

Phonon Spectroscopies

Raman & IR



An important optical spectroscopy technique
is

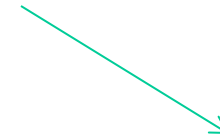
Inelastic Light Scattering.

(In solids) this technique can be used to measure both

Accoustic Phonons & Optical Phonons



Brillouin scattering



Raman Scattering

- **Inelastic light scattering** can only probe a small fraction around the center of the 1st Brillouin zone.

Inelastic light scattering

- Raman scattering: probes optical phonons
- Brillouin scattering: probes acoustic phonons

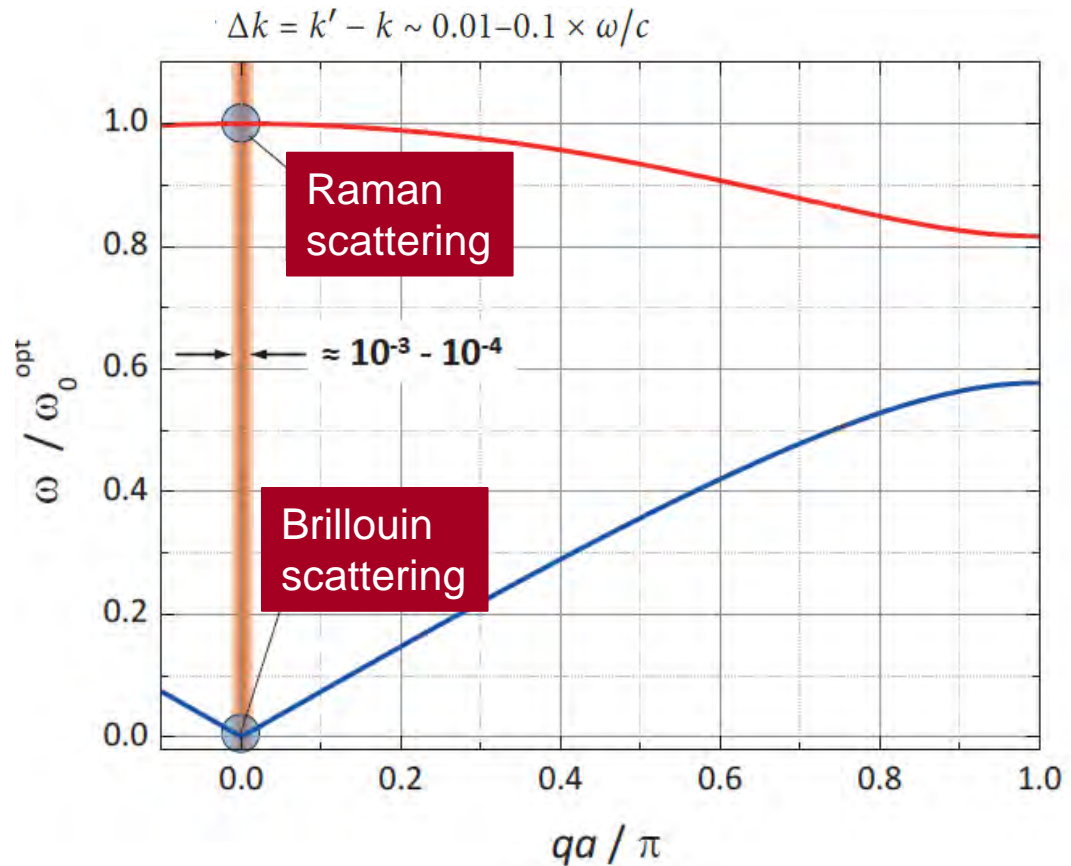
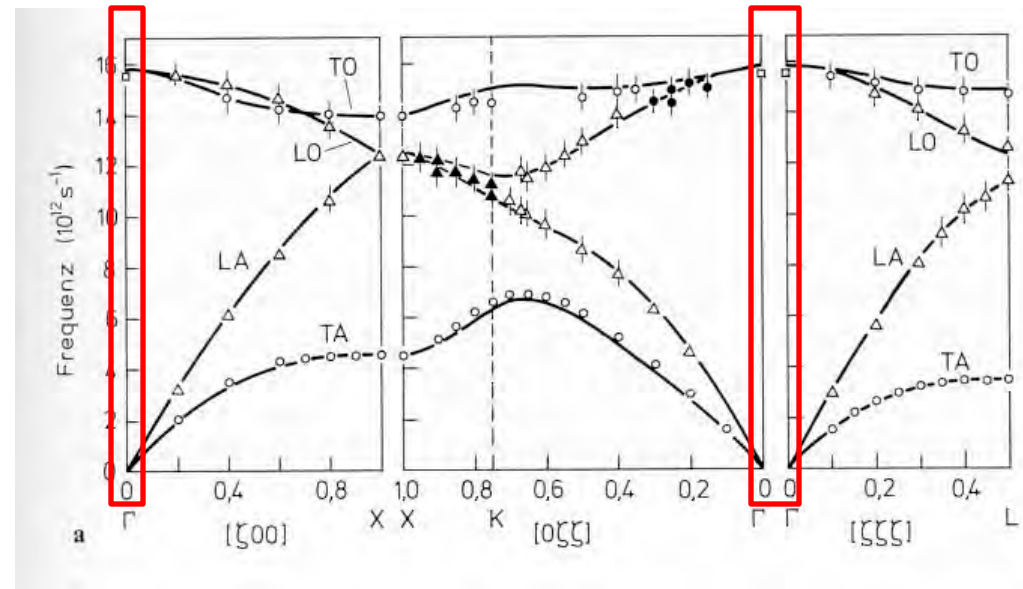


