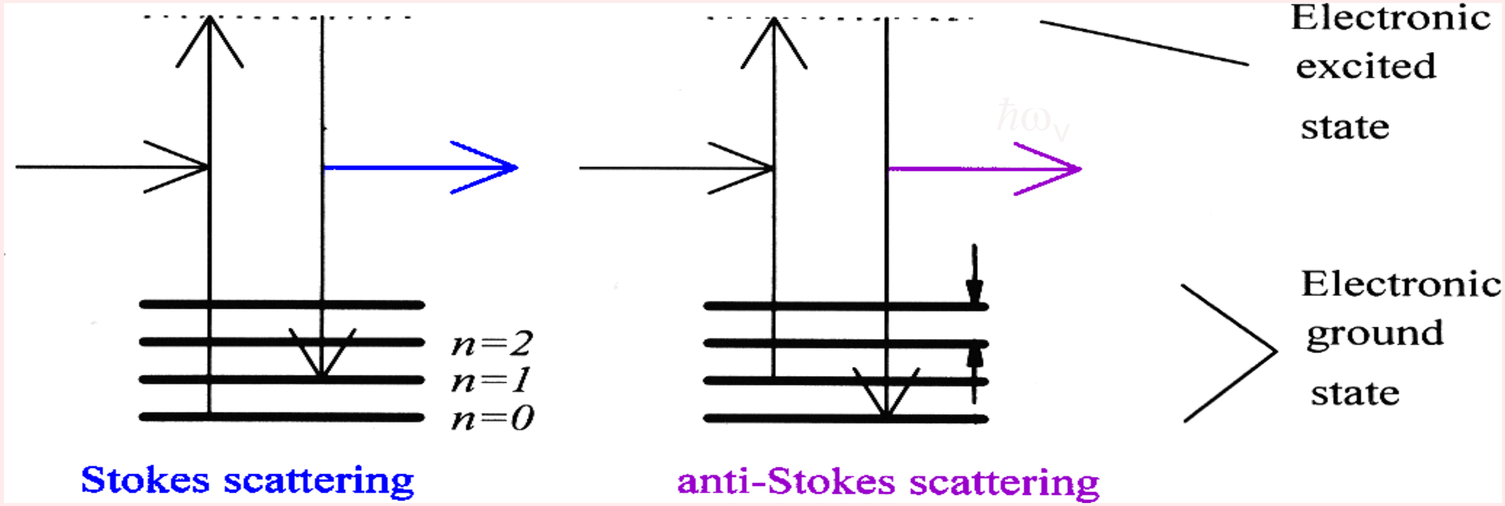


- Ground vibrational state is more populated than excited vibrational states.
  - ↳ intensity of Stokes lines are higher than Anti-stokes
- When temperature of the specimen is increased,
  - ↳ larger fraction of molecules are in vibrationally excited state
  - ↳ ratio of anti-Stokes/Stokes increases
- positions of Stokes & anti-Stokes lines are characteristic of materials
  - ↳ can be used to indentify materials

Stokes and anti-Stokes

I fotoni possono sempre creare quanti vibrazionali in un sistema → la probabilità di scattering Stokes non dipende dalla temperatura.

Al contrario, la probabilità di annichilazione di un fonone dipende dalla prob. di trovare il sistema in uno stato vibrazionale eccitato.



Il rapporto delle bande di Stokes e anti-Stokes è proporzionale al fattore di Boltzmann exp(- $\hbar\omega_v$ /kT) , essendo $\hbar\omega_v$ il quanto di energia vibrazionale.

Esempio: $\hbar\omega_v$ = 1000 cm^{-1}, T=300 K →
kT ~ 250 cm^{-1} → exp (– $\hbar\omega_v$ /kT) ~ 0.02.

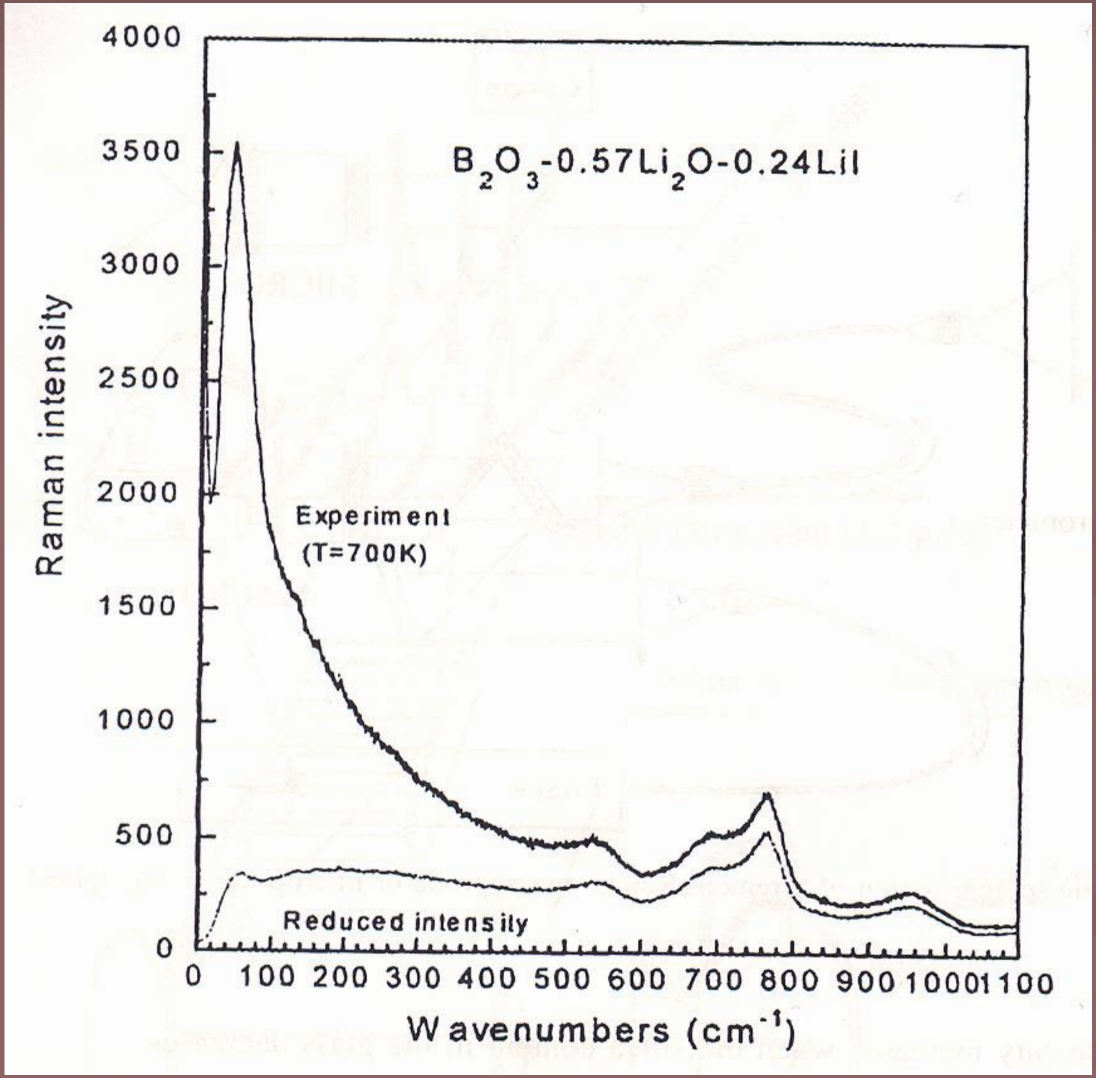
Temperature correction

- The thermal population factor can mask peaks or bands in the low-frequency region of the spectrum. The corrected (reduced) Raman intensity can be calculated from

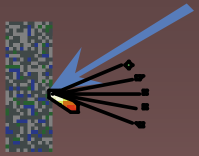
$$I_{reduced} = \frac{I_{observed}}{Exp\left[-\frac{\hbar\omega}{kT}\right]+1}$$

- This needs to be done before any peak assignments are made

Temperature correction



- The effect of the temperature correction can be seen at left, where the most dramatic change occurs at low wavenumbers.

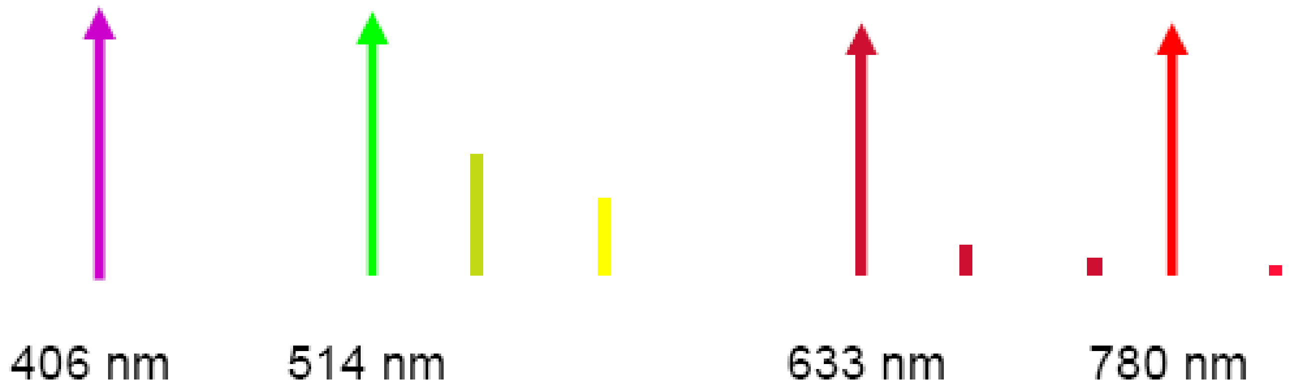


Scattering

- Classically, the observed intensity of Raman scattering is proportional to
  - $I_R = \mu(\nu_0 \pm \nu_j)^4 \alpha_j^2 Q_j^2$

where ν_0 is the laser light frequency, ν_j is the frequency of the jth mode, Q_j the displacement, and α is the polarizability of that mode. **Note the dependence on the fourth power of the laser light**, typical for dipole scattering.

Choice of excitation wavelenght



- Shorter wavelength lasers excite Raman scattering more efficiently — ν^4 dependence.
- *e.g.* efficiency$_{514\ \mathrm{nm}} \cong$ 5 x efficiency$_{780\ \mathrm{nm}}$

Resonance term

- the resonance term in the transition probability leads to an enhancement of the scattering intensity when the incident light is close to an electronic energy level. This allows to explore the energy spectrum of the mater in the light energy range.
- Only one term contribute the most, because it is the multiply of two resonances: that of the incoming beam and that of the outgoing beam.

In definitiva: $I_{scatt} = N_i(E_i)\sigma_R(i \to f) I_L$

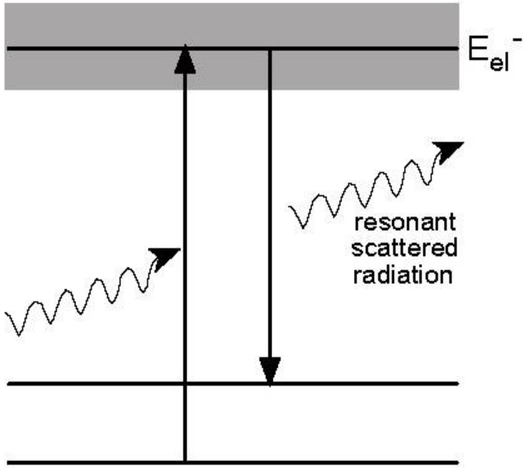
essendo σ_R (i→f) la sezione d'urto di scattering Raman. Si dimostra:

$$\sigma_R(i \to f) = \frac{8\pi\omega_s^4}{9\hbar c^4}\left|\sum_j\left[\frac{\langle\alpha_{ij}\rangle\hat{e}_L\langle\alpha_{jf}\rangle\hat{e}_s}{(\omega_{ij}-\omega_L-i\gamma_j)}+\frac{\langle\alpha_{ij}\rangle\hat{e}_s\langle\alpha_{jf}\rangle\hat{e}_L}{(\omega_{jf}-\omega_L-i\gamma_j)}\right]\right|^2$$

Some specific features of Raman Spectroscopy

1) Resonance Raman

… if incident radiation nearly conincides with the energy of an electronic transition of the sample.

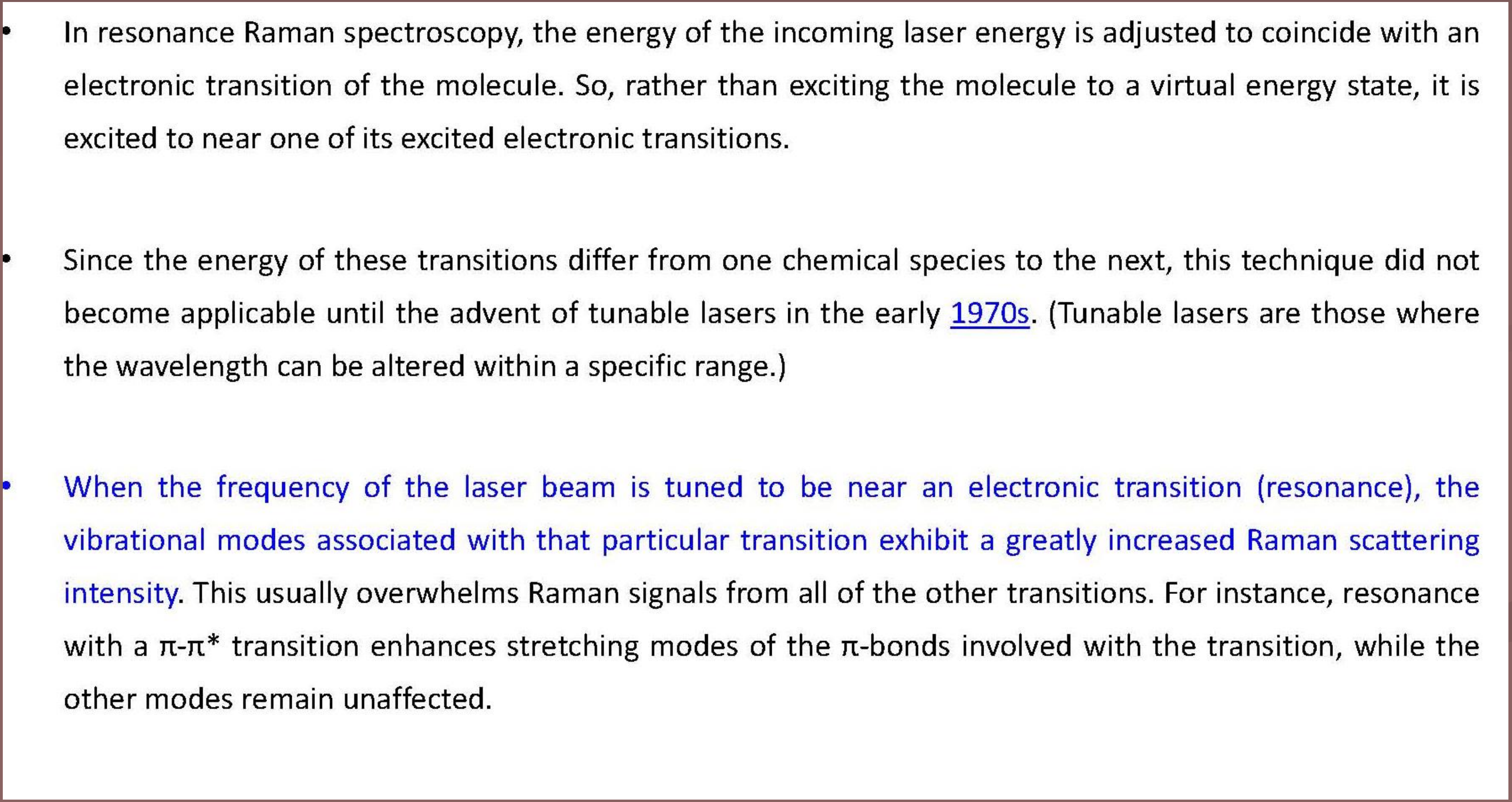


-> intensity of the Raman scattered radiation is strongly enhanced.

-> applications for pigments (β-carotene; chlorophyll; phthalocyanines etc.) with strong absorption in the UV and visible region of the spectrum.

-> This leads to a certain degree of selectivity if these pigments are bound to very large biological molecules, and only certain vibrational excitations in specific parts of the molecule are enhanced.

Resonance Raman Spectroscopy



- In resonance Raman spectroscopy, the energy of the incoming laser energy is adjusted to coincide with an electronic transition of the molecule. So, rather than exciting the molecule to a virtual energy state, it is excited to near one of its excited electronic transitions.

- Since the energy of these transitions differ from one chemical species to the next, this technique did not become applicable until the advent of tunable lasers in the early 1970s. (Tunable lasers are those where the wavelength can be altered within a specific range.)

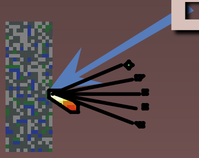
- When the frequency of the laser beam is tuned to be near an electronic transition (resonance), the vibrational modes associated with that particular transition exhibit a greatly increased Raman scattering intensity. This usually overwhelms Raman signals from all of the other transitions. For instance, resonance with a π-π* transition enhances stretching modes of the π-bonds involved with the transition, while the other modes remain unaffected.

Resonance Raman spectroscopy

- The main advantage of RR spectroscopy over traditional Raman spectroscopy is the large increase in intensity of the peaks in question (by as much as a factor of 10^6).
- This allows RR spectra to be generated with sample concentrations as low as 10^{-8} M.
- This is in stark contrast to conventional Raman spectra, which usually requires concentrations greater than 0.1 M. Also, as previously mentioned, RR spectra usually exhibit only a few peaks, and different peaks can be selected for by targeting specific electronic transitions. The main disadvantage of RR spectroscopy is the increased risk of fluorescence and photodegradation of the sample due to the increased energy of the incoming laser light. Both of these factors can be minimized by using an infrared laser instead of visible light.

Outline

- General principles
  - Light scattering
  - Electronic and vibrational energy levels
  - Experimental implementation
- Raman scattering in crystals
  - Resonant enhancement
- Signal enhancement
  - Resonant enhancement
  - Surface enhancement (SERS)



Energy and momentum conservation one phonon process

- Conservation of energy and crystal momentum requires (for one-phonon process)

$$\hbar\omega_s = \hbar\omega_i - \hbar\omega_0$$

$$\hbar\mathbf{k}_s = \hbar\mathbf{k}_i - \hbar\mathbf{q} + \hbar\mathbf{Q}$$

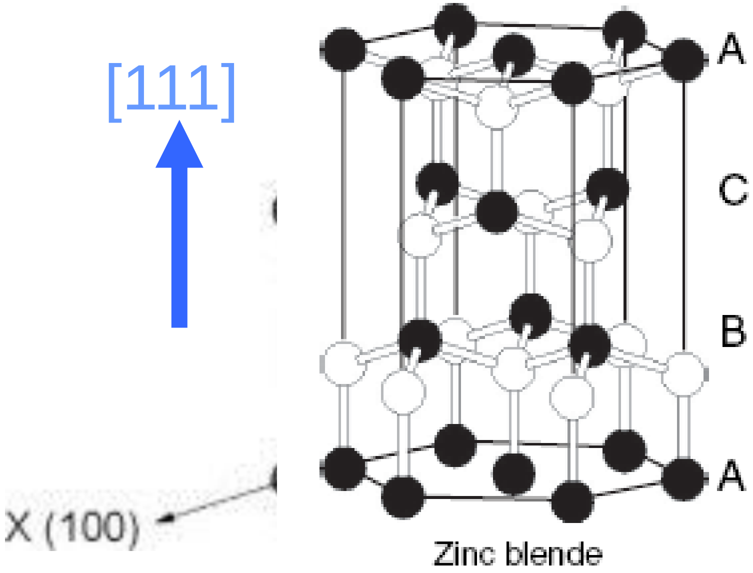
•Sizes of k,q,ω_i and ω_0

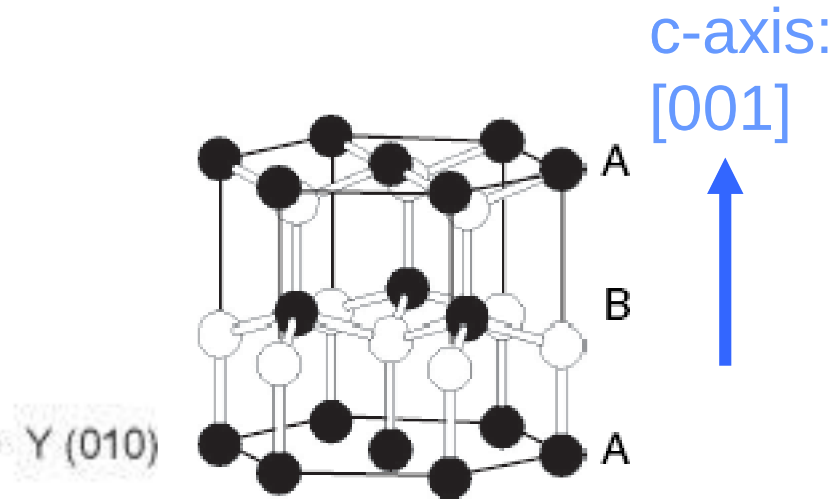
Wavevector of a visible light photon ~ 10^5cm^{-1}
Wavevector of phonons range typically 0-10^7cm^{-1}
Photons can exchange momentum only with zone center phonons (**q**~0) and **Q**=0

$$\hbar\omega_i \sim 1eV \qquad \hbar\omega_0 \sim 1-100meV$$

Raman scattering in crystals

- Vibrational modes in crystals: phonons
- Symmetry considerations = entire field of physics!





Zincblende: cubic crystal

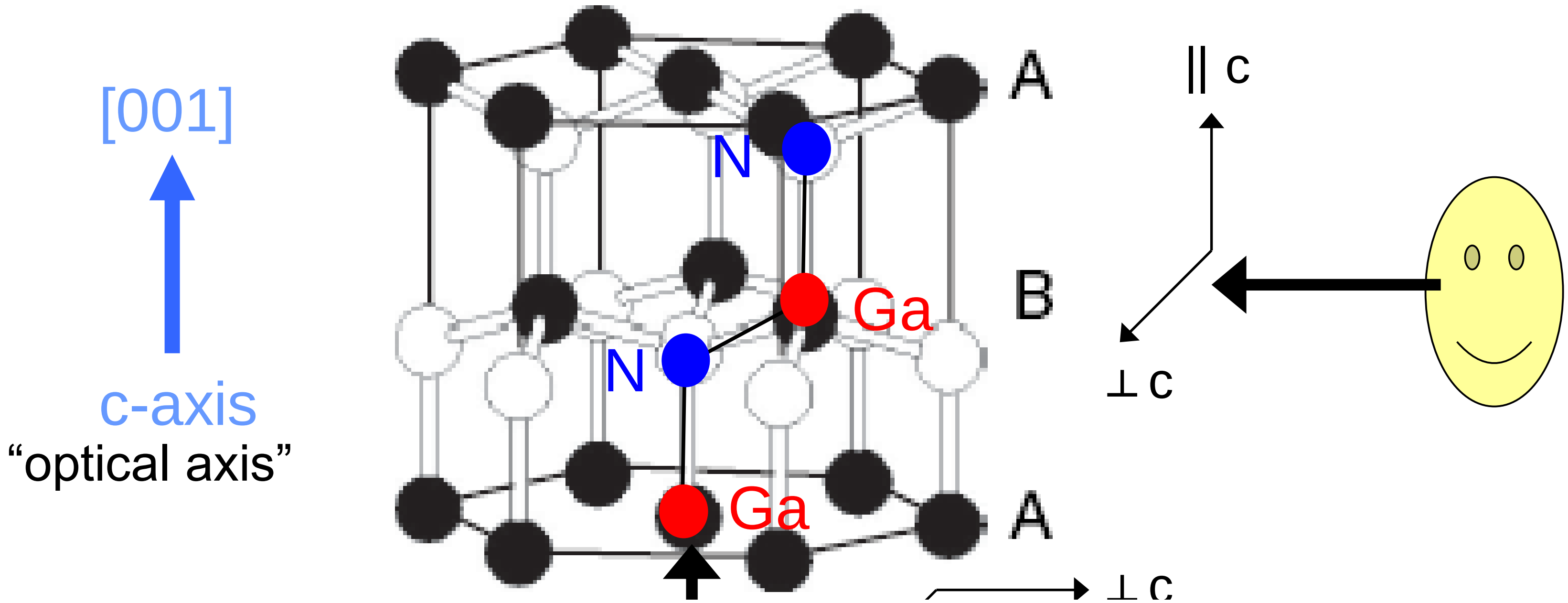
e.g. III-V semiconductors: usual for III-Arsenides and III-Antimonides, sometimes also III-Nitrides

Wurtzite: hexagonal crystal

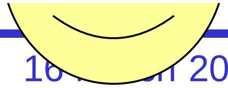
e.g. II-VI and III-Nitrides semiconductors: ZnO, ZnS, CdSe, GaN, etc.