Image source: Gross

How to determine experimentally the phonon frequency at the center of the Brillouin zone?

- Raman spectroscopy
(inelastic photon scattering)
- Brillouin spectroscopy
(inelastic photon scattering)
- Infrared absorption spectroscopy
(photon absorption)



Phonon dispersion for Silicon

Theoretical calculations ----lines in the graphs
Experimental measurements (neutron scattering): dots

The Raman effect:

→ variation of intensity, frequency/wavelength and therefore direction of incident light after going through a sample.

- The pattern of the Raman lines is characteristic of the particular species;
- The intensity is proportional to the number of scattering points in the path of the light.
- The energies corresponding to the Raman frequency shifts are found to be the energies associated with transitions between different vibrational states of the scattering points.

Raman Spectroscopy

- *High intensity laser radiation with wavelengths in either the **visible** or **near-infrared** regions of the spectrum is passed through a sample.
- *The Photons from the laser beam produce an oscillating (polarization) in the molecules, exciting them to a **virtual energy state**.
- *The oscillating polarization of the molecule can couple with other possible polarizations of the molecule, including vibrational and electronic excitations.
- *If the polarization in the molecule does not couple to these other possible polarizations, then it will not change the vibrational state and the scattered photon will have the same energy as the original photon: **Rayleigh Scattering**.



The **Raman interaction** leads to **3 possible outcomes**:

2 inelastic processes

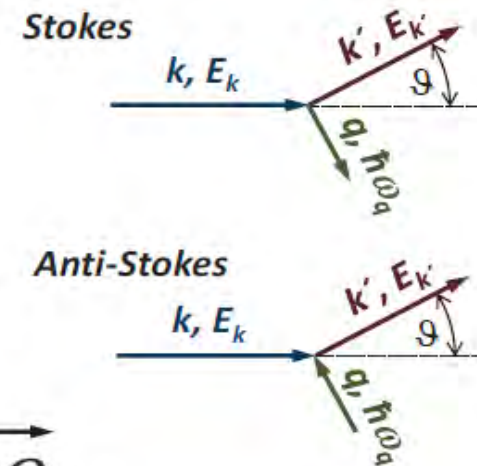
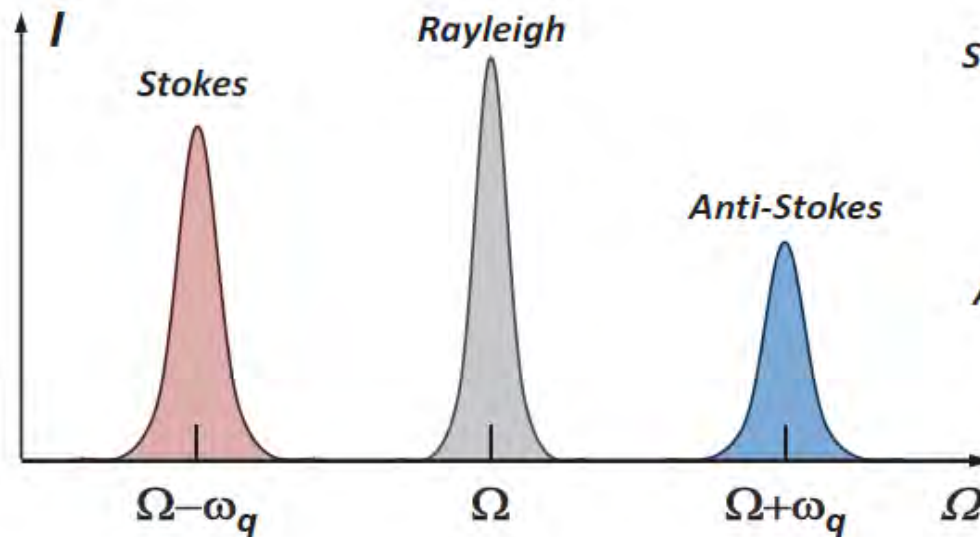
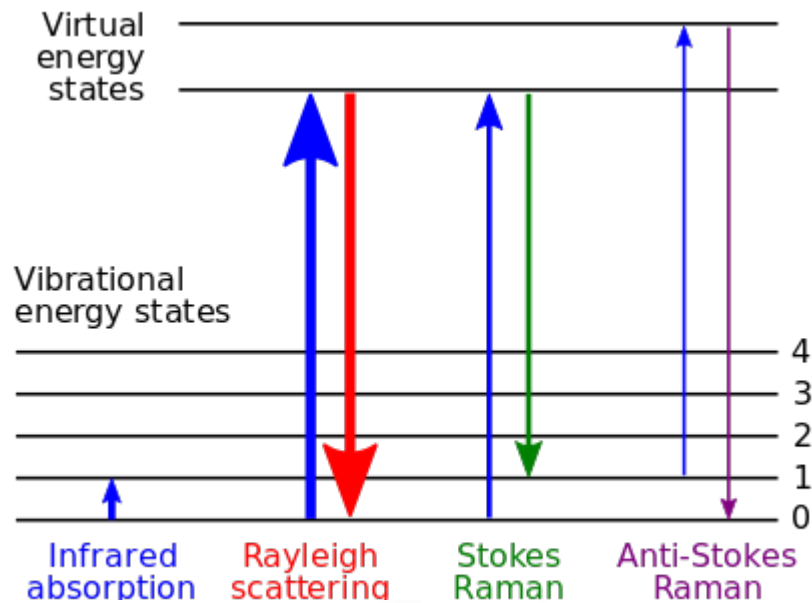
- the **material absorbs** energy and the emitted photon has a lower energy than the absorbed photon: **Stokes Raman scattering**.
- the **material loses** energy and the emitted photon has a higher energy than the absorbed photon: **anti-Stokes Raman scattering**.