Raman scattering in crystals

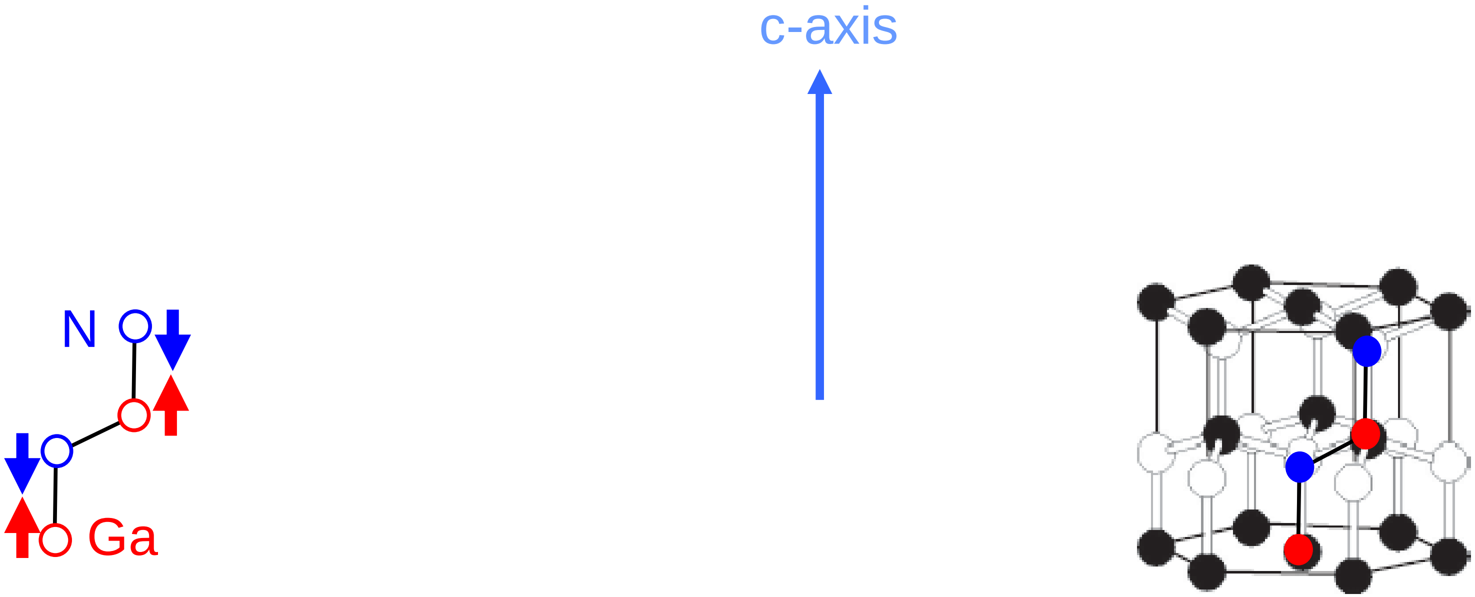
- Wurtzite crystal: hexagonal structure
  - Anisotropic crystal: Material properties like refractive index, effective masses depend on direction relative to c-axis



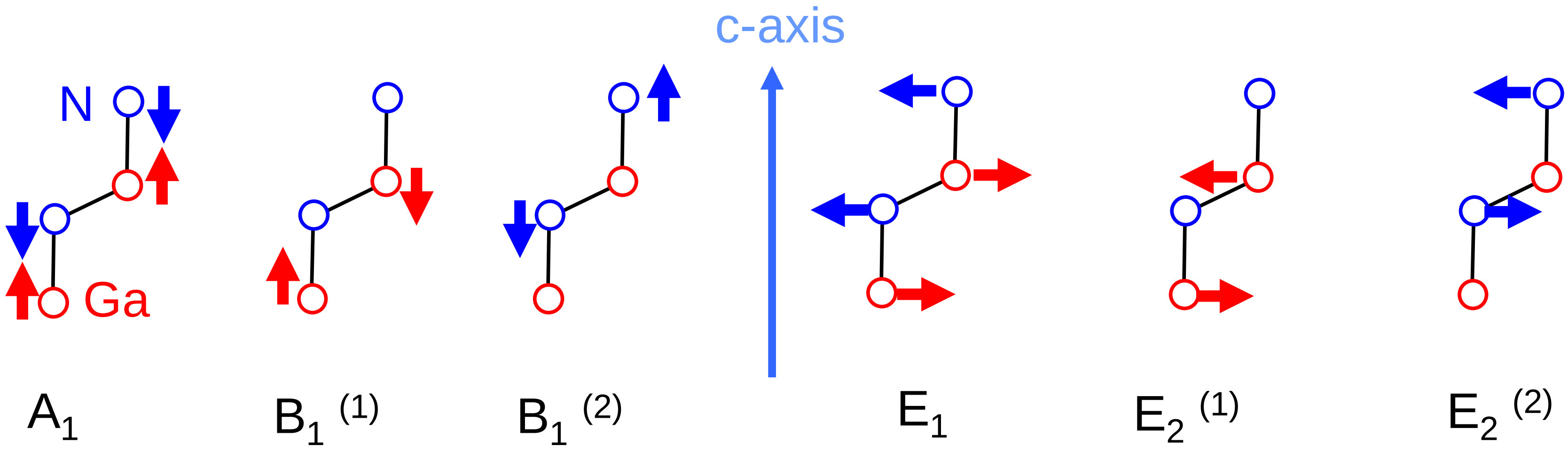
- Restoring forces for crystal vibrations also have c-axis dependence



Wurtzite crystal modes



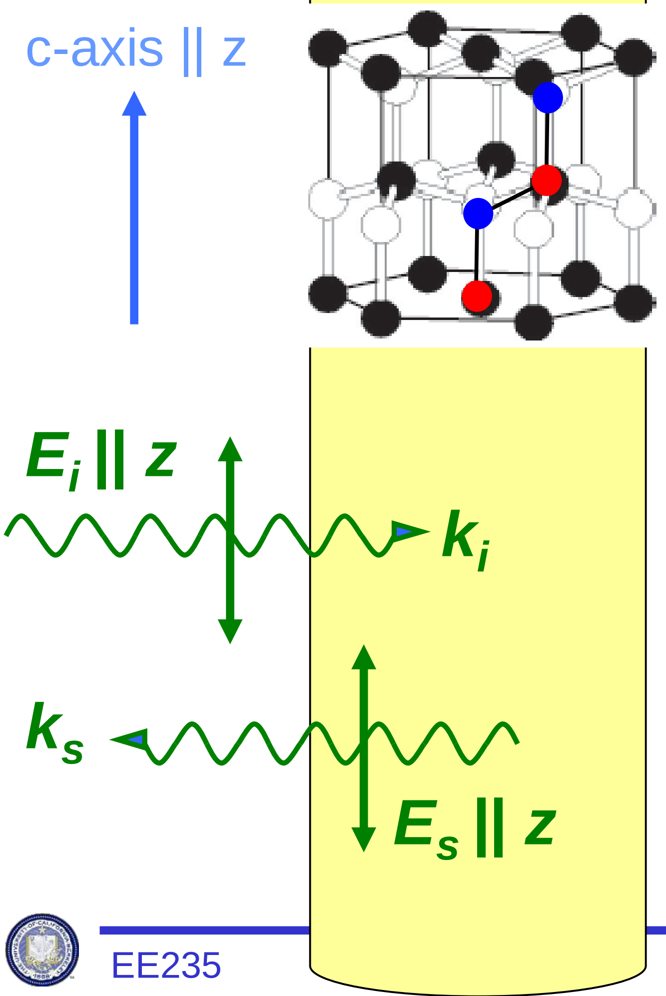
Wurtzite crystal modes

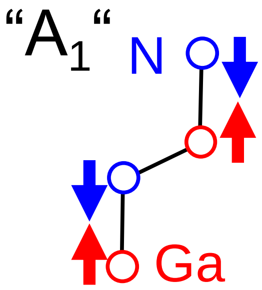


- Vibrational mode measured depends on form of tensor for a given measurement geometry

Raman mode polarization

- Vibrational mode measured depends on form of tensor for a given measurement geometry

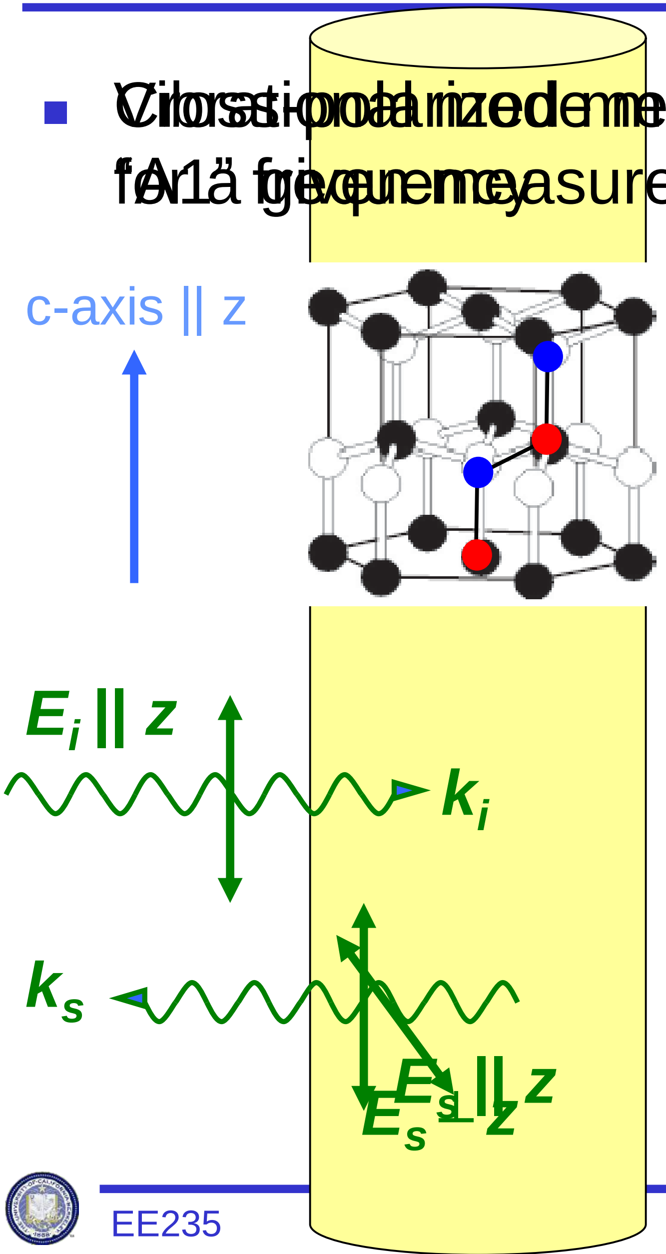


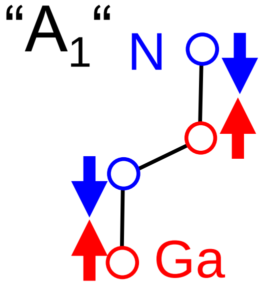


$$\overset{\leftrightarrow}{R}(A_1) = \begin{bmatrix} a & & \\ & a & \\ & & c \end{bmatrix}$$

Raman mode polarization

- Vibrational mode measurement depends on form of tensor for a given measurement geometry
- Cross-polarized measurement gives no mode at this “A1” frequency



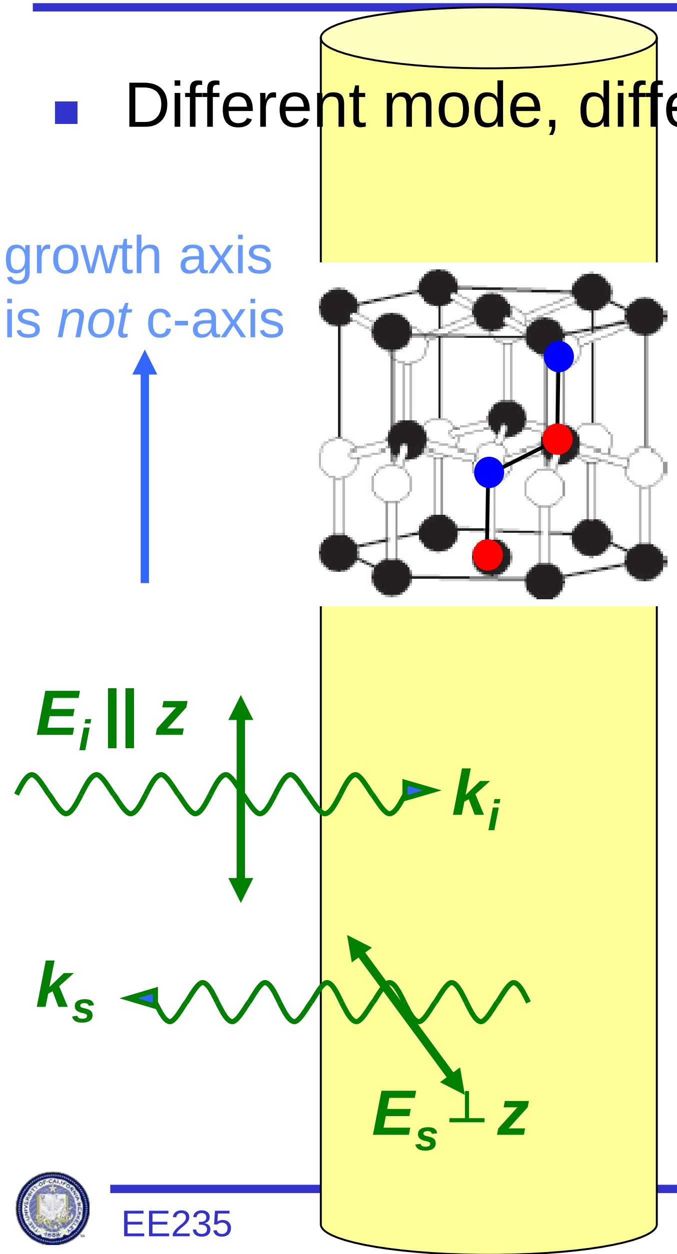


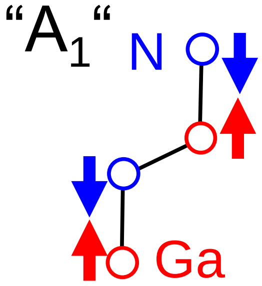
$$\overleftrightarrow{R}(A_1) = \begin{bmatrix} a & & \\ & a & \\ & & c \end{bmatrix}$$

$$I_s \sim \left| \hat{e}_i \cdot \overleftrightarrow{R} \cdot \hat{e}_s \right|^2$$

Raman mode polarization

- Different mode, different intensity



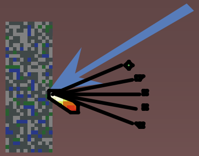


$$\overleftrightarrow{R}(A_1) = \begin{bmatrix} a & & \\ & a & \\ & & c \end{bmatrix}$$

e

e

$$I_s \sim \left| \hat{e}_i \cdot \overleftrightarrow{R} \cdot \hat{e}_s \right|^2$$



What can we learn from Raman Scattering

- The investigation of the Raman spectrum of a crystal should include the angular and polarization dependence of the scattering intensity, and also the width of peak and the efficiency. From this information can be extracted:
  - The frequency of an optic phonon
  - The symmetry of the phonon
  - Electron-Phonon interaction
- Two Phonon scattering process give information about Phonon density of states
- From the incident light frequency dependence of the intensity we can find electronic energy levels

Summary: Raman in crystals

- Measurement geometry / polarizations determine which modes can be Raman-scattered
- This example was looking at how one particular mode (A1) would change
  - 1) Knowing the nanowire direction but under different measurement geometries
  - 2) Not knowing crystal orientation: use mode selection to determine
- Non-destructive structural characterization tool for nanostructures!

For example:

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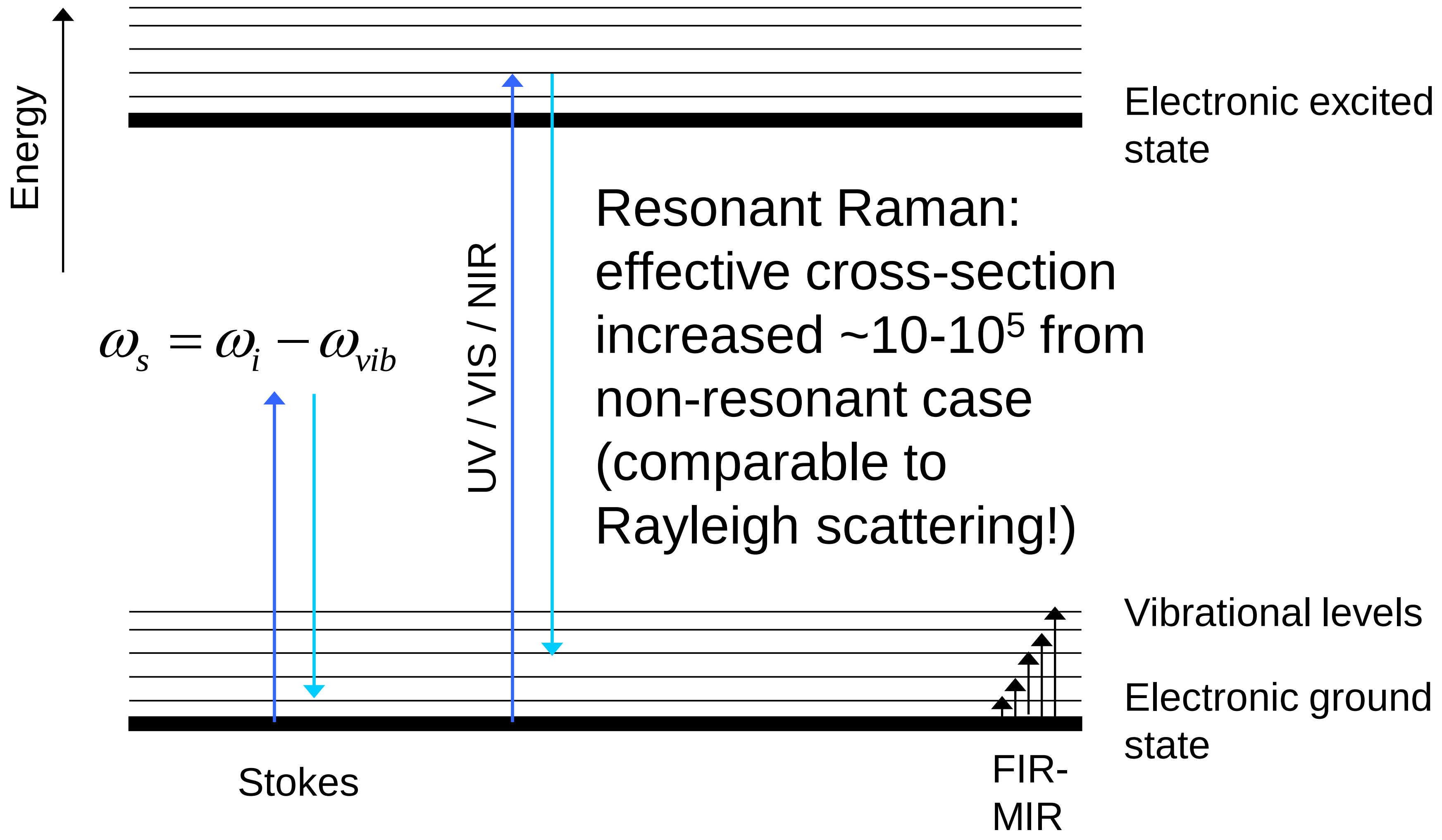
Polarized Raman scattering from single GaN nanowires

Tsachi Livneh,[1,*] Jinping Zhang,[2] Guosheng Cheng,[1] and Martin Moskovits[1,†]
[1]*Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, USA*
[2]*Department of Materials Engineering, University of California, Santa Barbara, California 93106-9510, USA*

Outline

- General principles
  - Light scattering
  - Electronic and vibrational energy levels
  - Experimental implementation
- Raman scattering in crystals
  - Resonant enhancement
- Signal enhancement
  - Resonant Raman - good or bad?
  - Surface-enhancement (SERS)

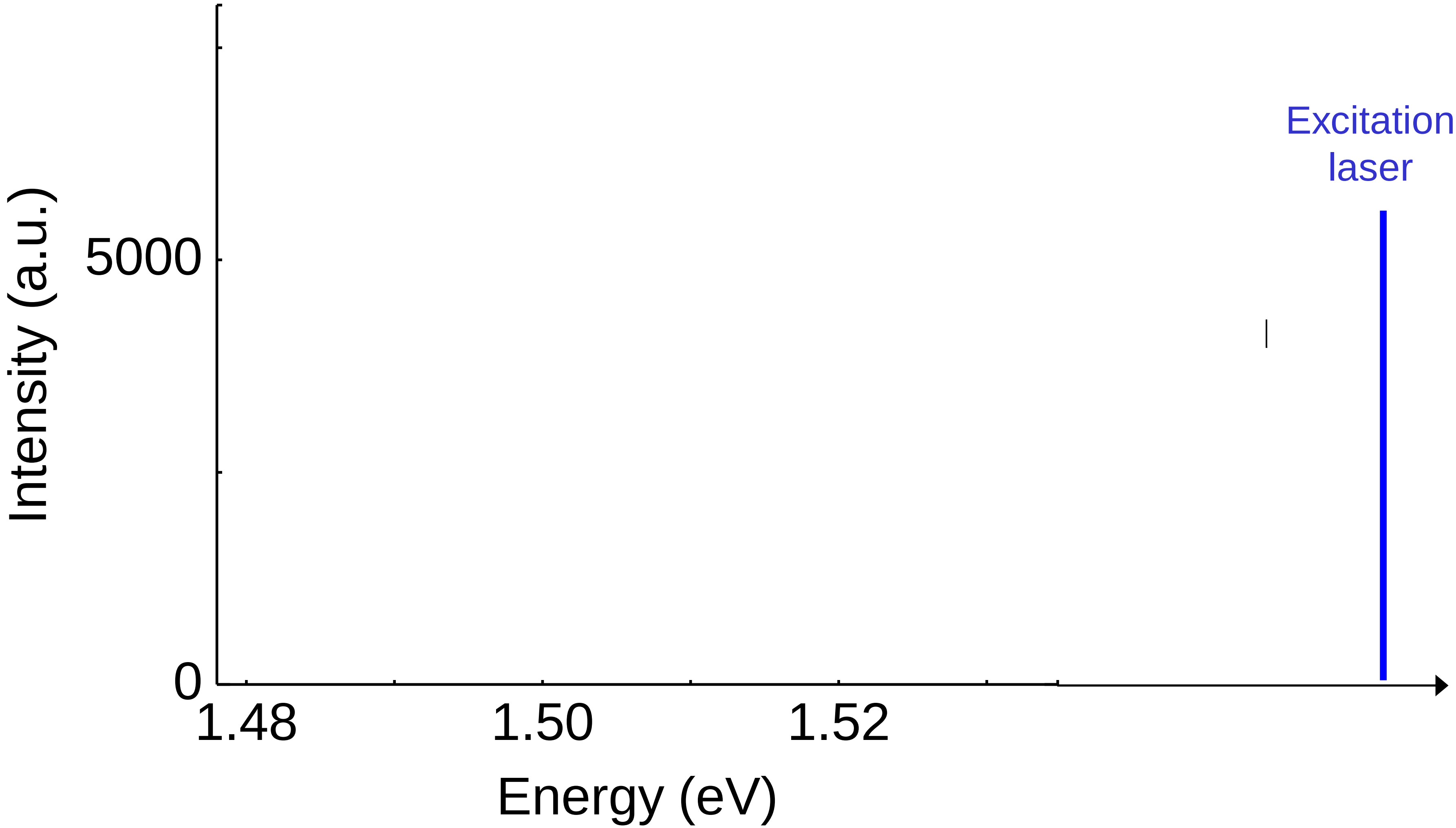
Electronic resonance



Resonant Raman: effective cross-section increased ~10-10^5 from non-resonant case (comparable to Rayleigh scattering!)

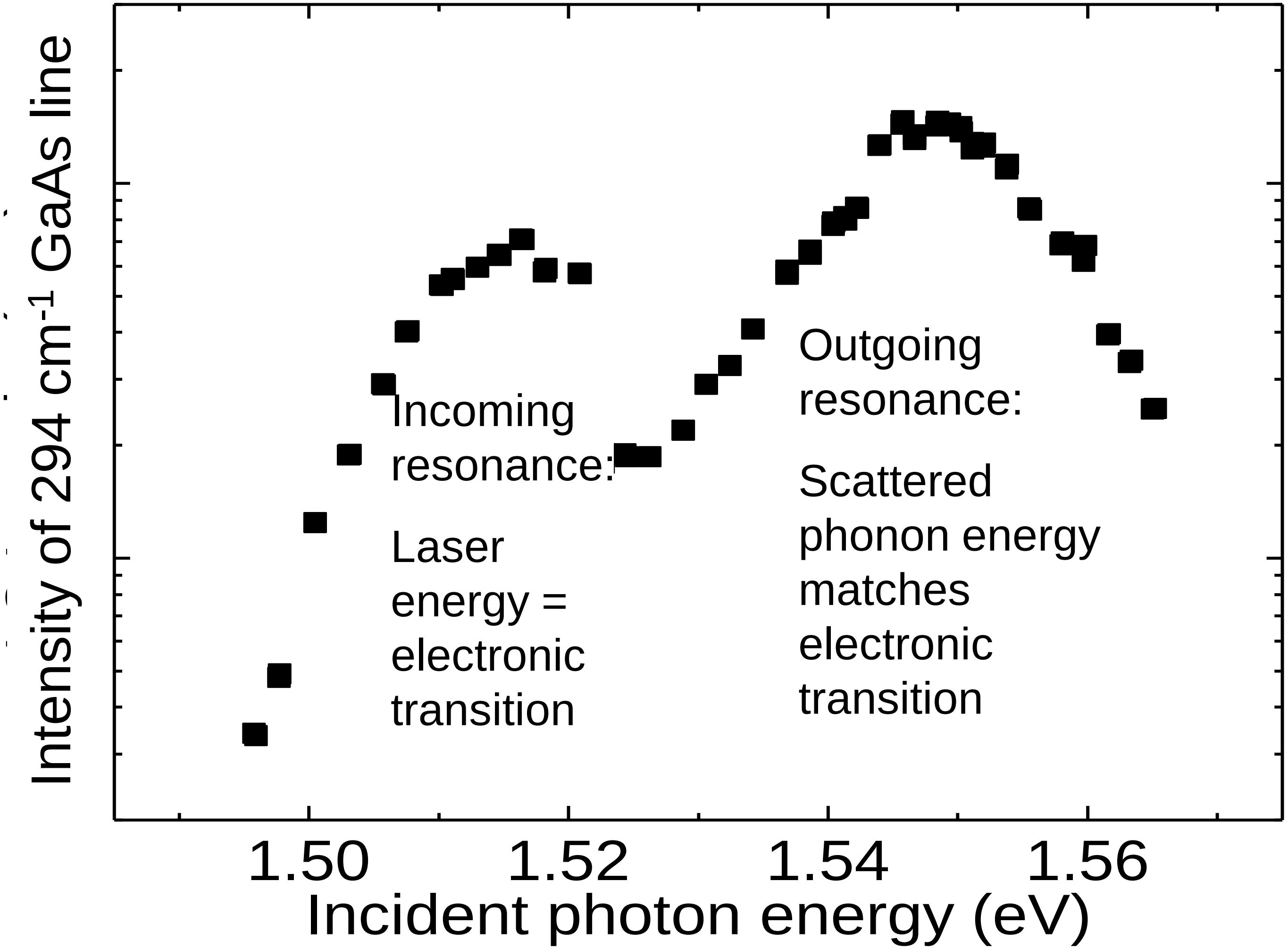
Resonant Raman - GaAs nanocrystals

- NIR used as excitation source, close to PL spectrum



Resonant Raman - GaAs nanocrystals

- Track intensity of single vibrational mode over laser excitation tuning range of electronic resonance



Incoming resonance:

Laser energy = electronic transition

Outgoing resonance:

Scattered phonon energy matches electronic transition

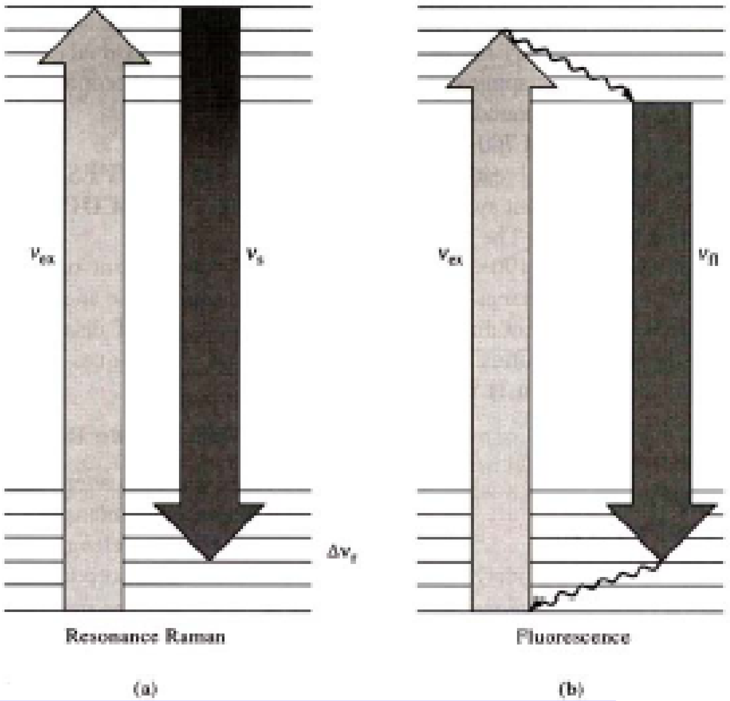
Resonant Raman

- Why not do this all the time?
- Energy of electronic resonance distinct from scattering process, does not follow laser (e.g. semiconductor bandgap)
  - → Excitation source must match electronic resonance
  - Much easier to match with *tunable* lasers (not readily available in the UV/VIS)
  - Could enhance a few particular lines, overwhelm others?

Resonant Raman

- Entirely sample-dependent.

  Chemical analysis: fluorescence always a bad word! end up choosing laser wavelength to avoid fluorescence



(a) Resonance Raman

(b) Fluorescence

In resonance Raman, relaxation to the ground state is not preceded by prior relaxation to the lowest vibrational level of the excited electronic state.

Time scale: Raman, 10^{-14}s; Fluorescence, 10^{-8}s

Weakness of resonance Raman: interference by fluorescence

Special types of Raman spectroscopy

(see Hollas, Modern Spectroscopy, Wiley)

Resonance Raman (RR) scattering

When the laser excitation frequency is near (or coincident) with an electronic absorption band, intensity enhancement can occur by a factor of 10^2-10^6, compared with normal Raman scattering. Electronic transitions are often localized in one part of a molecule, so that RR provides information about vibrations of the chromophore, especially those exhibiting a large change in geometry between the two electronic states.

RR is used in analytical chemistry to achieve detection limits 10^{-6}-10^{-8} M.

Surface enhanced Raman spectroscopy (SERS):

Raman scattering is enhanced (typically by 10^3-10^6 times) when the analyte is adsorbed on colloidal metallic surfaces,

e.g. on colloidal Ag prepared by reduction of Ag^+ with citrate, in particle size range 25-500 nm.

Stimulated Raman scattering (SRS)

The Raman scattering from a laser is observed in the forward direction from the sample (i.e. in the same direction, or at a small angle to the incident laser radiation).

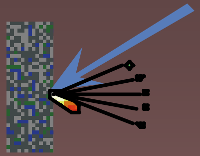
Vibrational progressions are observed for certain modes.

Coherent anti-Stokes Raman spectroscopy (CARS)

Radiation from two lasers is incident on the sample, and the intensity of the outgoing wave energy gives information about the vibrational modes of the sample.

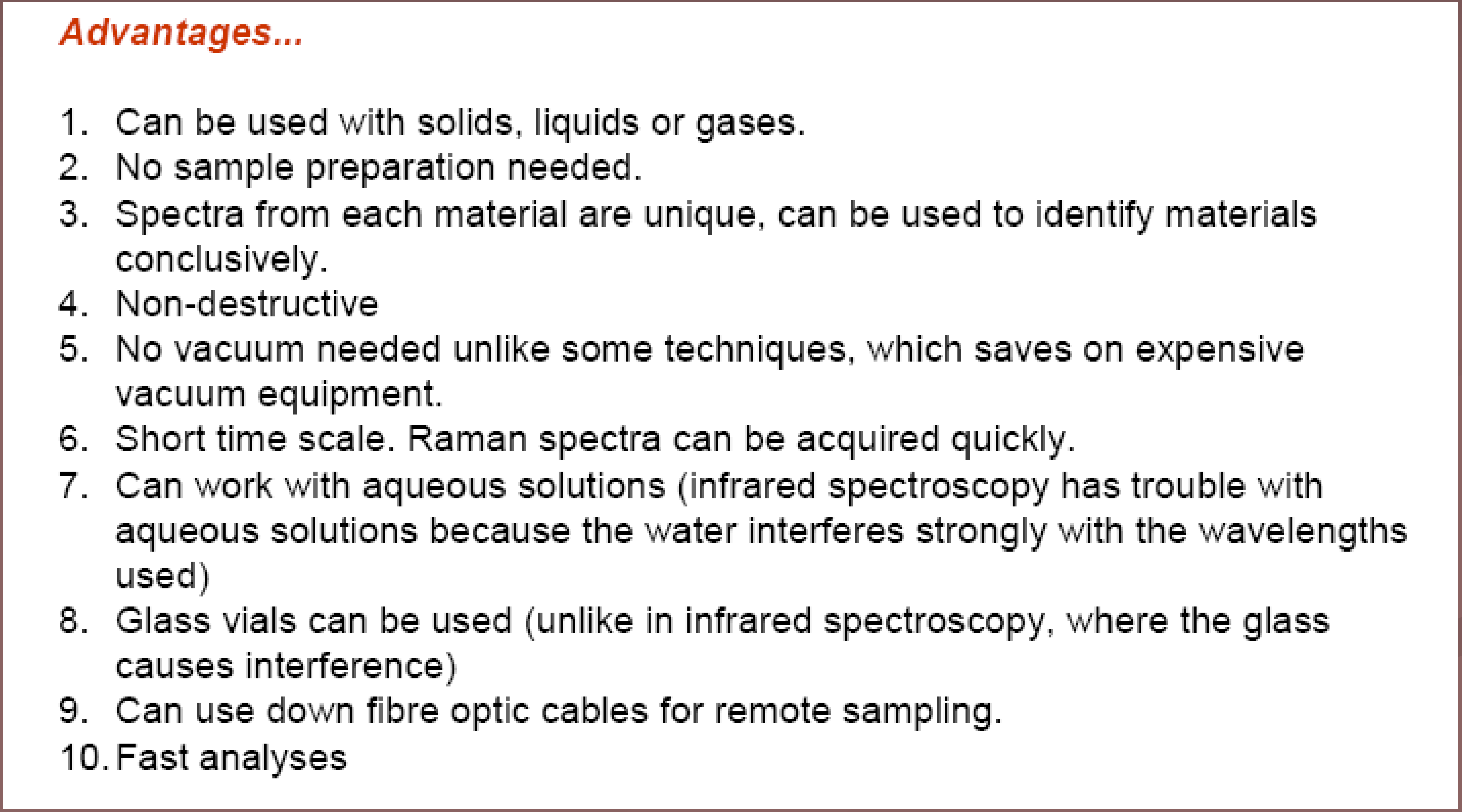
Hyper-Raman spectroscopy

Very weak scattering at twice the laser frequency, $2\nu_0$, is called Hyper-Rayleigh scattering. Similarly, Stokes and anti-Stokes hyper-Raman scattering occur at $2\nu_0 \pm \nu_{vib}$, where ν_{vib} is a vibration frequency. The selection rules differ from those of Raman scattering.



Raman Scattering

Advantages and disadvantages



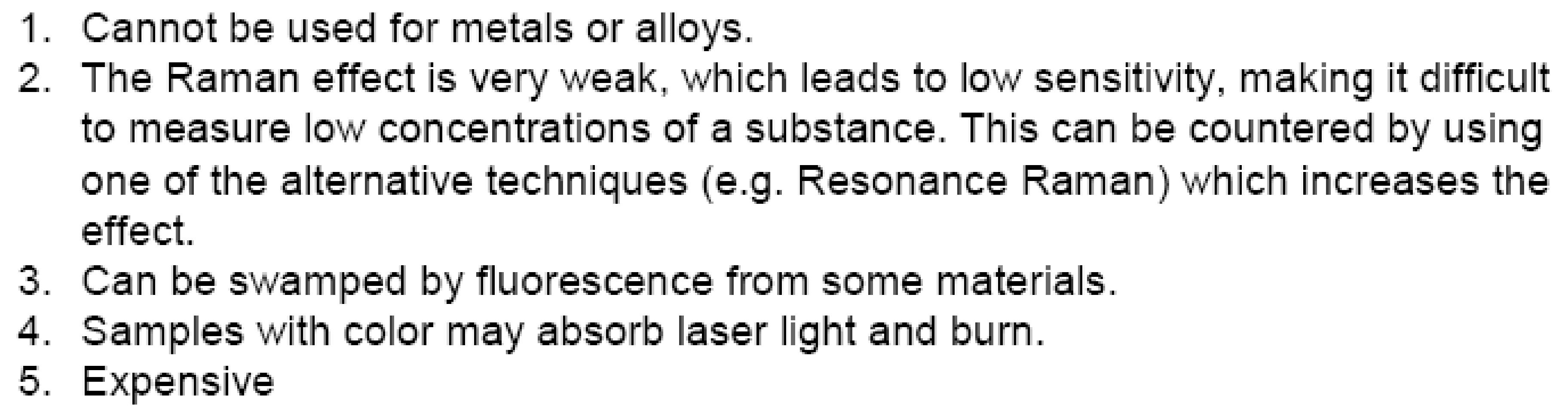
Advantages…

1. Can be used with solids, liquids or gases.
2. No sample preparation needed.
3. Spectra from each material are unique, can be used to identify materials conclusively.
4. Non-destructive
5. No vacuum needed unlike some techniques, which saves on expensive vacuum equipment.
6. Short time scale. Raman spectra can be acquired quickly.
7. Can work with aqueous solutions (infrared spectroscopy has trouble with aqueous solutions because the water interferes strongly with the wavelengths used)
8. Glass vials can be used (unlike in infrared spectroscopy, where the glass causes interference)
9. Can use down fibre optic cables for remote sampling.
10. Fast analyses

…Advantages of Raman

- Selection rules allow for some vibrations (normally symmetric) to be seen only by Raman spectroscopy.
- Measurements of depolarization ratios yield information about molecular symmetry.
- Only a small sample area is needed (laser spot).
- Water is a weak Raman scatterer, allowing for the use of aqueous solutions. Can also sample through glass container walls.
- The region 4000 cm^{-1} to 50 cm^{-1} can be covered in a single scan without changing gratings, splitters, detectors, etc.

Disavantages of Raman



1. Cannot be used for metals or alloys.
2. The Raman effect is very weak, which leads to low sensitivity, making it difficult to measure low concentrations of a substance. This can be countered by using one of the alternative techniques (e.g. Resonance Raman) which increases the effect.
3. Can be swamped by fluorescence from some materials.
4. Samples with color may absorb laser light and burn.
5. Expensive

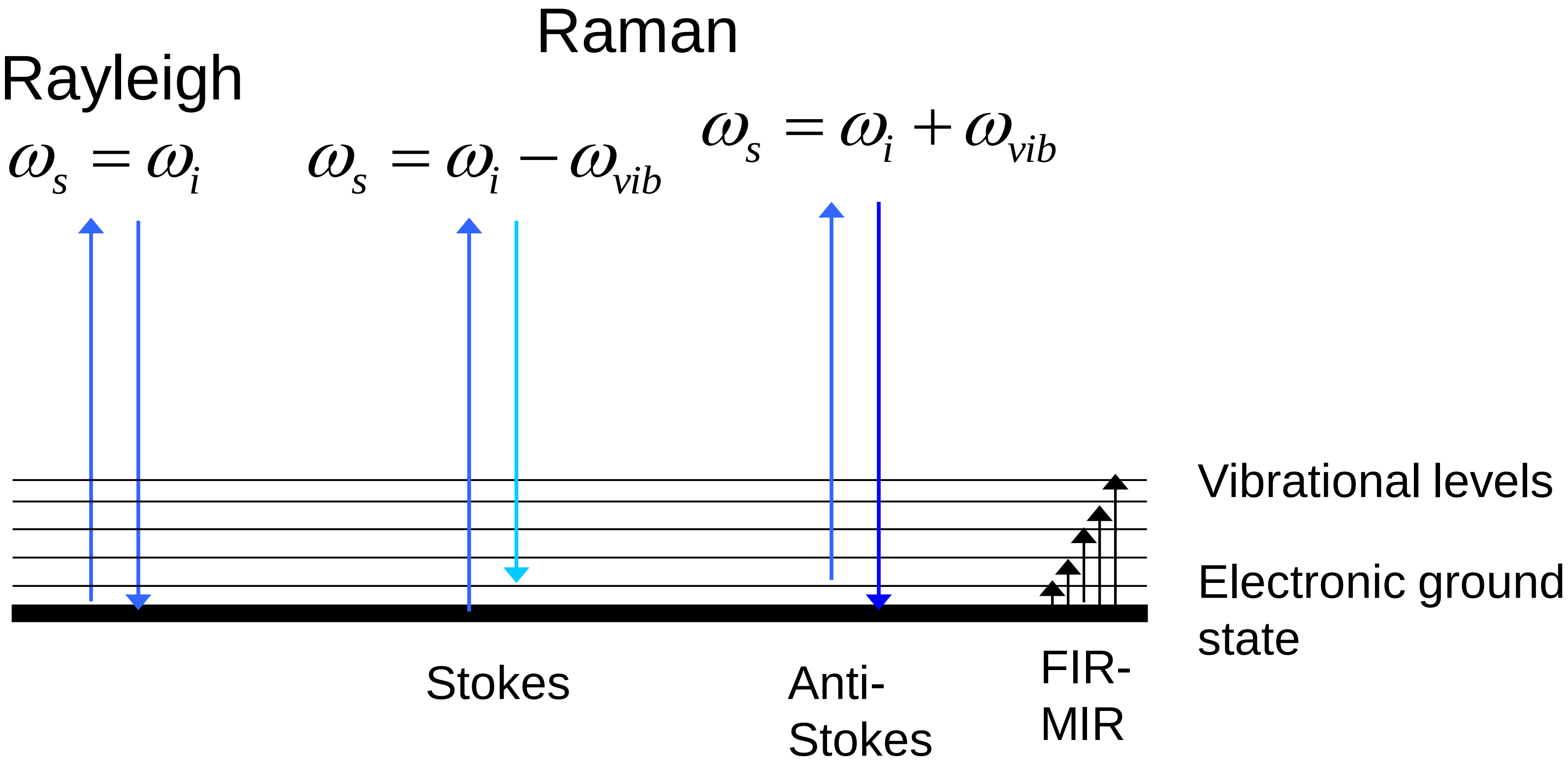
..Disadvantages of Raman

- Laser source is needed, which can cause local heating/decomposition.
- Can cause fluorescence.
- More difficult to obtain rotational and ro-vibrational spectra with high resolution
- Way more expensive: 150-200 k$ vs. 40-60 k$ for FTIR.

3. System components and common techniques

Scattering processes

- In principle, any laser wavelength shorter (i.e. higher energy) than the vibrational mode of interest will work as a source



Raman

Rayleigh

$$\omega_s = \omega_i$$

$$\omega_s = \omega_i - \omega_{vib}$$

$$\omega_s = \omega_i + \omega_{vib}$$

Vibrational levels

Electronic ground state

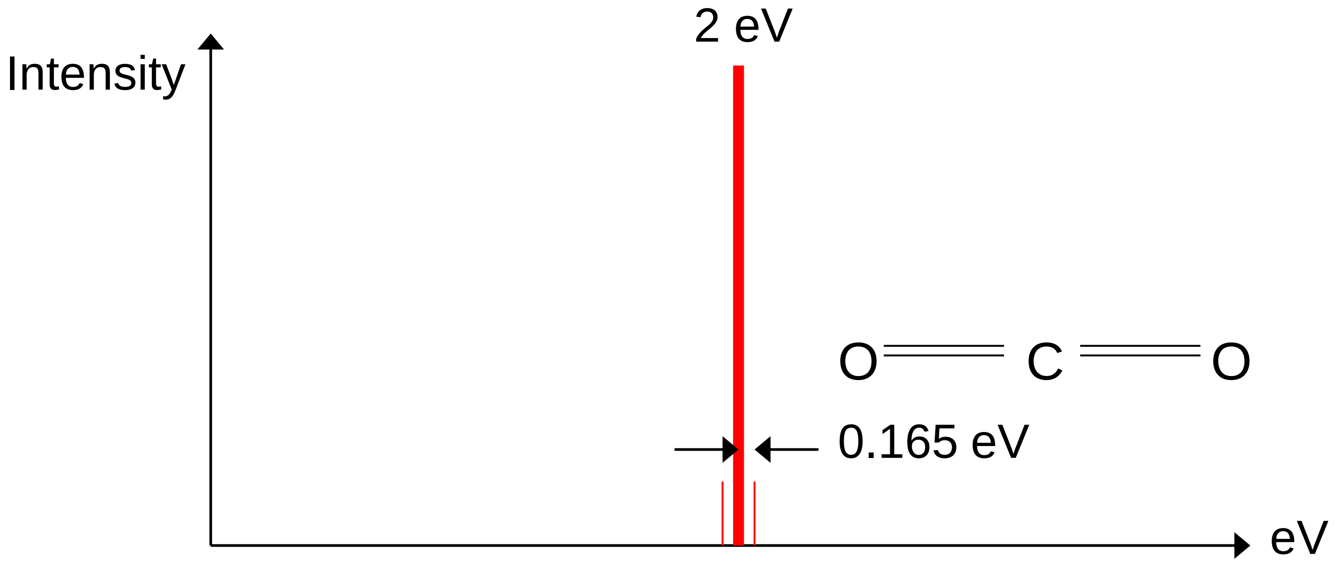
Stokes

Anti-Stokes

FIR-MIR

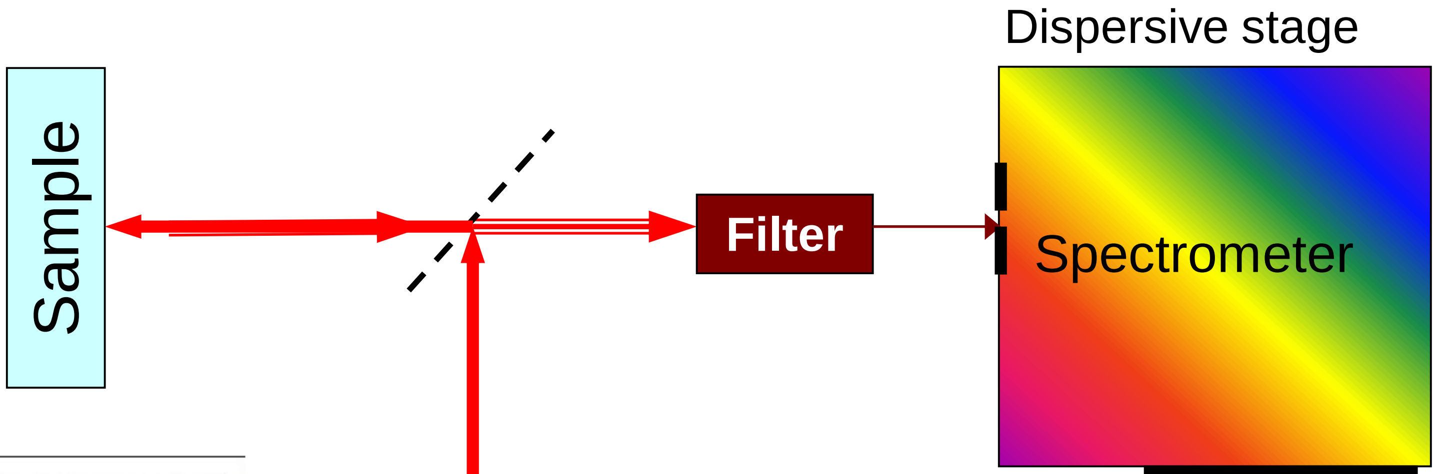
Implementation issues

- Weak Raman-scattered light close to strong source laser + Rayleigh-scattered light
- Need high rejection of unwanted “carrier frequency” light very close to Raman-shifted signal light



Implementation issues

- Need: very clean source line
- Very sharp edge discrimination



Narrow excitation source

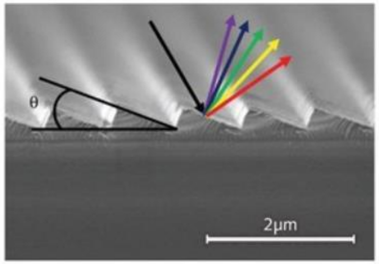
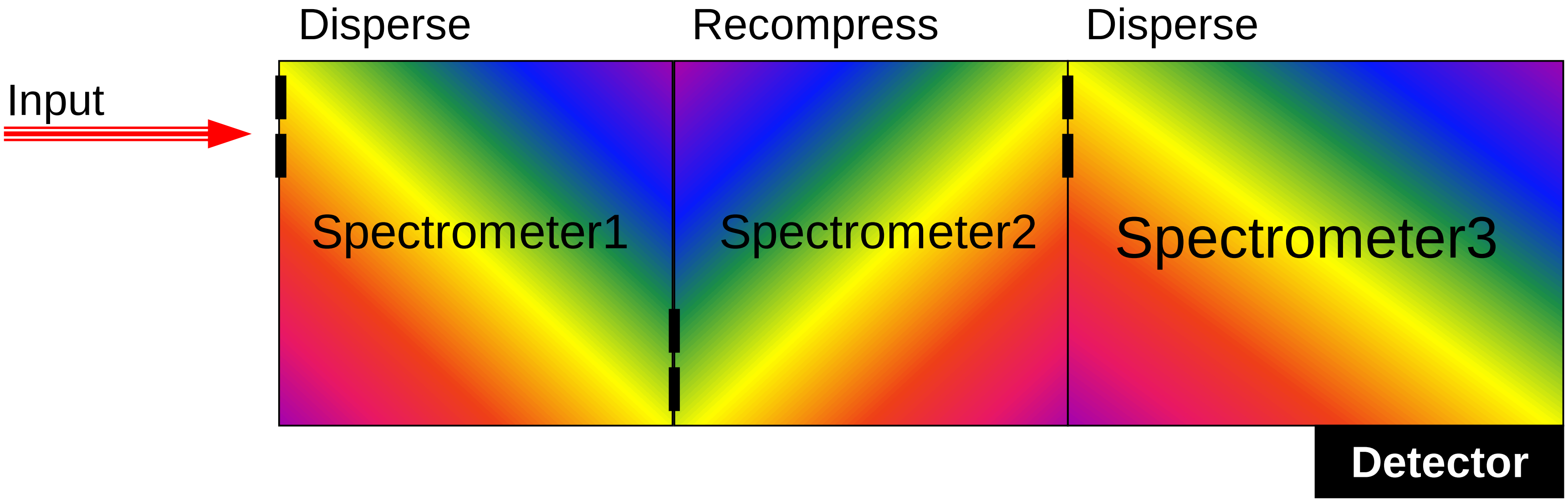