1 elastic process: **Rayleigh Scattering**

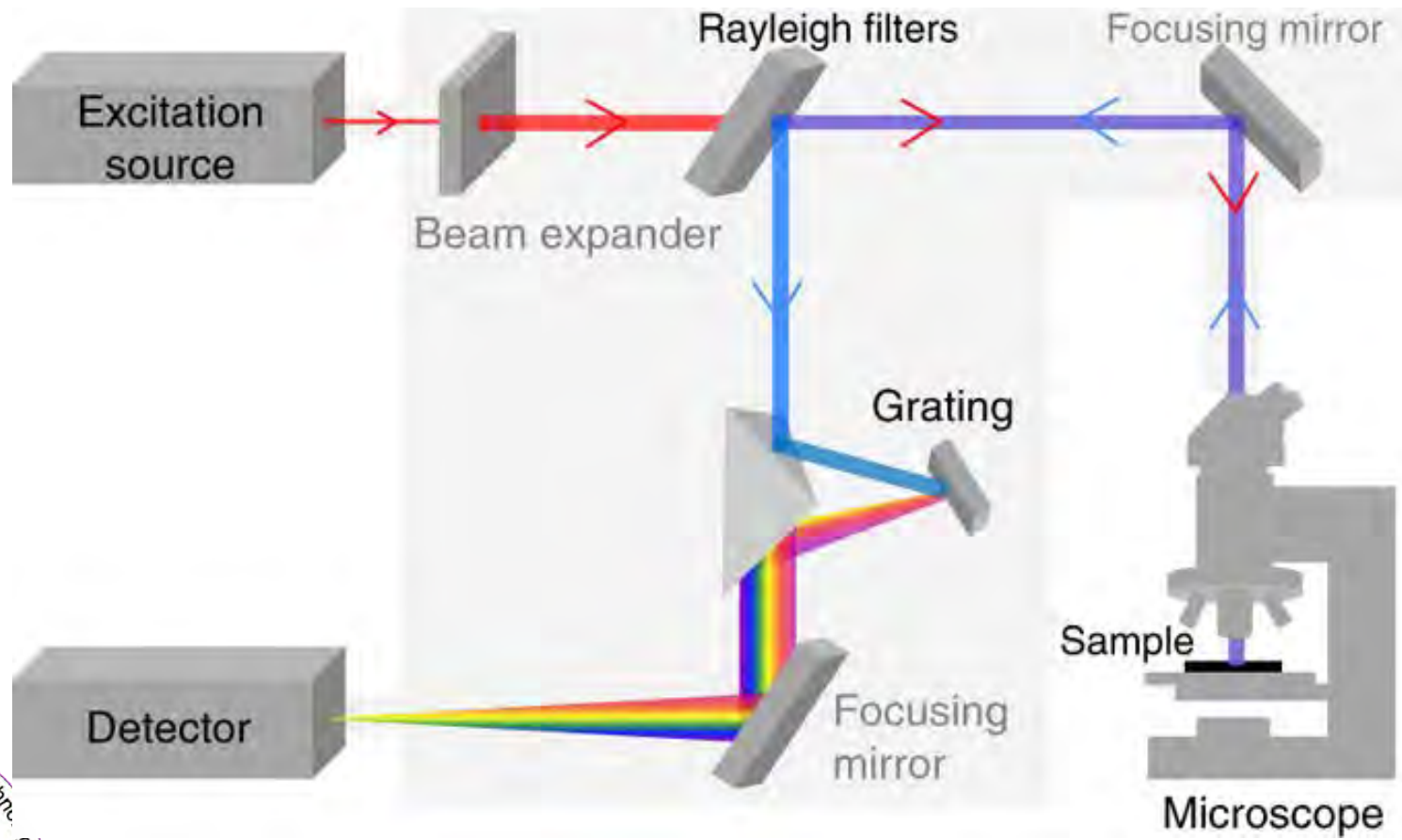
The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the material and is independent of the absolute energy of the photon.