FIGURE 2. Illustration of how a grating separates light according to wavelength and a typical structure for the surface of a grating.[1] *(Adapted from reference 1, with kind permission from the authors.)*

Raman instrumentation

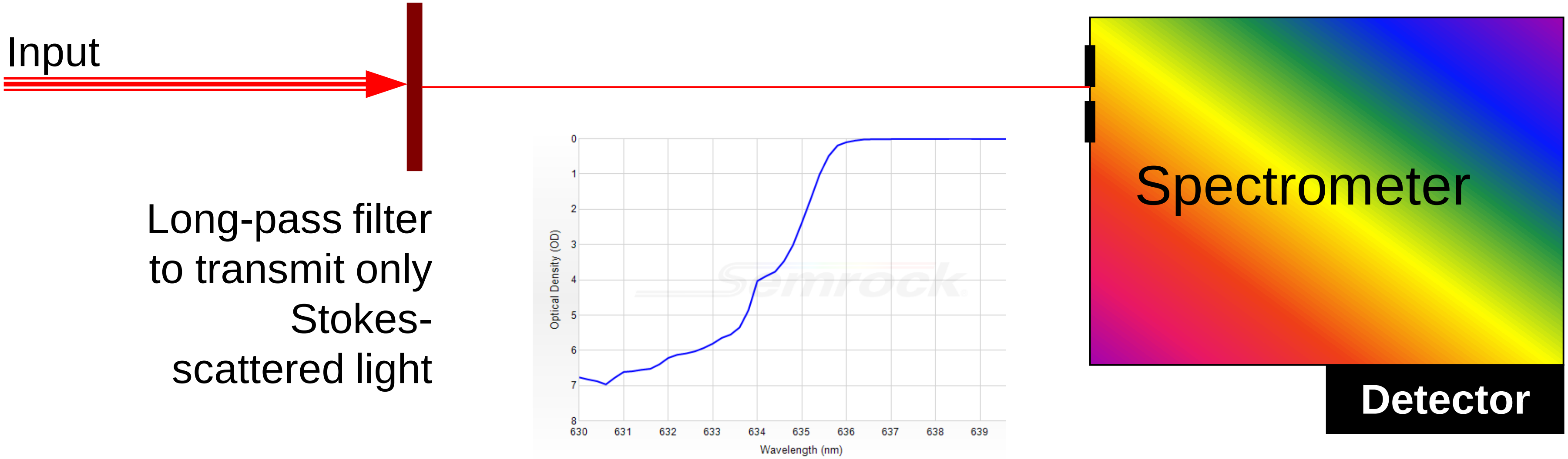
- Multi-stage spectrographs



- Excellent stray light rejection, can measure very close to laser line (few cm^{-1})
- Large and expensive

Raman instrumentation

- Single spectrometer, strong filters
  - Longpass filter in collection path
  - Line-pass filter (shortpass for tunable lasers) for laser line clean-up in excitation path

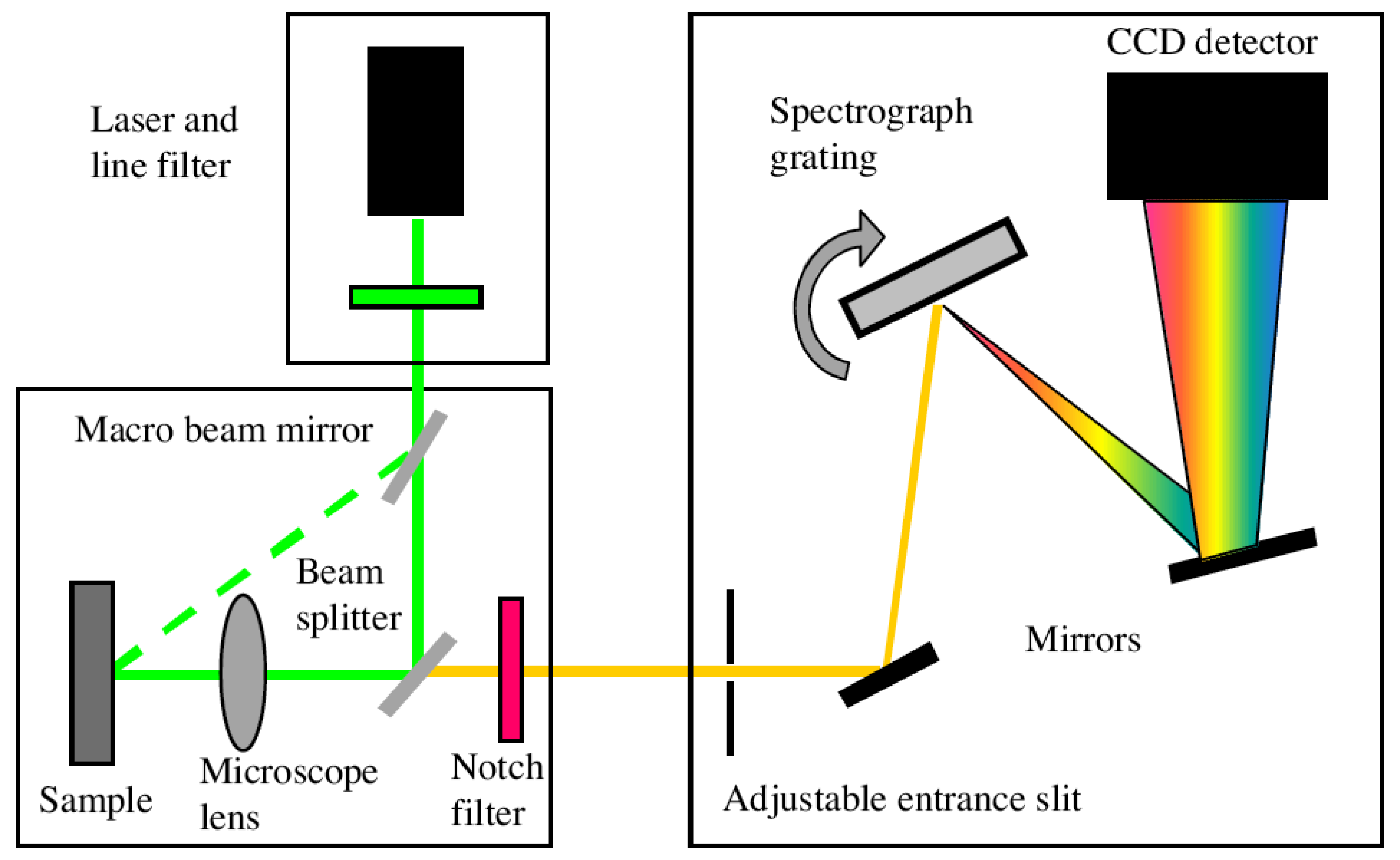


Long-pass filter to transmit only Stokes-scattered light

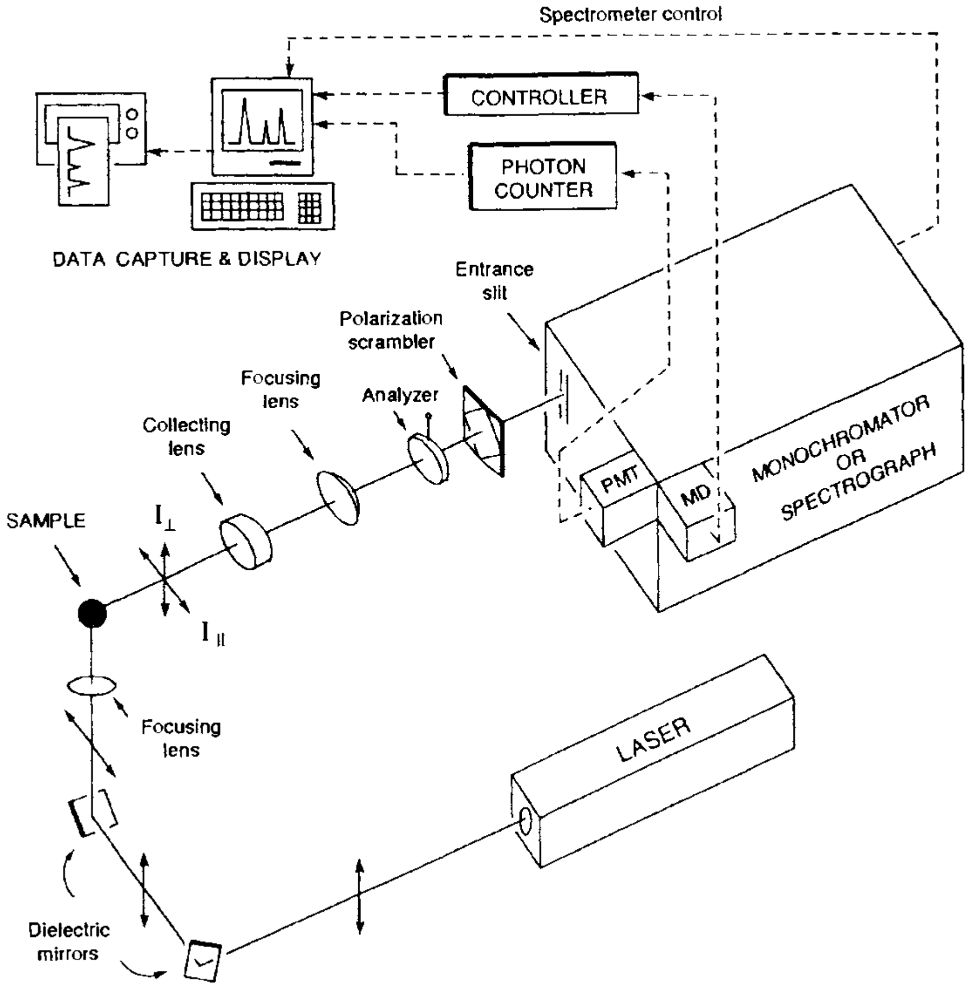
- Final resolution depends on spectrograph and detector; filter limitation ~tens of cm^{-1}

semrock LP-633RE

Simplified Raman spectrometer layout



INSTRUMENTATION for CONVENTIONAL RAMAN SPECTROSCOPY



The major components of a RAMAN spectrometer are:

1. **Excitation source**, which is generally a continuous wave (CW) laser
2. **Sample illumination** and **collection system**
3. **Filters**
4. **Wavelength selector**
5. **Detection** and computer control/processing systems.

EXCITATION SOURCE

CW LASER is the ideal excitation source for Raman spectroscopy due to the following characteristics of the laser beam:

- ☐ Single lines can easily provide 1-2 W of power
- ☐ Laser beams are highly monochromatic (bandwidth ~ 0.1 cm^{-1} for Ar^+ laser)
  - ➢ Extraneous lines are much weaker and can be eliminated easily by using a pre - monochromator.
- ☐ Small diameter (1-2 mm) of laser beam, which can be reduced by using simple lens systems or microscope objective.
  - ➢ All the radiant flux can be focused on a small sample.
  - ➢ Sample area as ~ 2 μm in diameter can be studied (RAMAN MICROSCOPY)
- ☐ Laser beams are almost completely linearly polarized

EXCITATION SOURCE: CW GAS LASER

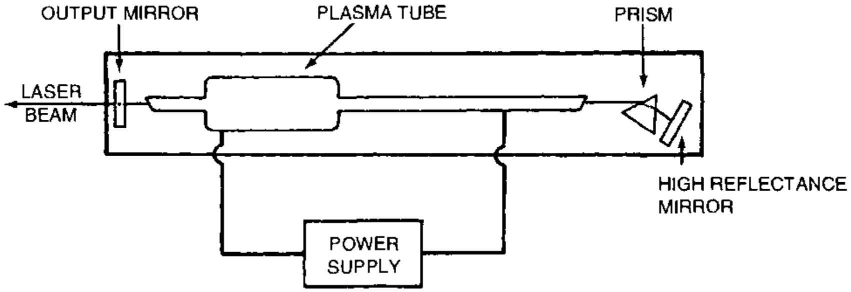
CW GAS LASER commonly used for Raman spectroscopy:

❑ Ar^+ (351.1-514.5 nm)

❑ Kr^+ (337.4-676.4 nm)

❑ He-Ne (632.8 nm)

Schematic of a typical gas CW laser



The outside of the tube is water jacketed to cool the tube.

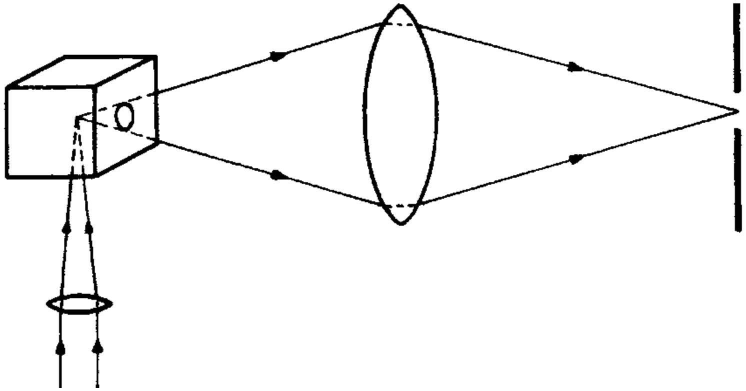
- A very high current discharge passes through Ar or Kr gas contained in the plasma tube.
- The discharge ionizes the gas and populates the excited state involved in the lasing.
- The resonant cavity, defined by the semitransparent output mirror and the high-reflectance mirror, provide a mechanism for amplification of photons emitted parallel to the cavity axis. (both mirrors are coated to reflect the light of wavelength(s) of interest.
- The end of the tube is enclosed with Brewster windows , so the output beam is almost completely polarized in a fixed direction.
- A prism is inserted between the two mirrors to force the laser to output a specific wavelength.

SAMPLE ILLUMINATION and COLLECTION SYSTEM

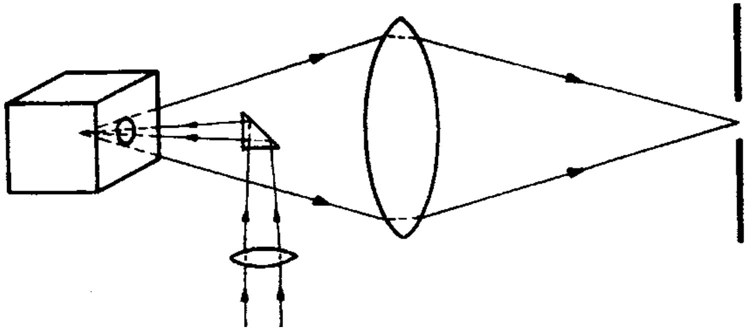
Since Raman scattering is inherently weak:

- the laser beam must be focused properly onto the sample
- the scattered radiation must be collected efficiently.

Collection optics consist of an achromatic lens system with a collecting lens and a focusing lens.



90° scattering geometry



180° scattering geometry

The light-gathering power of a lens is expressed in terms of *f-number,* defined by:

$$f_{number} = \frac{f}{D}$$

f is the focal length of the lens
D is the lens diameter

The smaller the *f-number*, the larger is the light gathering power (i.e., either a larger D or a smaller focal length f).

Optical FILTERS

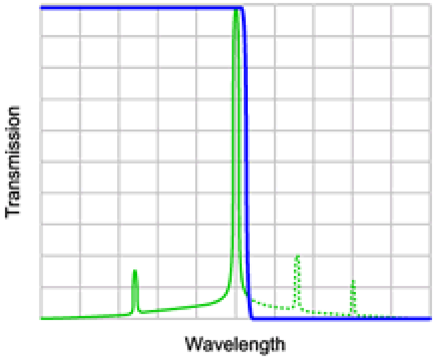
- Sono filtri interferenziali progettati ad-hoc per ogni singola lunghezza d’onda

Laser Transmitting Filters

Laser Blocking Filters

Filters for only Stokes measurements

SWP Edge Filter



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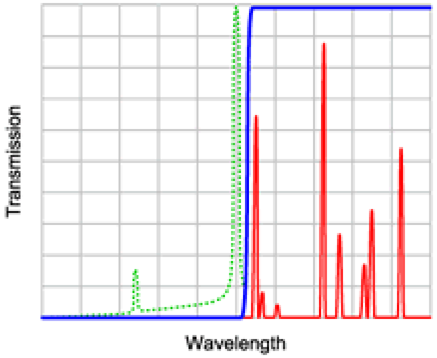
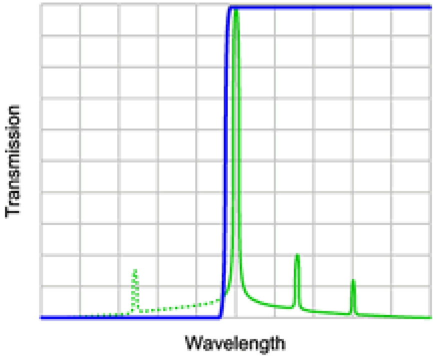
LWP Edge Filter



Filters for only Anti-Stokes measurements



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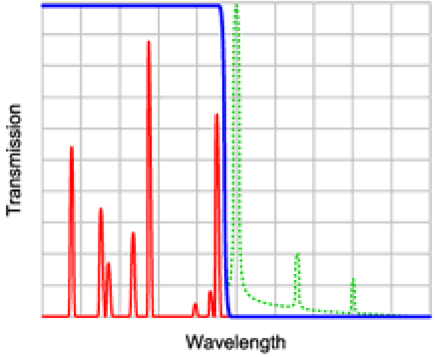


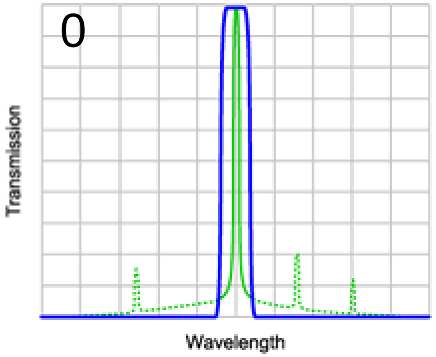
NOTCH FILTERS

- Sono filtri progettati ad-hoc per rimuovere o far passare un singola lunghezza d'onda

Filters for simultaneous Stokes and Anti-Stokes measurements

Laser Transmitting Filters

Laser-line Filter



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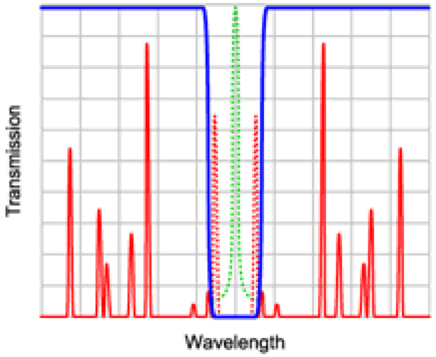
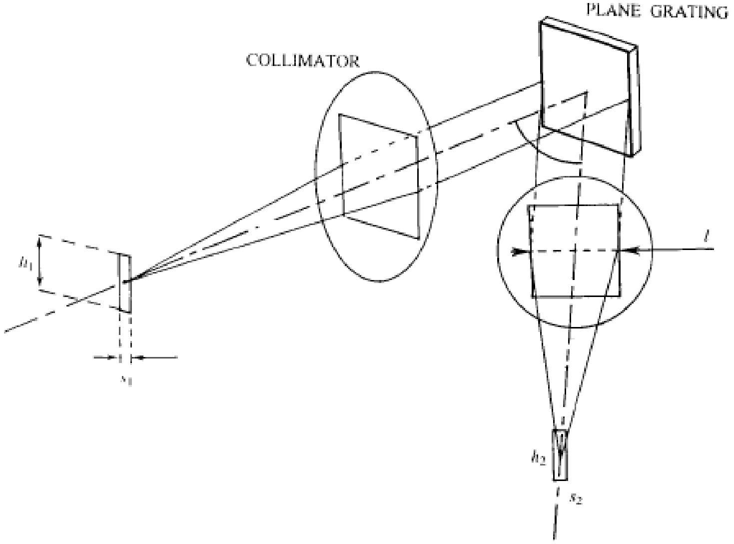
Laser Blocking Filters

Notch Filters



WAVELENGTH SELECTOR: MONOCROMATOR

- A dispersive element (a plane grating) is illuminated by a parallel light beam which is produced by a collimator consisting of an entrance slit placed at the focus of a convergent lens or a mirror of focal length f.
- A second collimator collects the light beam diffracted at a given angle and focuses it onto the exit slit.



The basic schematic diagram of a monochromator

- The *f-number* of a grating monochromator is also determined by previous equation (f is the focal length of mirror). D is calculated by:

$$\frac{1}{4}\pi D^2 = L^2$$

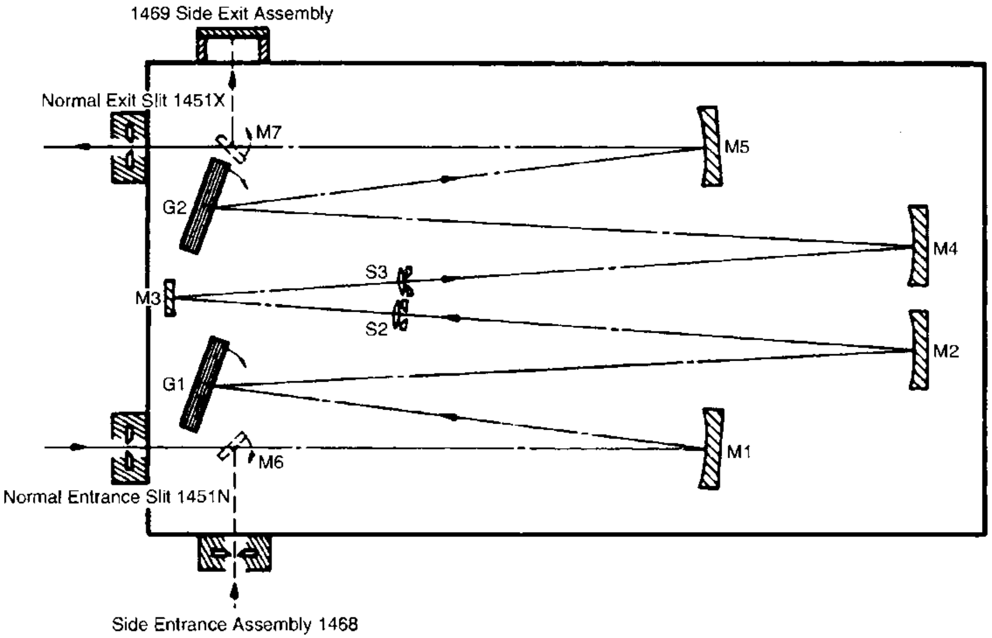
L is the side length of a square grating

- To make *f-number* smaller, f should be smaller and D should be larger.
- However, the resolution decreases as f became small and so to maintain good resolution D must be large, and this requires a large (and expensive grating).
- Grating determine the resolution of a spectrometer to a large extent.
- The more grooves per mm, the better is the dispersion, and the greater is the resolution.
- The signal loss due to improved resolution can be compensated by widening the slit width.

WAVELENGTH SELECTOR:
DOUBLE or TRIPLE MONOCHROMATOR

- In a single monochromator, extraneous or straight light (i.e. caused by undiffracted light being scattered from the face of grating) overlaps the weak Raman scattered light

- Such straight light can be reduced by arranging two spectrometers in tandem so that the output of one is filtered by the second



The basic schematic diagram of a double monochromator

- A triple monochromator has even greater stay light rejection than a double monochromator and allows observation of Raman bands located very close to the Rayleigh line.