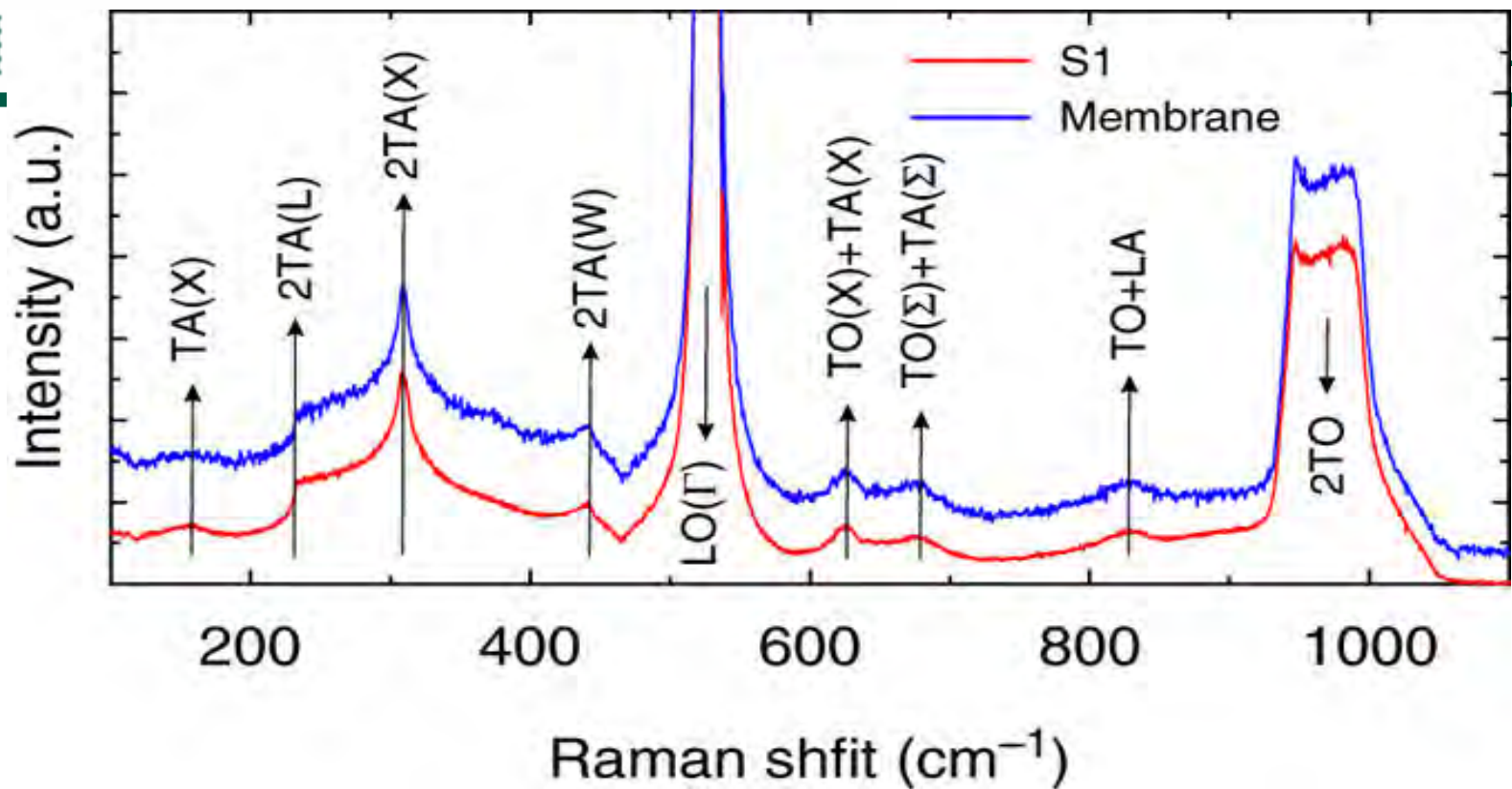


The **Raman Spectrum** is therefore the spectrum of the scattered photons.



Basic Diagram of a Raman Spectrometer





- Raman shifts are typically reported in wavenumbers, which have units of inverse length, which is directly related to energy.
- To convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used:

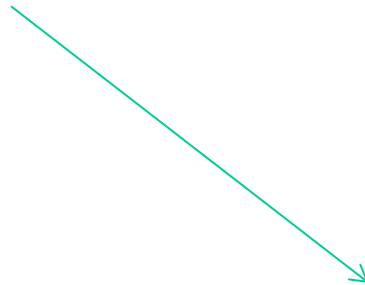
$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \longrightarrow \Delta w(\text{cm}^{-1}) = \left(\frac{1}{\lambda_0(\text{nm})} - \frac{1}{\lambda_1(\text{nm})} \right) \times \frac{(10^7 \text{ nm})}{(\text{cm})}$$

- $\Delta\omega$ is the Raman shift expressed in wavenumber
 -
 - λ_0 is the excitation wavelength
 - λ_1 is the Raman spectrum wavelength.
- Most commonly, the unit chosen for expressing wavenumber in Raman spectra is inverse centimeters (cm^{-1}).
- Since wavelength is often expressed in units of nanometers (nm), the previous relation can scale for this unit conversion explicitly.