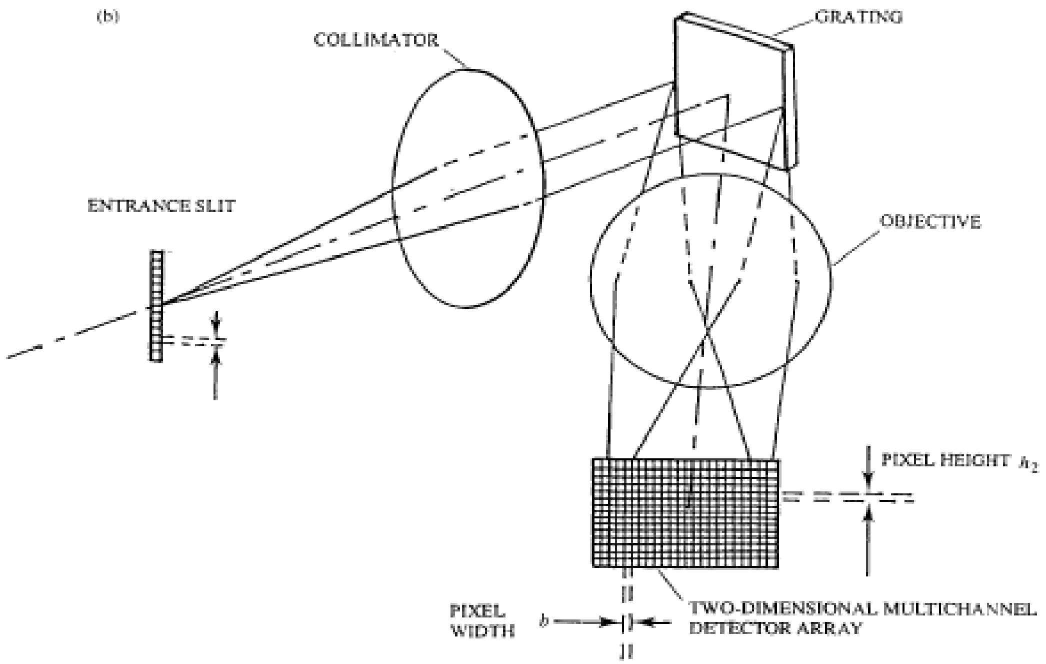
DETECTION

- **Single-channel detection technique**

The detection of Raman signals is made for each frequency and the Raman spectrum is obtained through scanning the entire frequency range.

- **Multi-channel detection technique**

Simultaneous detection of Raman signals in the entire frequency range.



Multi-channel photon detectors consist of an array of small photosensitive devices that can convert an optical image into a charge pattern that can be read as a Raman spectrum.

DETECTION
CHARGE-COUPLED DEVICE (CCD)

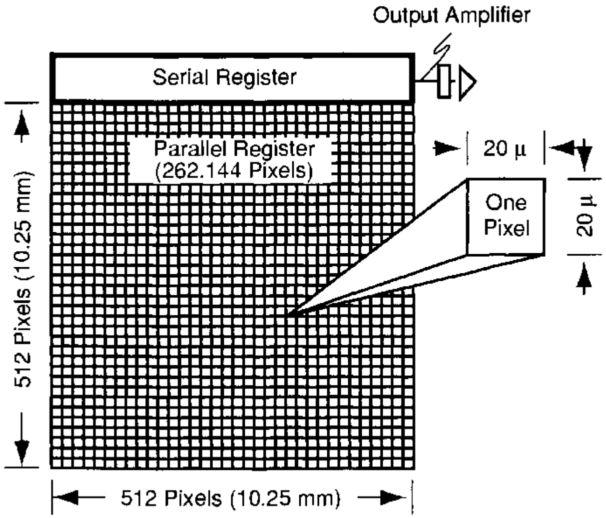
❑ A CCD is a silicon-based semiconductor arranged as an array of photosensitive elements, each one of which generates photoelectrons and stores them as a small charge.

❑ Charges are stored on each pixel as a function of the number of photons striking the pixel.

❑ On command, the charges from each row are shifted to the next higher row.

❑ Charges on pixels in the top row are shifted from left to right on request and read by a single analogue-to-digital converter.

❑ The charge-transfer process is noise-free, and almost all the noise contributed to the signal by CCD is from the output stage (readout noise)

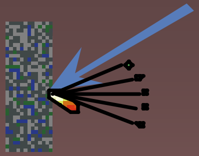


Schematics of a CCD detector.

In other words, to read the entire array, the top row is read one element at a time by moving the elements from left to right, and afterwards, all the rows are shifted up one to start the reading of the next row.

ADVANTAGES of the CCD:

1. Low readout noise
2. Optical intensification unnecessary
3. High quantum efficiency
4. High sensitivity in a wide wavelength range (120-1000 nm)



CCD Detectors

- Most of the current dispersive Raman set-ups are now equipped with multichannel two-dimensional CCD detectors. The main advantages of these detectors are the high quantum efficiency, the extremely low level of thermal noise (when effectively cooled), low read noise and the large spectral range available. Many CCD chips exist, but one of the most common spectroscopy sensor formats is the 1024 x 256 pixel array.

micro-Raman spectroscopy

- Spatial imaging down to diffraction limit of excitation wavelength used

- Confocal setup - small sample volume probed
- Vibrational map of sample

JobinYvon

Microscope Objectives

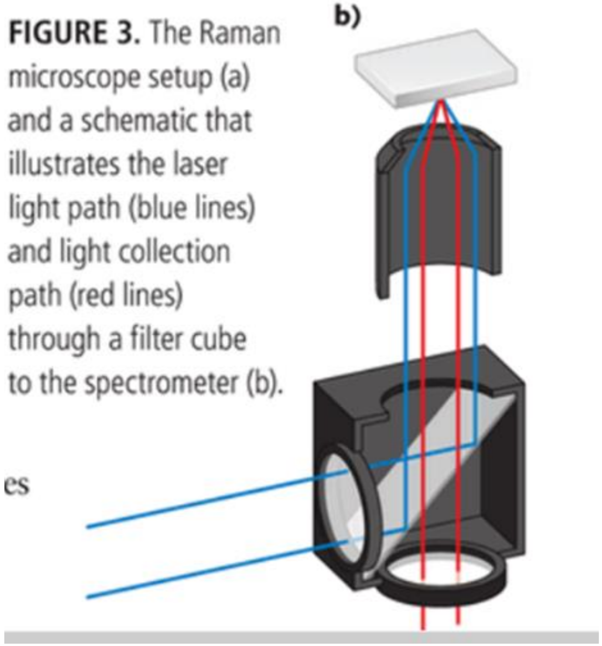


FIGURE 3. The Raman microscope setup (a) and a schematic that illustrates the laser light path (blue lines) and light collection path (red lines) through a filter cube to the spectrometer (b).

Objectives

∞ - Infinity corrected

PLAN-APO-40X 1.30 N.A. 160/0.22

Flat field *Apochromat* *Magnification Factor* *Numerical Aperture* *Tube Length* *Coverglass Thickness*

Objectives

Limit for smallest resolvable distance **d** between 2 points is (Rayleigh criterion):

$$\mathbf{d = \lambda/2\ N.A.}$$

$$\mathbf{d = 0{,}61\lambda/N.A.}$$

This defines a “resel” or “resolution element”

Thus high **NUMERICAL APERTURE** is critical for high magnification

Numerical Aperture

- The wider the angle the lens is capable of receiving light at, the greater its resolving power
- The higher the NA, the shorter the working distance

Numerical Aperture

- Resolving power is directly related to numerical aperture.
- The higher the NA the greater the resolution
- Resolving power:

The ability of an objective to resolve two distinct lines very close together

$$\boxed{NA = n \sin \mu}$$

  - (n=the lowest refractive index between the object and first objective element) (hopefully 1)
  - μ is 1/2 the angular aperture of the objective

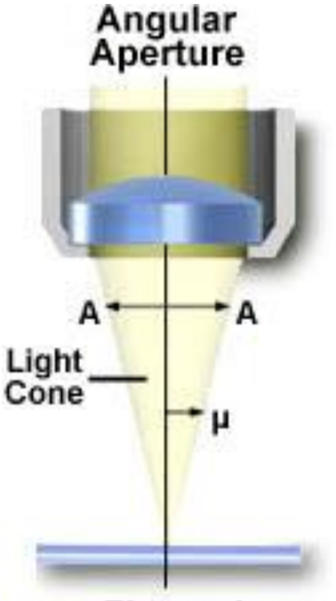
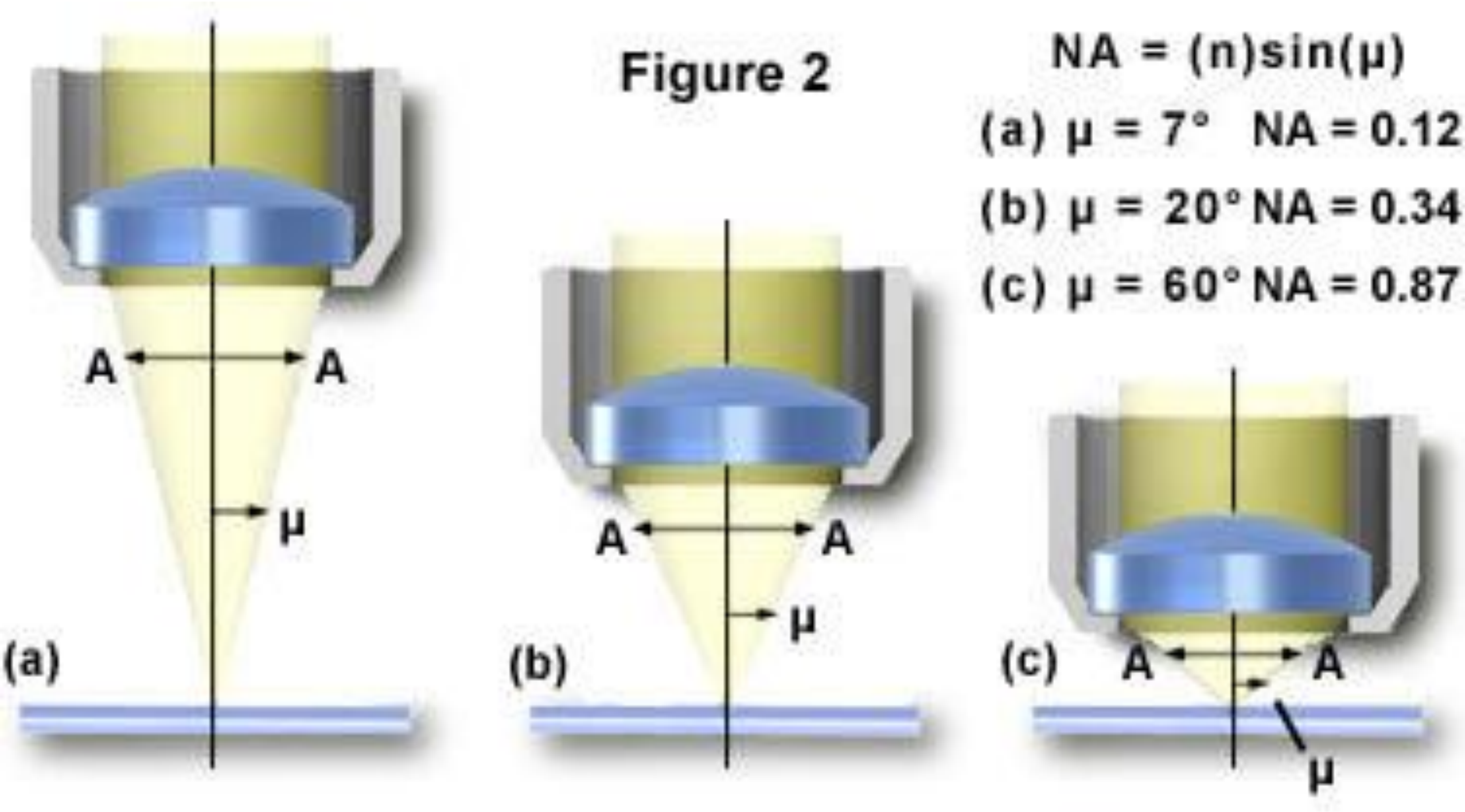


Figure 1

Numerical Aperture



http://www.microscopy.fsu.edu/primer/anatomy/numaperture.html

Object Resolution

- Example:

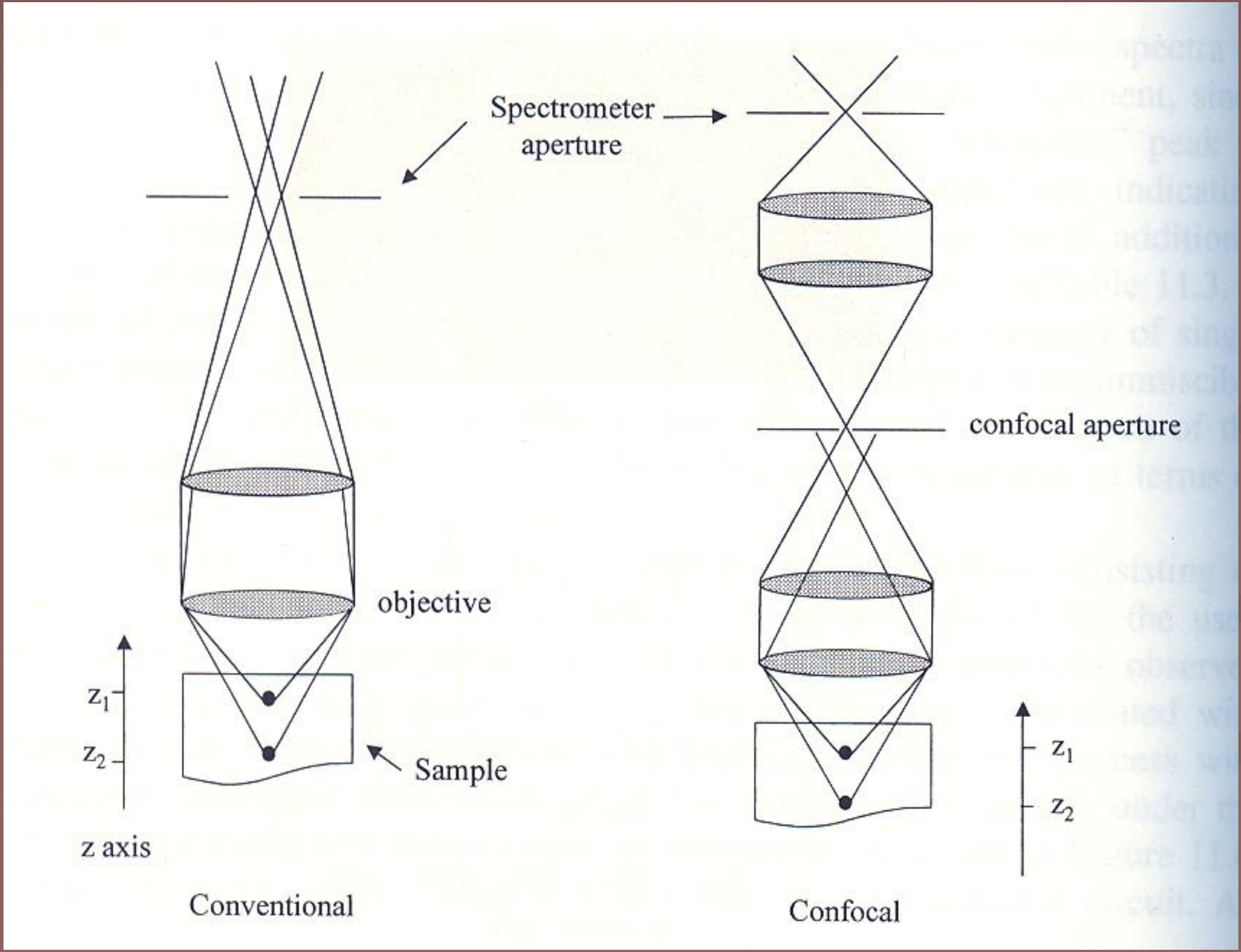
40 x 1.3 N.A. objective at 530 nm light

$$\frac{\lambda}{2 \text{ x } NA} = \frac{.00053}{2 \text{ x } 1.3} = 0.20\ \mu m$$

40 x 0.65 N.A. objective at 530 nm light

$$\frac{\lambda}{2 \text{ x } NA} = \frac{.00053}{2 \text{ x } .65} = 0.405\ \mu m$$

Conventional *vs.* Confocal



Principi della Microscopia Confocale

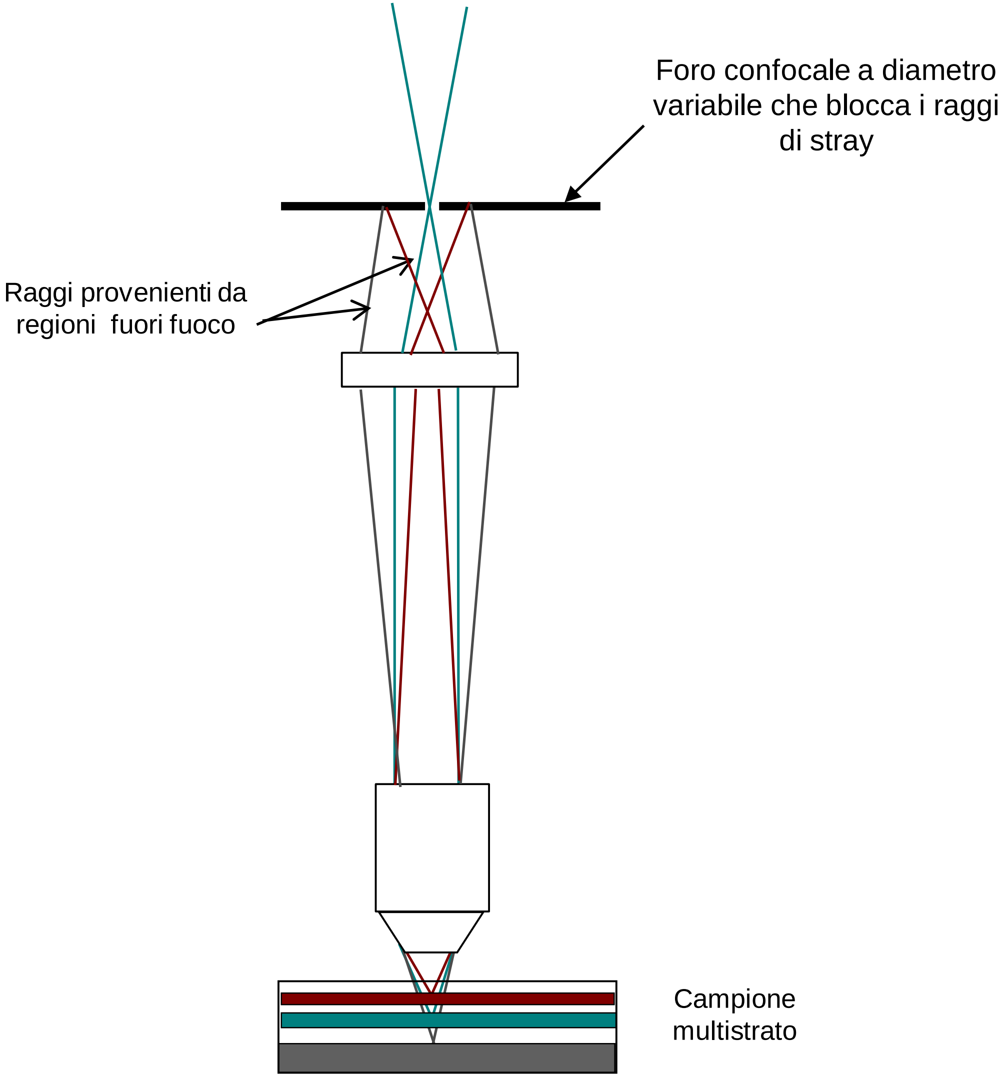
- Il segnale proveniente dal punto del campione irradiato dal laser é focalizzato su di un “foro confocale” e rivelato da un rivelatore ad esso otticamente coniugato.

- Mediante il foro confocale solamente il segnale generato da un punto nel piano P viene rivelato.

- Se il segnale é generato nei piani P’ o P’’ non viene focalizzato sul foro confocale e risulta quindi parzialmente rigettato e non rivelato.

Vantaggi I

- Un primo vantaggio della microscopia confocale é una sensibile riduzione della profonditá di fuoco e di conseguenza un **incremento di discriminazione lungo Z**.
- Ció significa che mediante un ottica confocale il segnale proveniente da ogni singolo strato del campione puó essere acquisito escludendo il segnale proveniente dagli strati adiacenti.
- Qualora il campione fosse incluso in un mezzo se ne potrebbe comunque acquisire lo spettro con il minimo , o addirittura nessun, contributo da parte della matrice.



Foro confocale a diametro variabile che blocca i raggi di stray

Raggi provenienti da regioni fuori fuoco

Campione multistrato

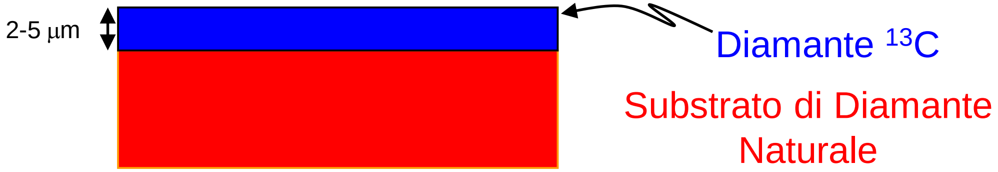
Vantaggi II

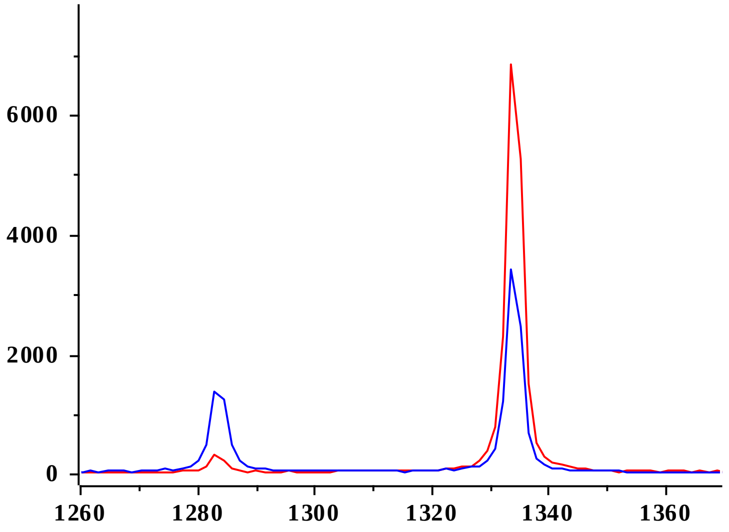
Un’altro aspetto importante della configurazione confocale é il maggior controllo della superficie analizzata. Il foro limita la regione del campione dalla quale si ottiene il segnale. Le dimensioni di questa regione possono essere facilmente correlate a quelle del foro confocale. Il foro ricopre cosí anche il ruolo di filtro spaziale, **incrementando la risoluzione spaziale.** Per un campione trasparente il foro non seleziona, come ovvio, un area, ma un volume.

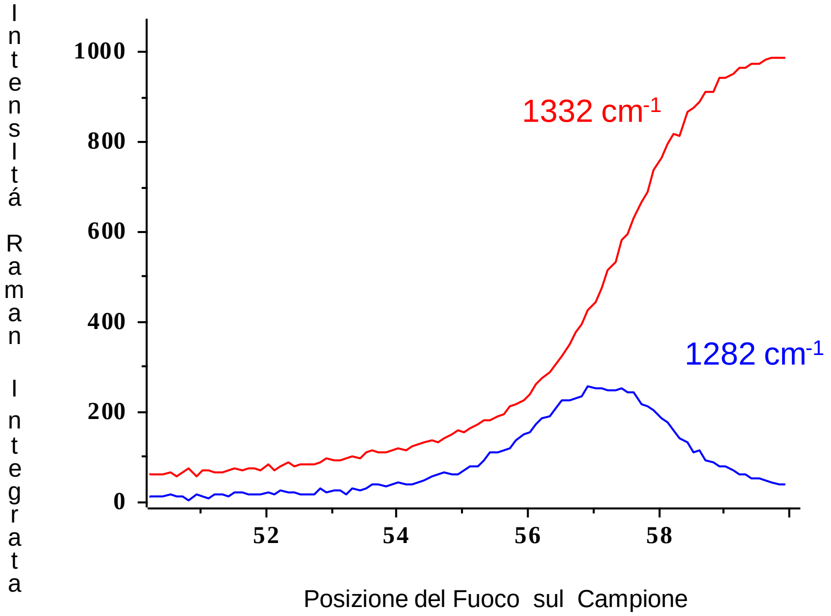
Per dettagli si veda JY note: *Study of different confocal techniques*.

Esempio

Profilo in funzione della profonditá di un film di 2-5 µm di diamante ^{13}C depositato su di una scheggia di diamante naturale



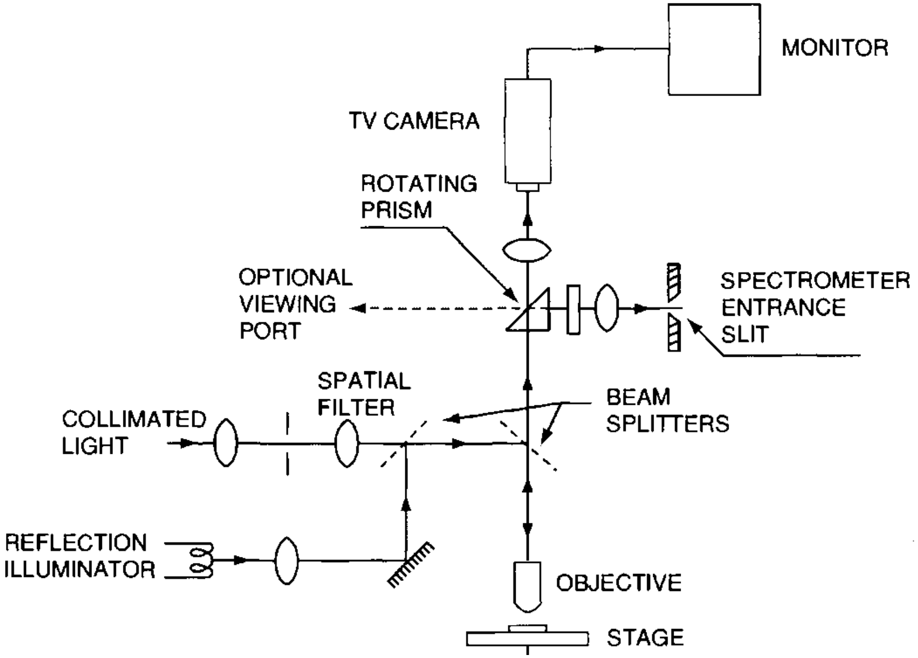




SAMPLE ILLUMINATION and COLLECTION SYSTEM
RAMAN MICROSCOPY

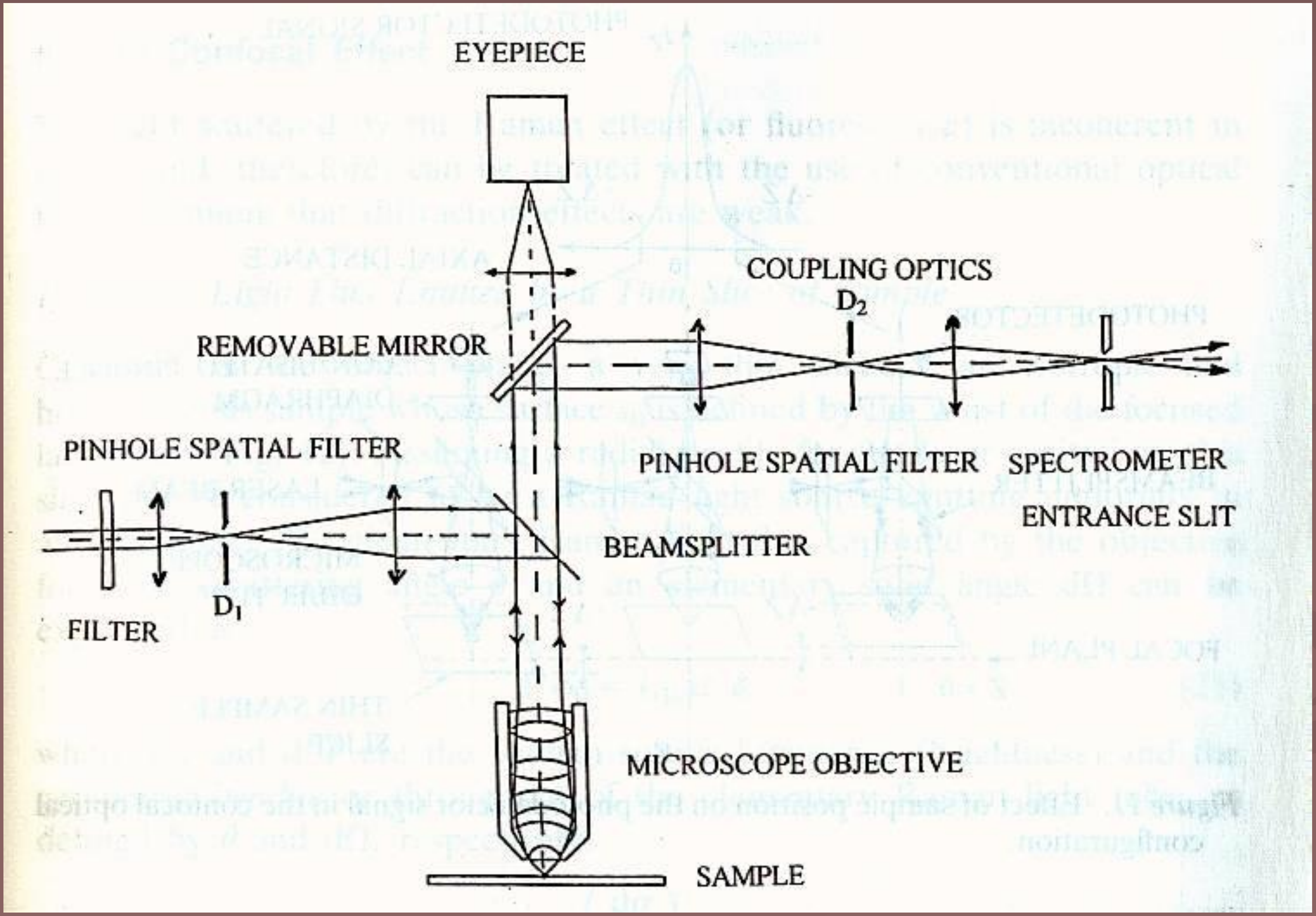
Raman MICROSCOPY provide the capability of obtaining analytical-quality Raman spectra with 1-2 µm spatial resolution.

- A high numerical aperture (NA) is necessary to collect the light scattered over a large solid angle to assure that more Raman scattered light from the sample is detected.



- The sample is placed on the stage of the microscope and is illuminated by light from illuminator.
- The focus on the sample is adjusted by moving the objective.
- TV camera is switched on by rotating the prism.
- The illuminator lamp is switched off and the laser beam is directed on by rotating the prism.
- The scattered light from the sample is collected by the objective and sent into the spectrometer.

Microscope schematic



Raman microscopy

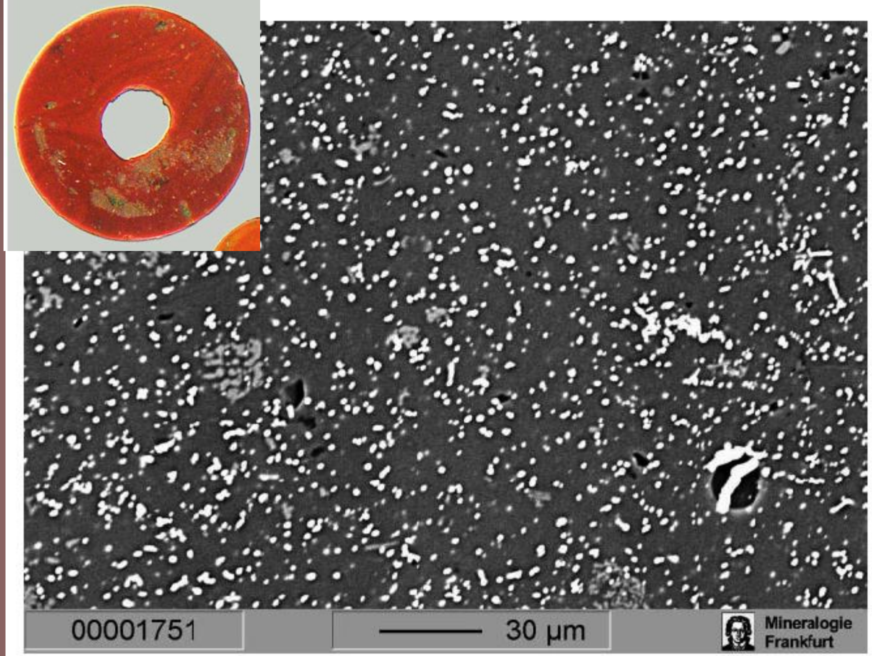


Figure 4. Small cuprite crystals of micrometre size interspersed in the glass matrix of red opaque disc-shaped beads: back-scattered image.

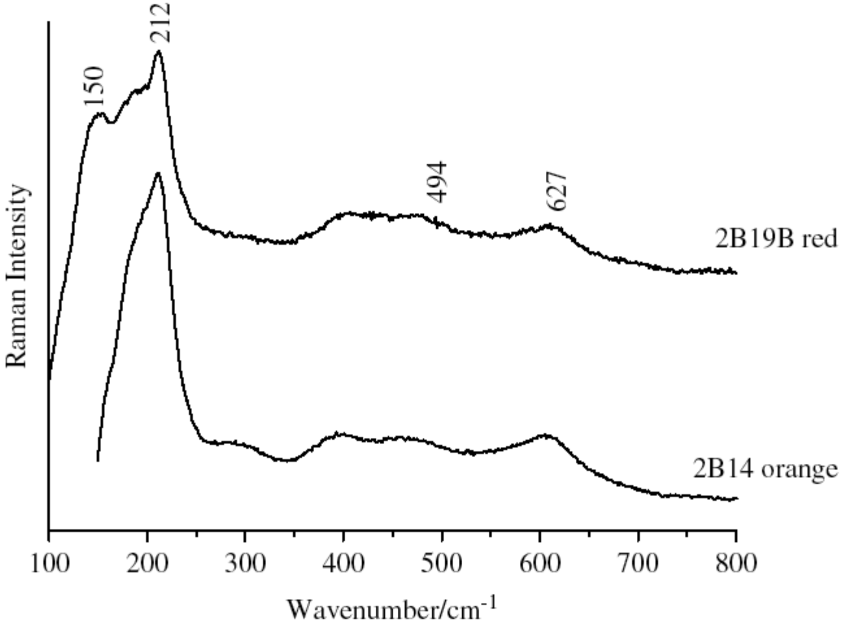
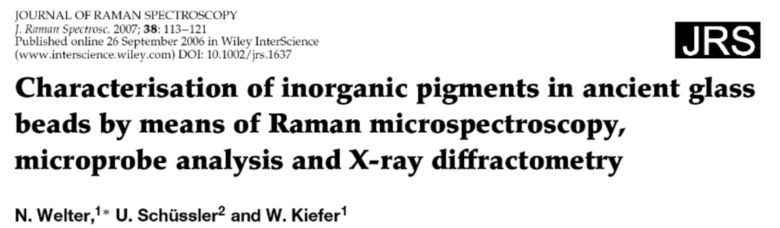


Figure 5. Raman spectra of cuprite (Cu_2O) in the red disc-shaped beads 2B19B and 2B14: excitation wavelength $\lambda = 514.5$ nm.



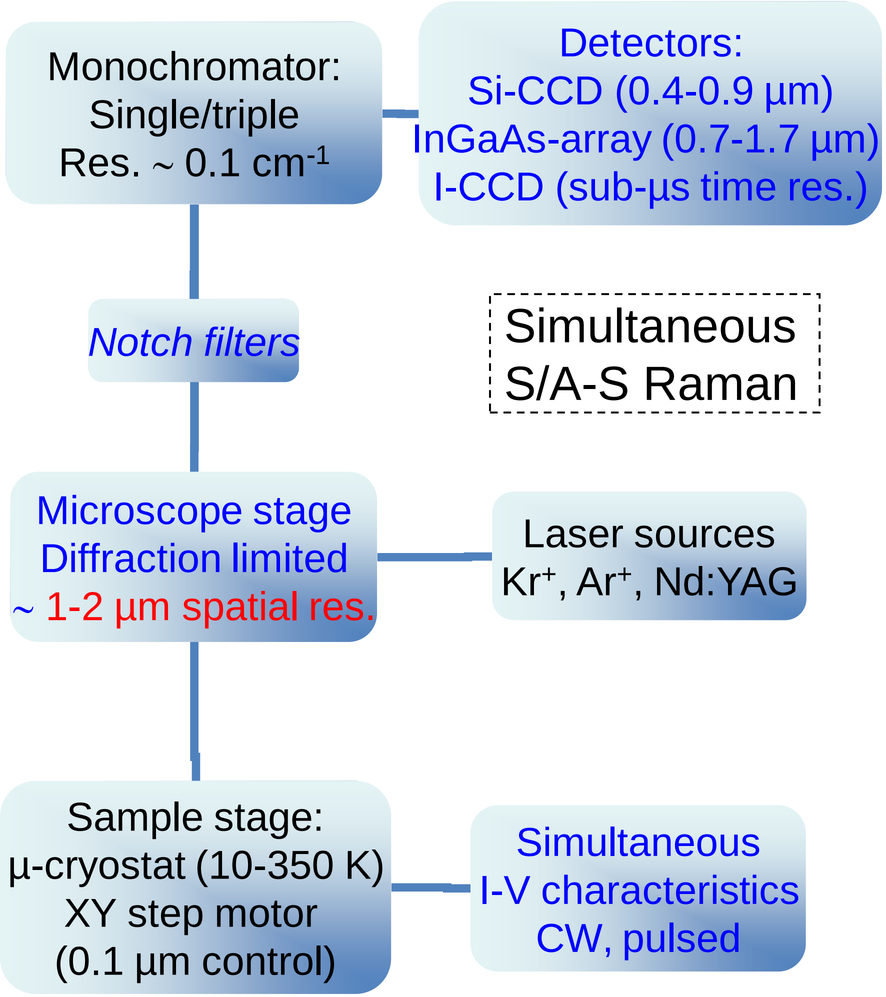
JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2007; **38**: 113–121
Published online 26 September 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/jrs.1637

JRS

Characterisation of inorganic pigments in ancient glass beads by means of Raman microspectroscopy, microprobe analysis and X-ray diffractometry

N. Welter,[1]* U. Schüssler[2] and W. Kiefer[1]

μ-probe optical spectroscopy set-up



Monochromator:
Single/triple
Res. ~ 0.1 cm^{-1}

Detectors:
Si-CCD (0.4-0.9 μm)
InGaAs-array (0.7-1.7 μm)
I-CCD (sub-μs time res.)

Notch filters

Simultaneous
S/A-S Raman

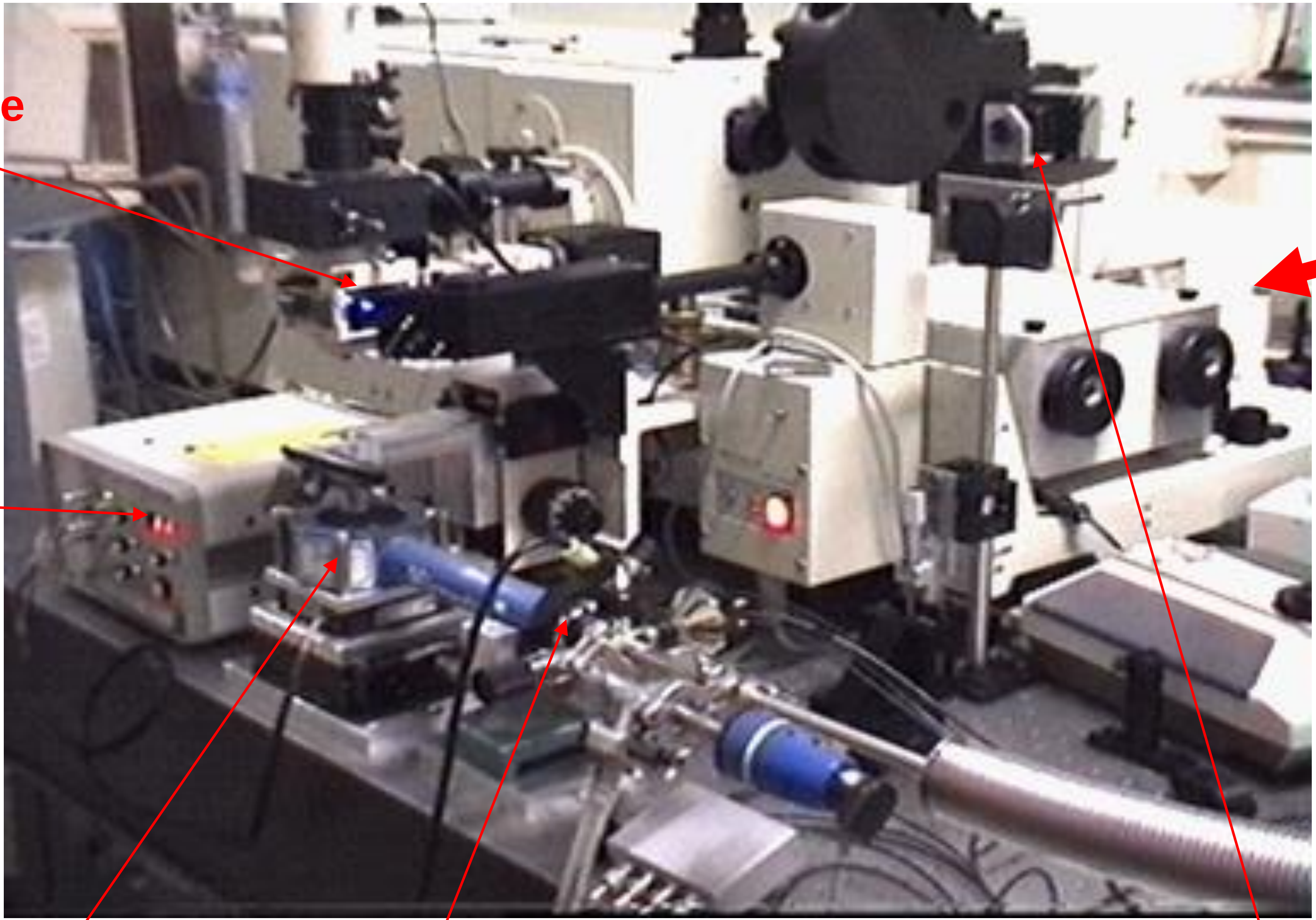
Microscope stage
Diffraction limited
~ 1-2 μm spatial res.

Laser sources
Kr^+, Ar^+, Nd:YAG

Sample stage:
μ-cryostat (10-350 K)
XY step motor
(0.1 μm control)

Simultaneous
I-V characteristics
CW, pulsed

Experimental Setup



Microscope

Laser Kr$^+$

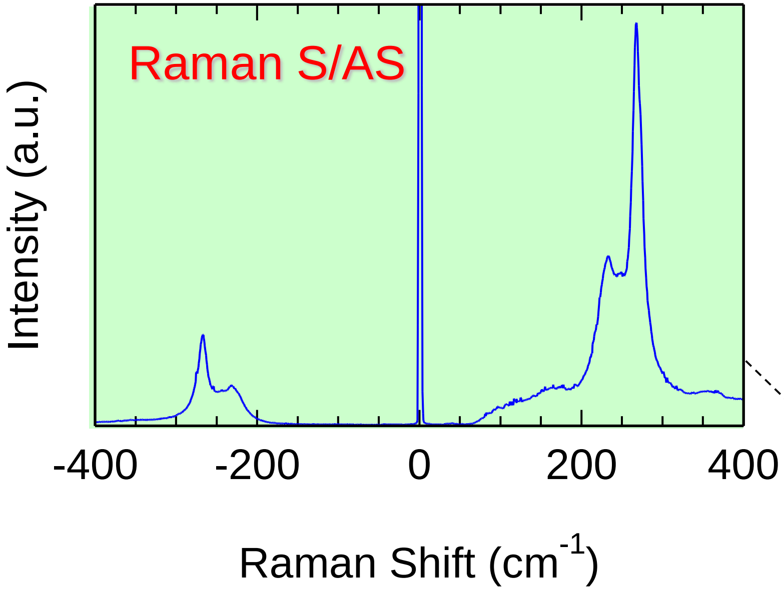
Piezo x-y

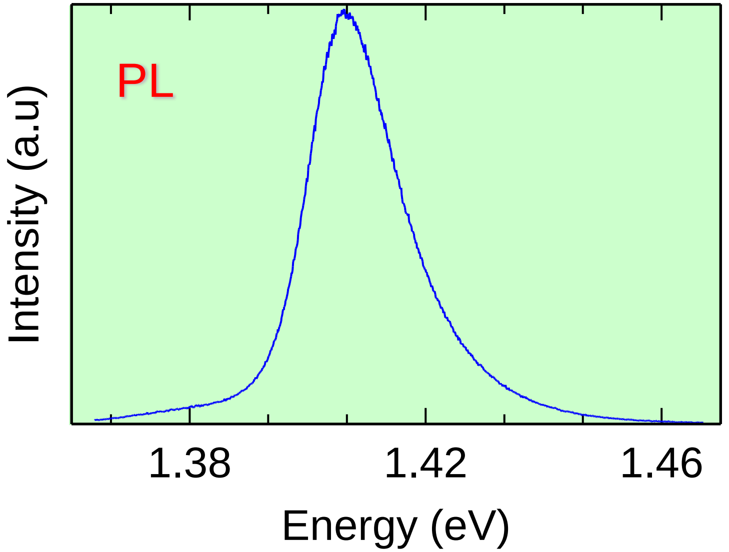
QC devices

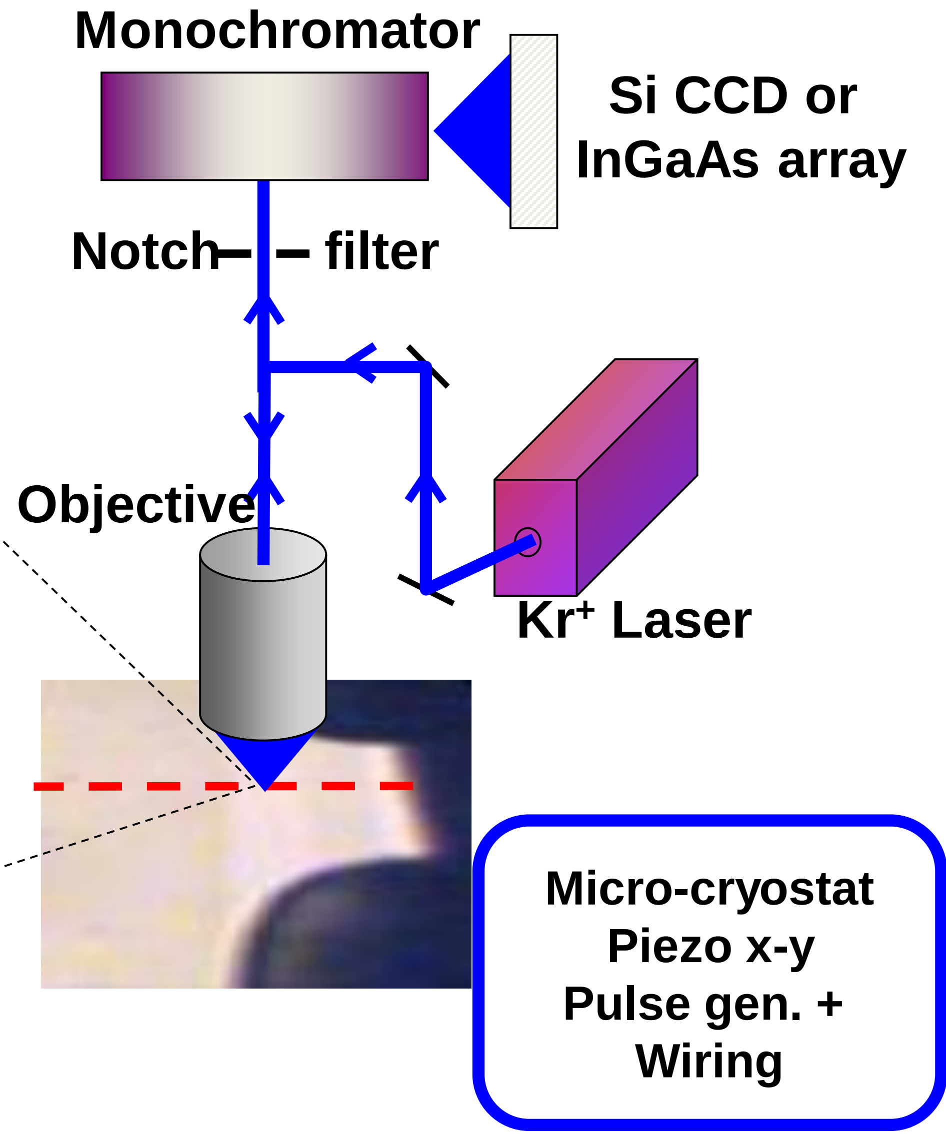
μ-Cryostat

Notch filter

Experimental Technique

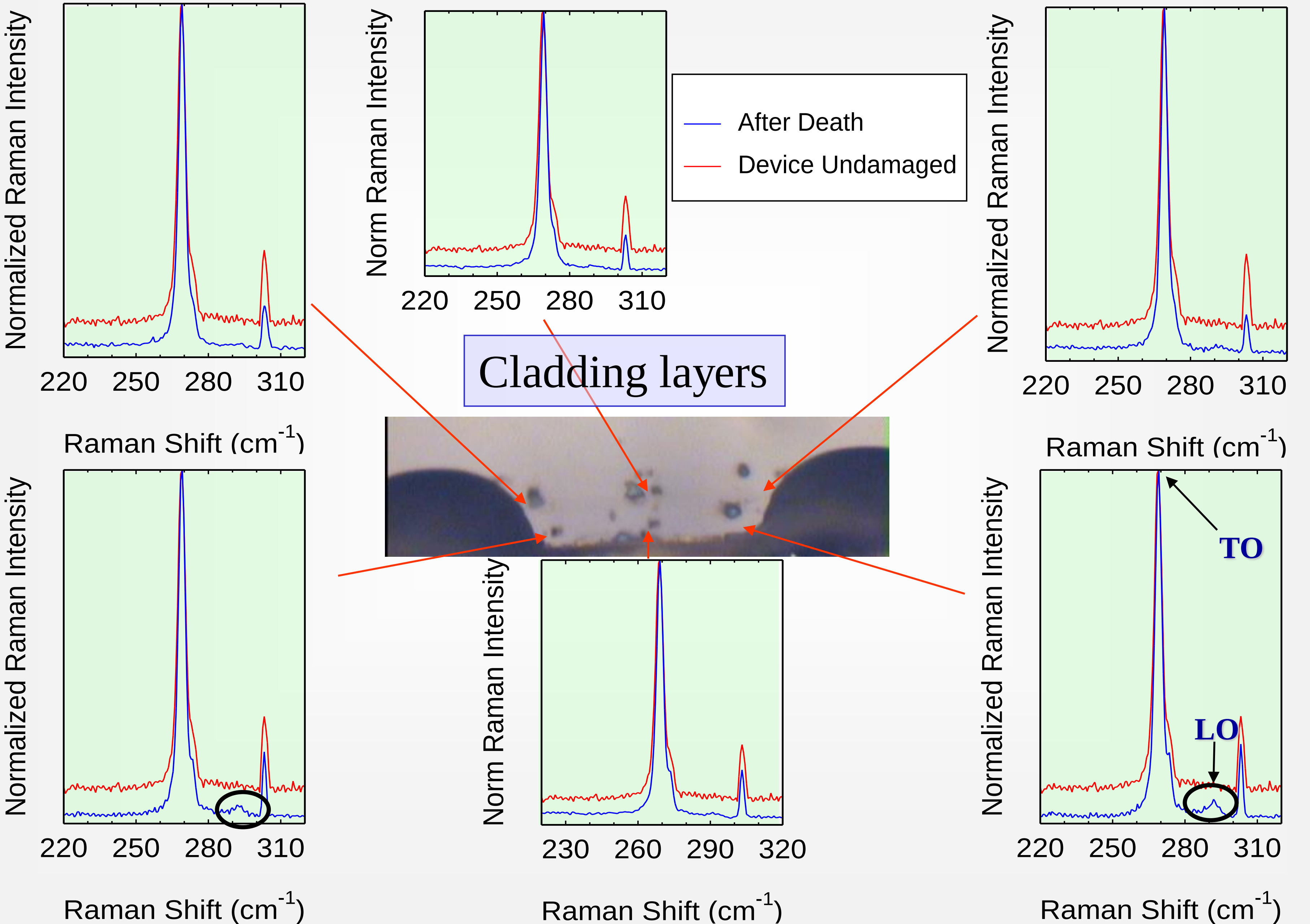






Micro-cryostat
Piezo x-y
Pulse gen. +
Wiring

Breakdown of Raman selection rules induced by **lattice damage**



Effect of Biaxial STRAIN on optical phonons in GaAs layers (*along [001] and [110]*)

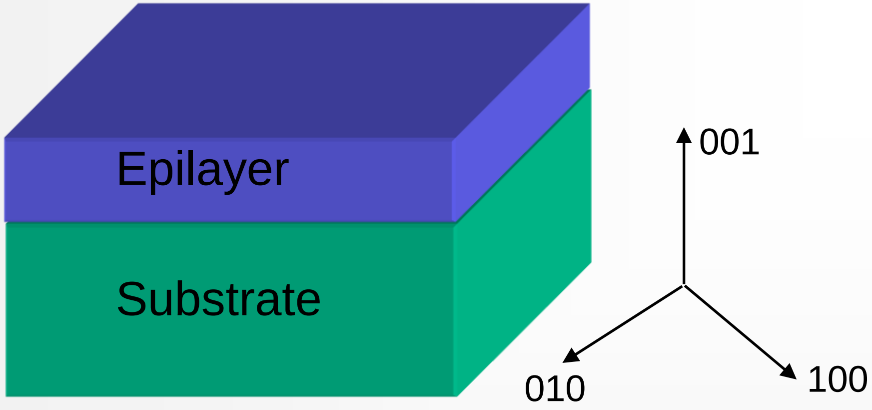
Application of stress on GaAs

↓

lowering of the crystal simmetry

Splittings of the triple TO and LO degeneracy in a doublet (D) and a singlet (S) levels

Shift of the TO and LO energy



Strain uniform in the epitaxial layer

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{//} = \Delta a_{//}/a = (S_{11} + S_{12})X$$

$$\varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{xz} = 0$$

$$\varepsilon_{zz} = \varepsilon_{\perp} = S_{12}X$$

Longitudinal Optical Phonon

$$\cancel{\Delta\omega_{\mathrm{LO_D}} = -2.3X = -0.29\times10^{3}\varepsilon_{//}}$$

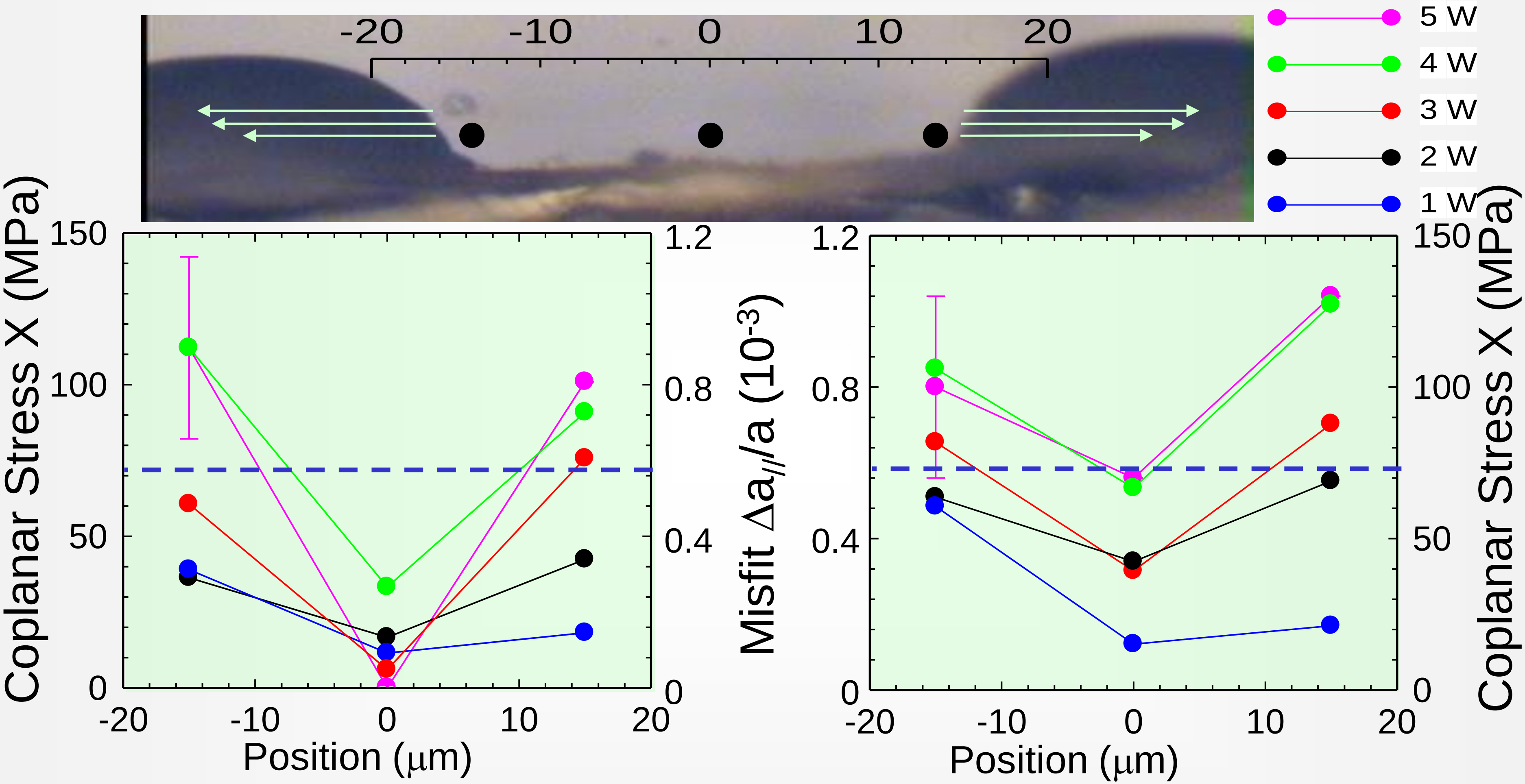
$$\cancel{\Delta\omega_{\mathrm{LO_S}} = -3.9X = -0.49\times10^{3}\varepsilon_{//}}$$

Transverse Optical Phonon

$$\Delta\omega_{\mathrm{TO_D}} = -2.7X = -0.34\times10^{3}\varepsilon_{//}$$

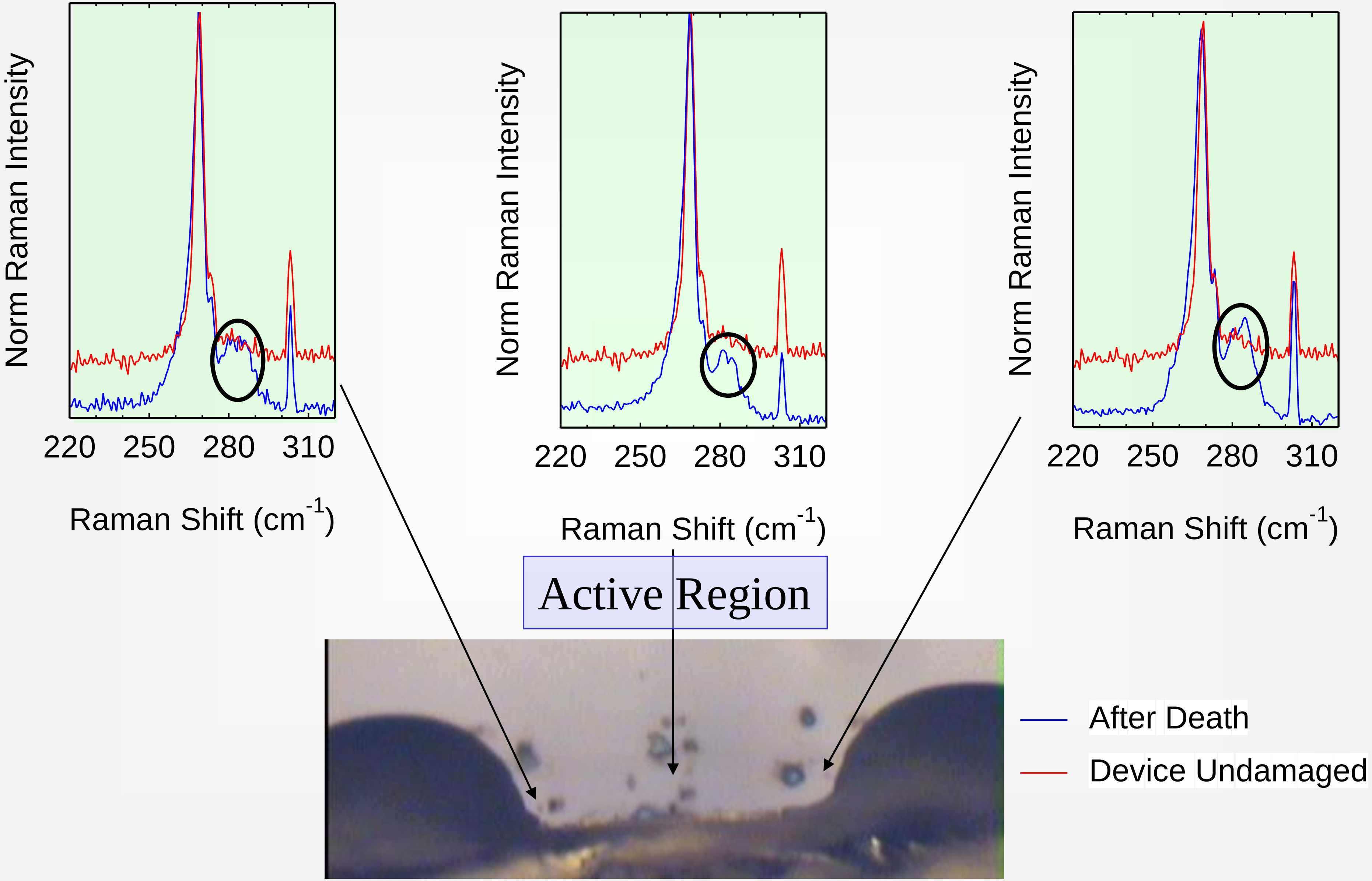
$$\cancel{\Delta\omega_{\mathrm{TO_S}} = -3.3X = -0.41\times10^{3}\varepsilon_{//}}$$

Stress and **misfit** in the upper GaAs cladding of operating epilayer-down mounted devices



The cladding layers suffer a TENSILE strain due to the large thermal expansion coefficient of the solder that, at dissipated power P> 3W, leads to misfit dislocation injection and so to device failure

Breakdown of Raman selection rules induced by **lattice damage**

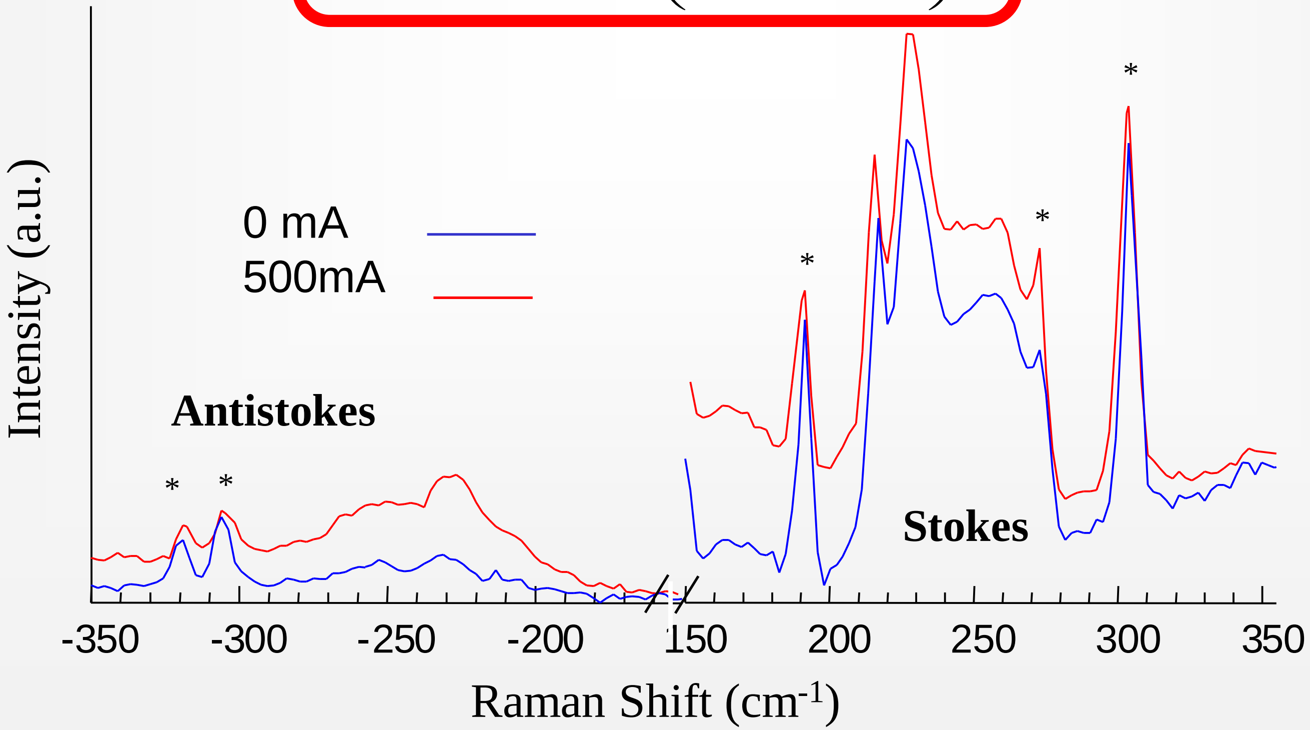


DETERMINATION OF OPTICAL PHONONS ENERGY DISTRIBUTION

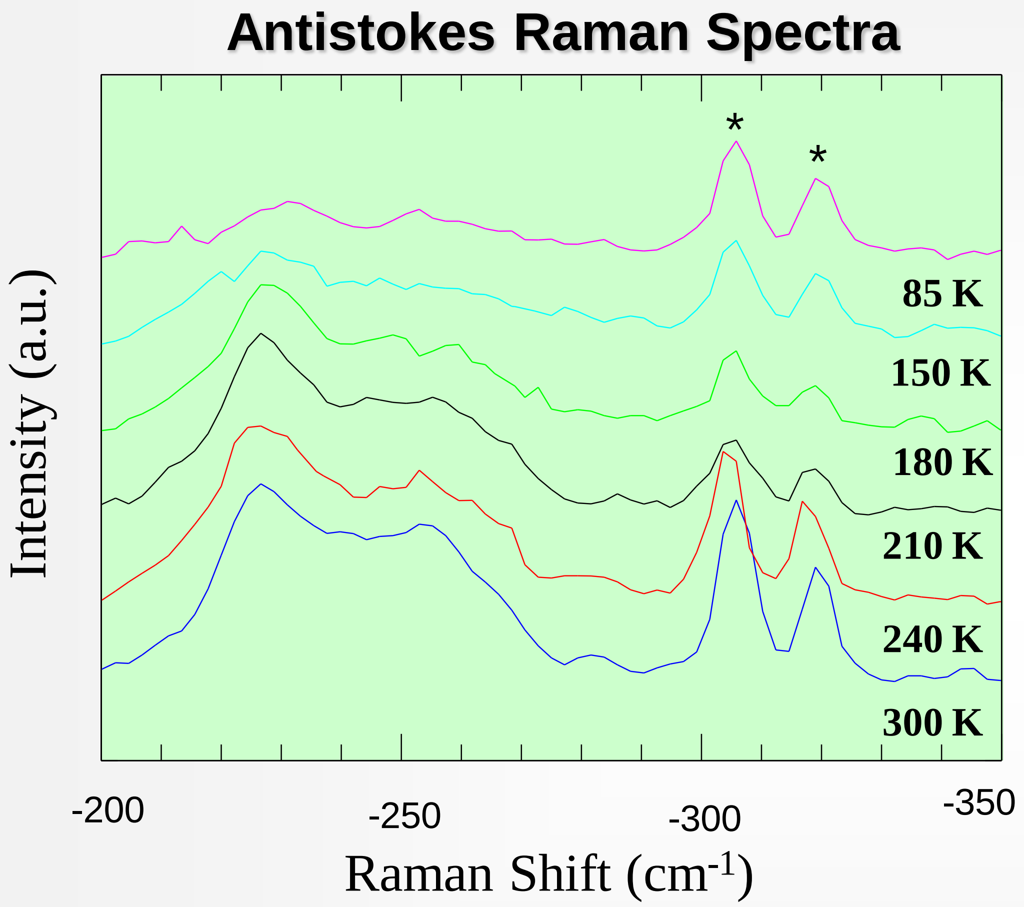
$$n = \frac{1}{\exp\left(\hbar\omega_0 / kT\right) - 1}$$ *(Bose-Einstein)*

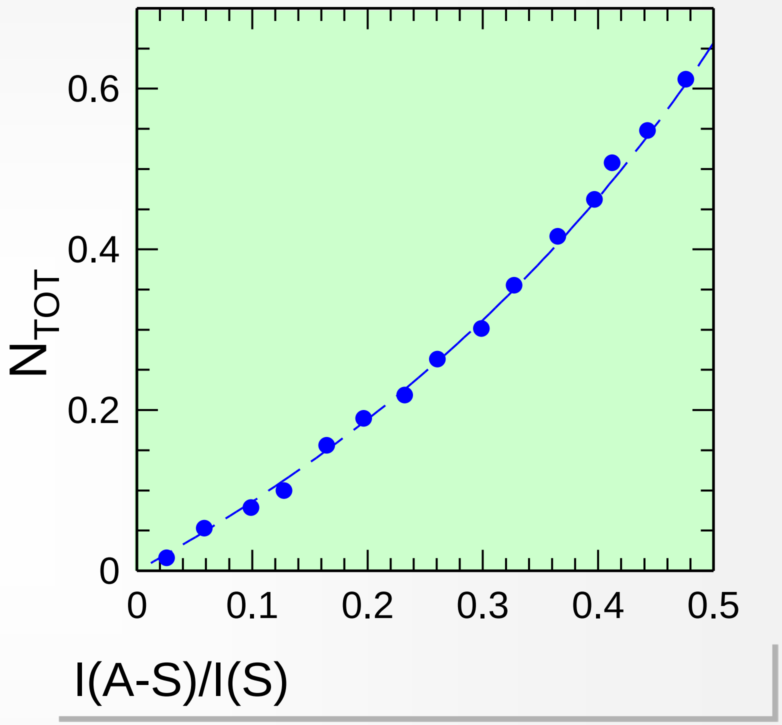
$$\frac{A - Stokes}{Stokes} \propto \frac{n}{n+1}$$

$$\boxed{T_{phonon} = f\left(\frac{AS}{S}, \hbar\omega_o\right)}$$



Raman Stoke/Antistokes Calibration Curve

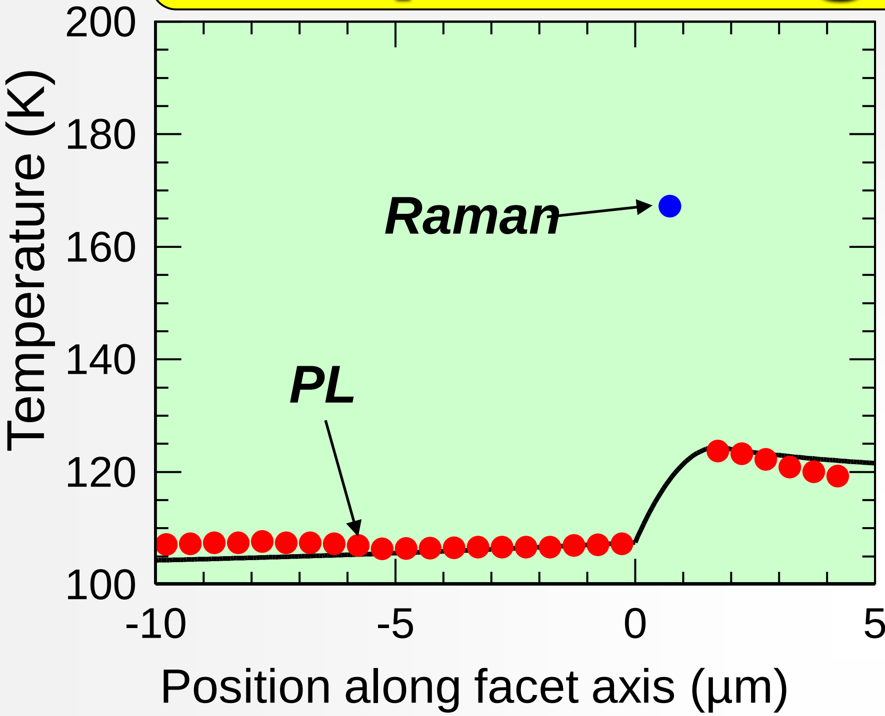

Antistokes Raman Spectra

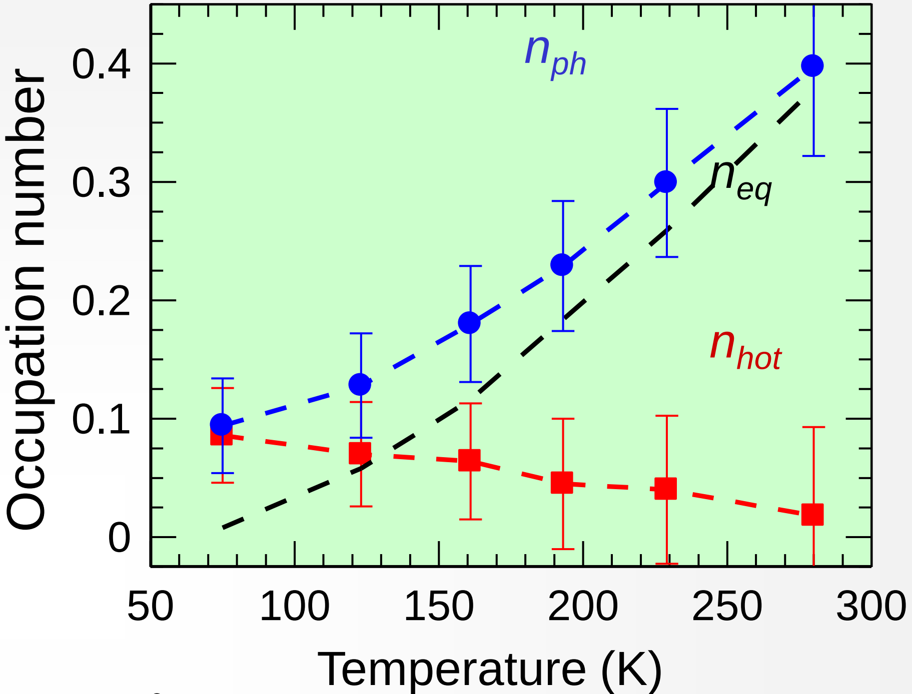


PL Spectra @ device on → PL energy peak position → Local Lattice temperature

Raman Spectra @ device on → AntiStokes/Stokes ratio → Optical Phonon “temperature”

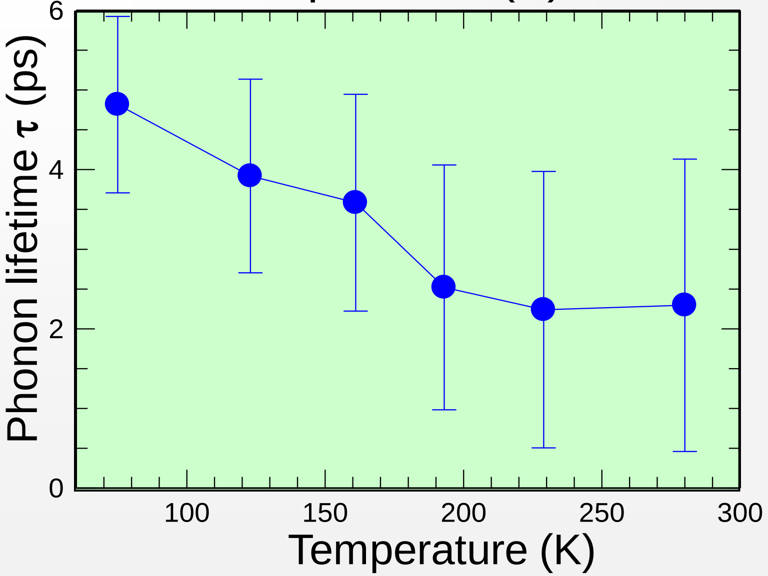
Hot phonon generation *APL 80, 4303 (2002)*





Interface Optical Phonon Lifetime

$$\tau \propto \frac{n_{tot} - n_0}{I \cdot \Delta V}$$



Analisi Raman

λ=476.2nm P=10mW

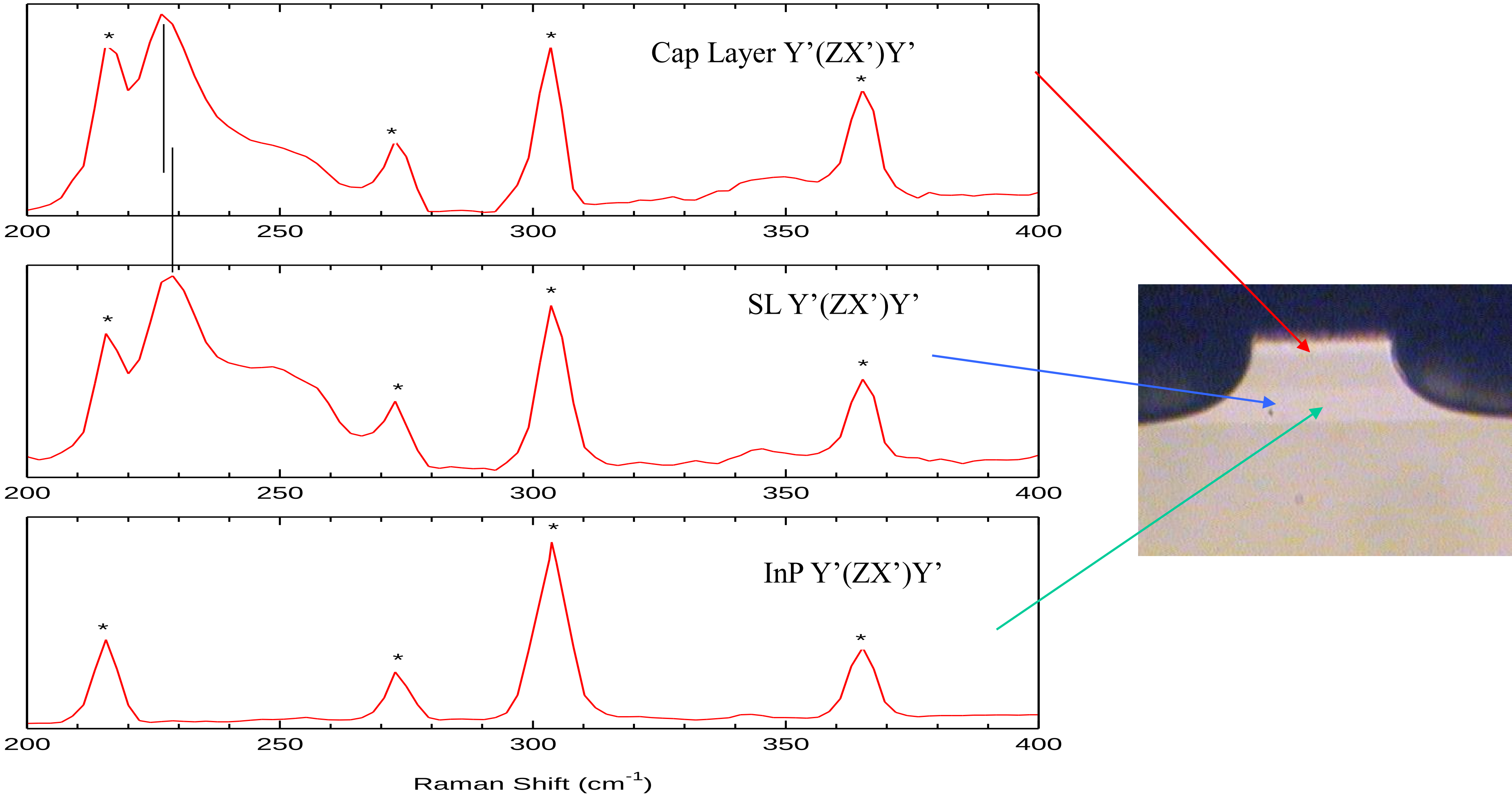
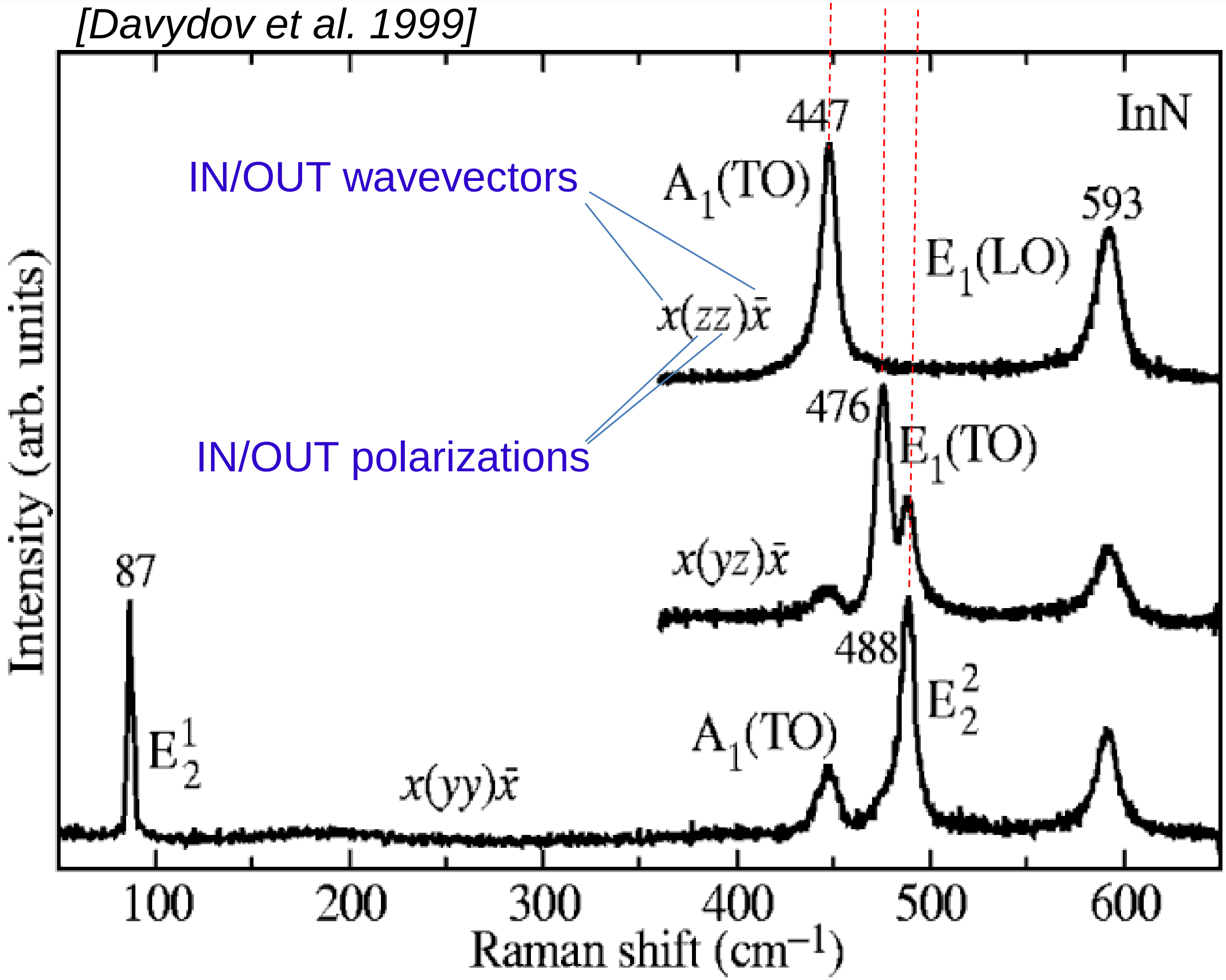


Figura 4

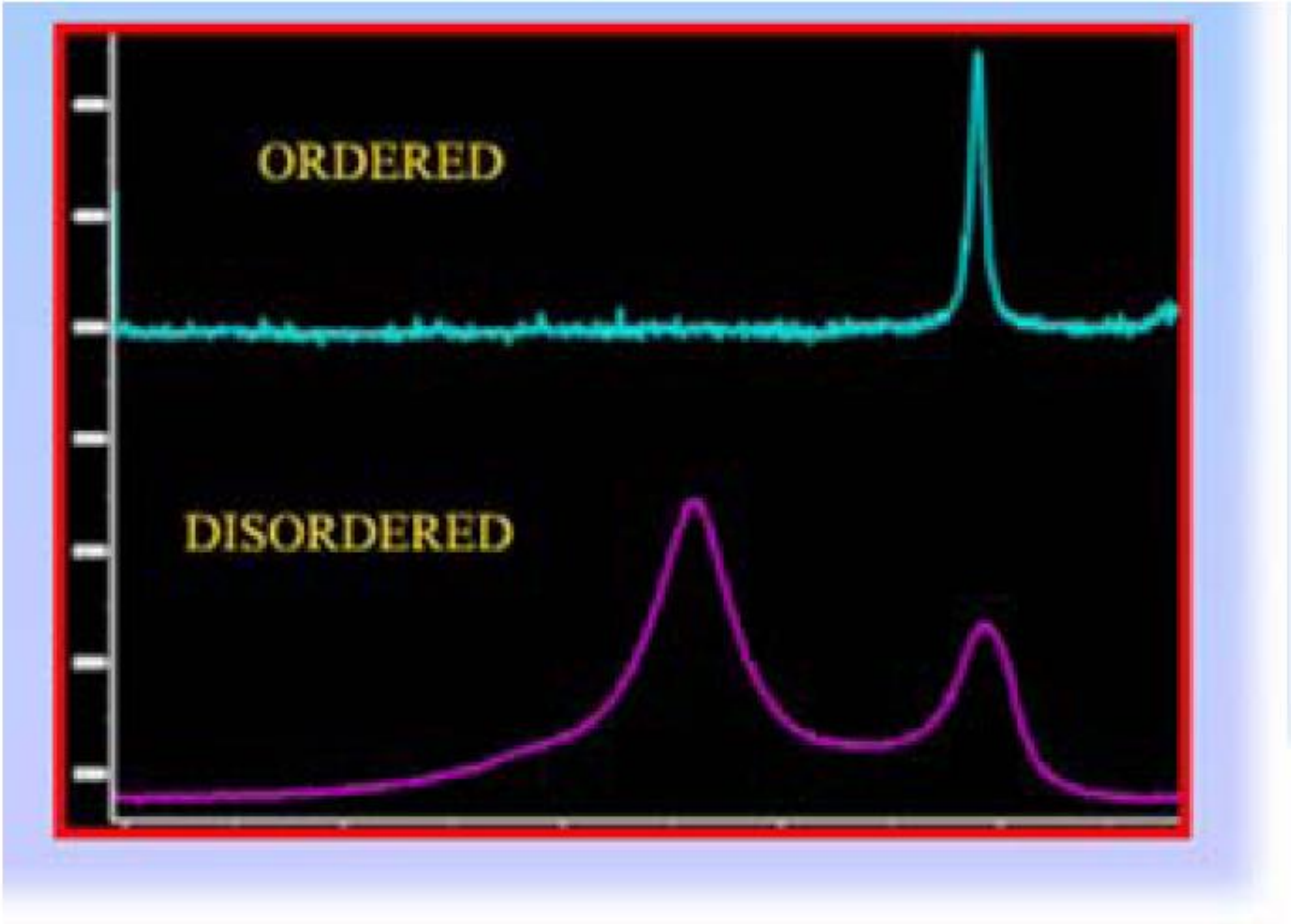
Polarized Raman spectrum of InN

[Davydov et al. 1999]



PHASE & CRYSTAL STRUCTURE EFFECTS

graphite



La Serie LabRam

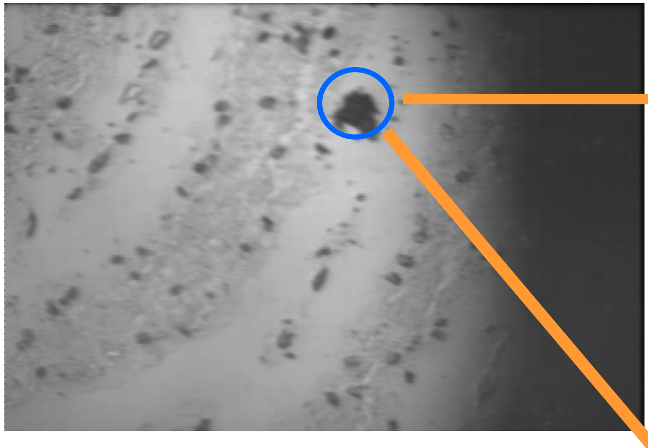
Una Nuova Generazione di Strumentazione per l'Analisi

***Il LabRam*, con il suo elevato livello di raffinatezza ed una tecnologia ottica unica nel suo genere consente l'analisi di routine di differenti campioni quali :**

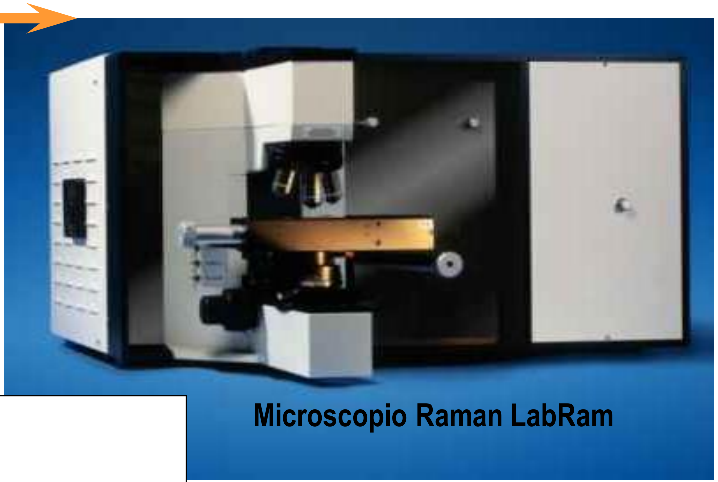
- **Narcotici e Sostanze Controllate**
- **Inchiostri**
- **Esplosivi**
- **Residui Chimici**

La Serie LabRam

Una Nuova Generazione di Strumentazione per l’Analisi

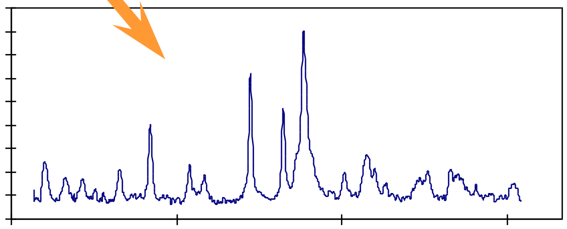


Immagini Video di Impronte Digitali



Microscopio Raman LabRam

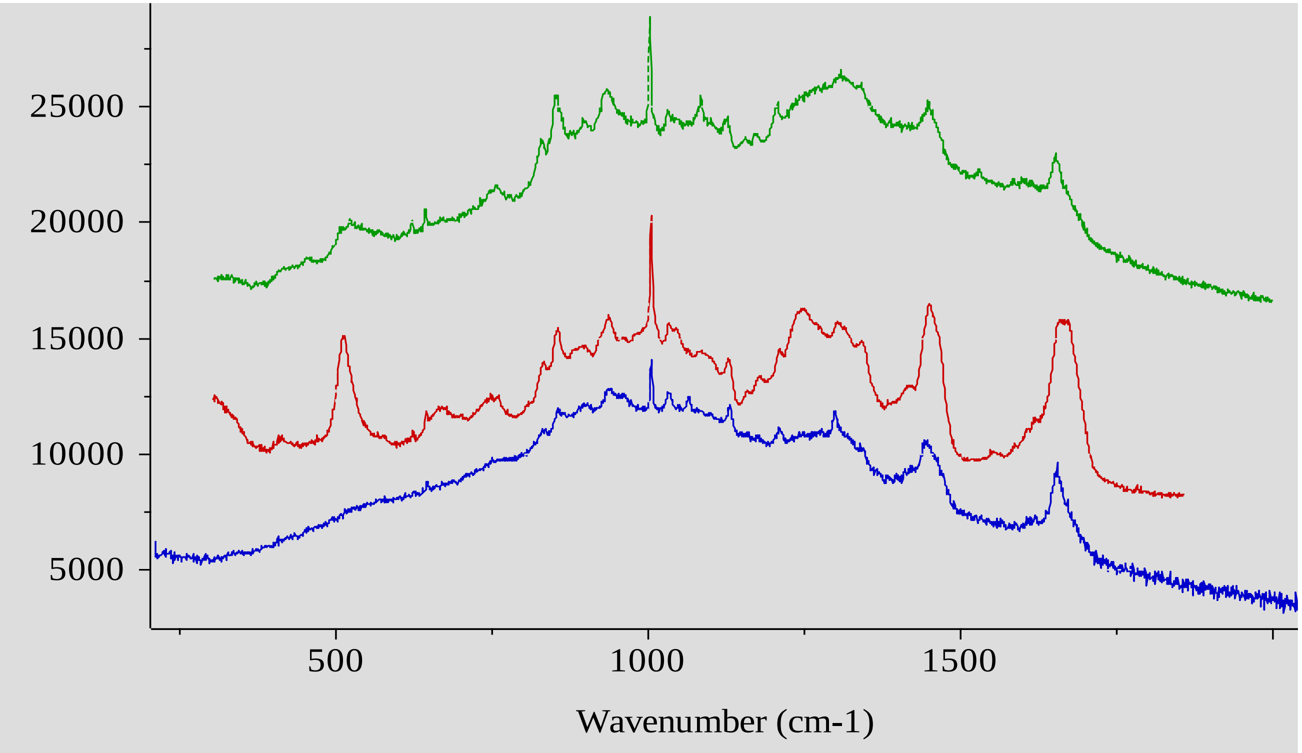
Identificazione di sostanze a livello microscopico...



Raman Spettro di MDMA

Esempio

Spettri Raman di Campioni Biologici di interesse Forense:
Unghia umana (sopra), Capello umano (al centro) e Pelle umana (in basso)



DROGHE ILLECITE

Identificazione di Cocaina: Crack vs. HCl

Lo Spettro Raman contrassegna le due.

L'esame puó essere eseguito:

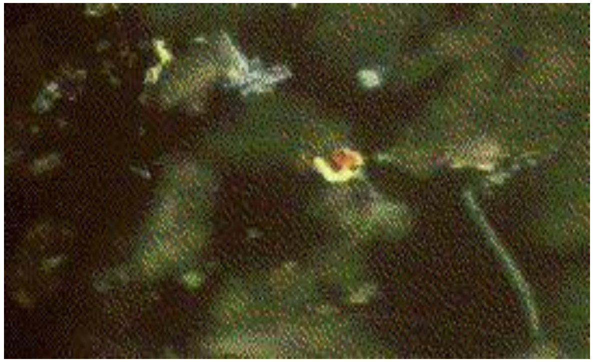
- **in fiale da 1cm preparate per altre analisi**
- **sulla polvere in pacchetti di plastica**

Ció significa che non vi é alcuna ulteriore preoccupazione riguado ai *processi di custodia* e/o *contaminazione*.

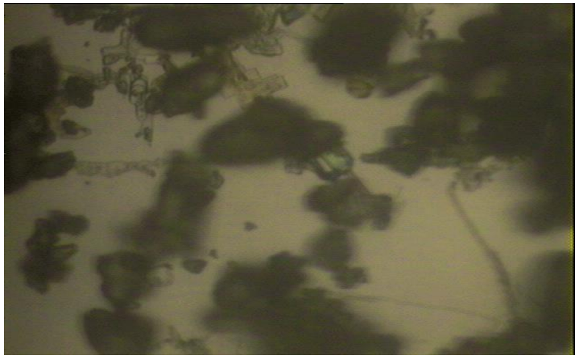
Micrografico Polarizzato di un Cristallo di Cocaina in presenza di Agenti Taglianti

Il Comportamento Cromatico indica Cocaina

L’uso di una lente a bassa magnificazione aiuta nell’identificazione visuale in luce polarizzata di particelle sospette, e nell’acquisire lo spettro Raman



Polarizzatori Trasversi

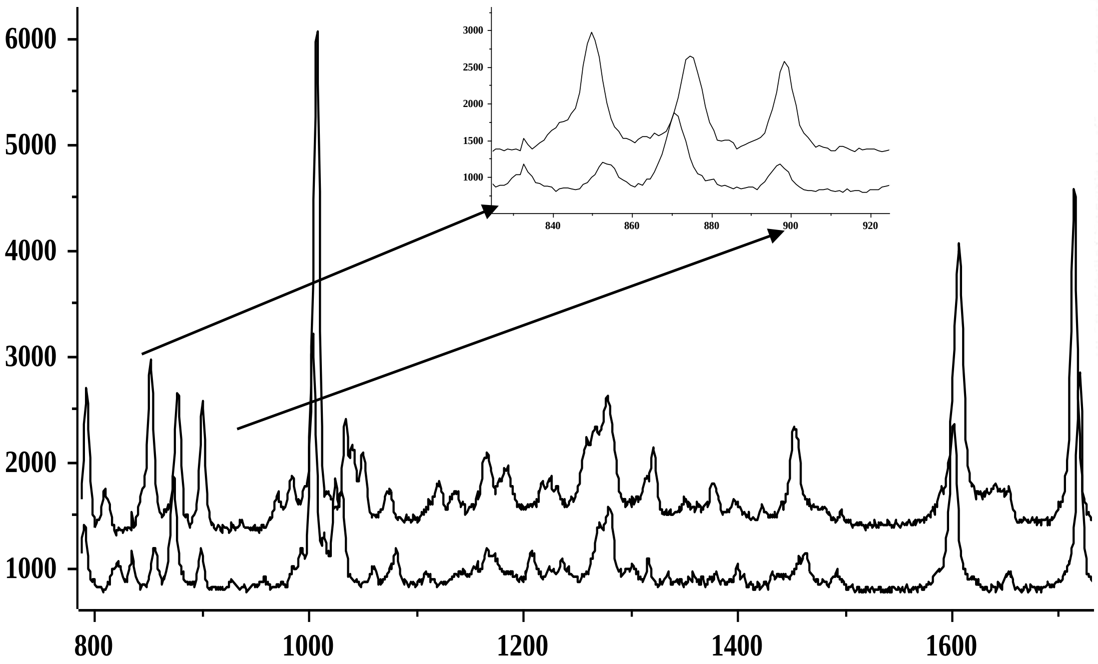


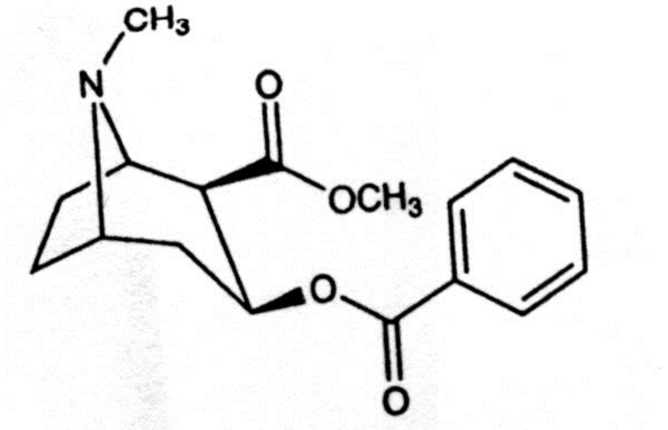
Polarizzatori Paralleli

Metodologia sviluppata da Deborah Cole e Tom Brettell

DROGHE ILLECITE

Spettri acquisiti con la Microsonda Raman di Cocaina HCl [sotto] vs. Cocaina Free Base (Crack) [sopra]





Crack (free base)

HCl

DROGHE ILLECITE

Anello acroamtico singolarmente sostituito:
bande intorno ai 1000 e 1600 cm^{-1}

>C=O banda carbonile intorno ai 1750 cm^{-1}

>CH_2 e -CH_3 deformazioni intorno ai1450 cm^{-1}

Lo spettro tra gli 840 e i 900 cm^{-1} fornisce una facile "impronta digitale" della specie

Conclusioni:

•Lo Spettro Raman fornisce un’ “impronta digitale” di una sostanza e ne consente l’identificazione

•E’ una tecnica non invasiva e non distruttiva

•La confocalitá fornisce un incremento in termini di risoluzione spaziale e consente di effettuare misure:

- **in presenza di campioni di dimensioni microscopiche**
- **senza alcun problema in termini di *processi di custodia* e/o *contaminatione del campione*.**