Line width of the spectral lines

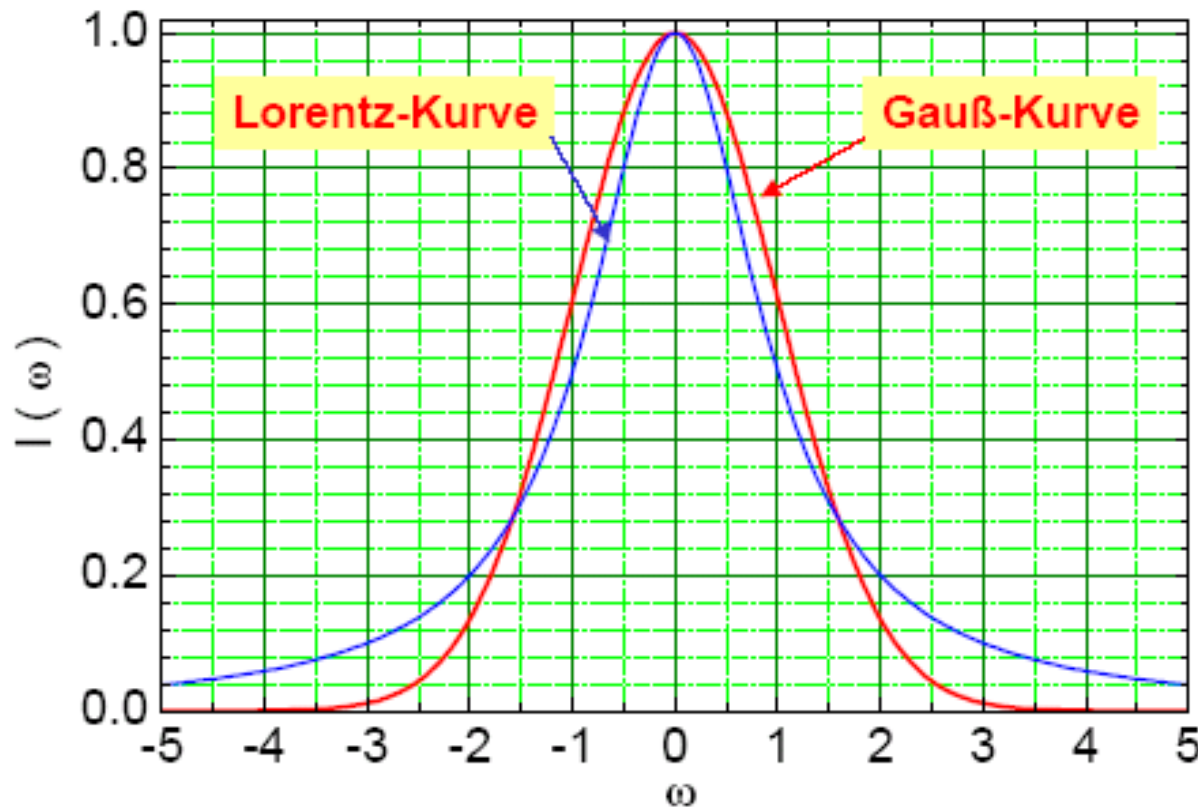
- natural line width: phonon lifetime
Lorentz profile

- instrumental broadening:
Gauss profile



Rayleigh line width

Natural & Real line width of the spectral lines



- Gauss-Profil

$$y = a \cdot \exp \left[- \left(\frac{\omega - \omega_0}{\gamma} \right)^2 \right]$$

- Lorentz-Profil

$$y = \frac{a \cdot \gamma^2}{(\omega - \omega_0)^2 + \gamma^2}$$

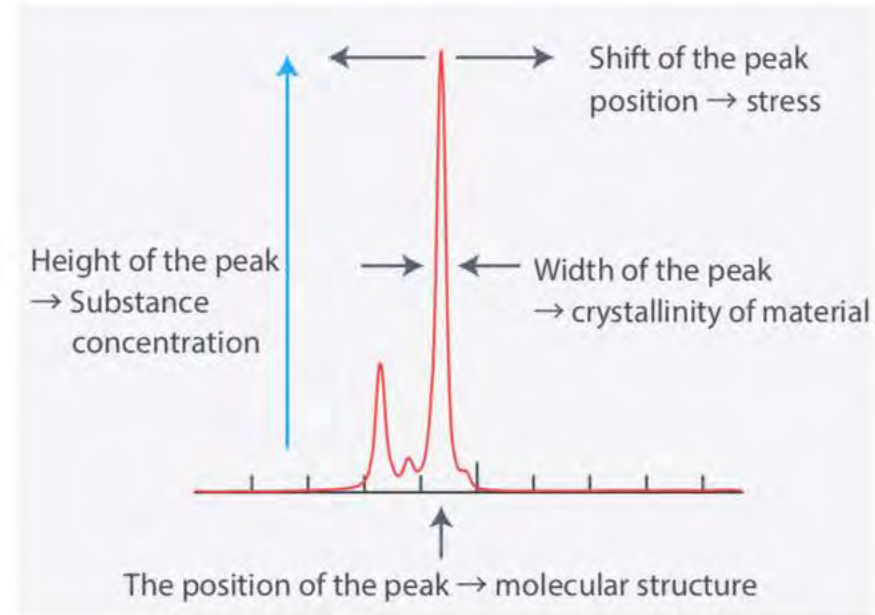
The use of Raman Spectroscopy in Solid State Physics

In solid-state physics, Raman spectroscopy is used to **characterize materials**, and find the **crystallographic orientation or phase** of a sample.

- A solid material can be **identified** by characteristic phonon modes.
- Information on the **population of a phonon mode** is given by the ratio of the Stokes and anti-Stokes intensity of the spontaneous Raman signal.



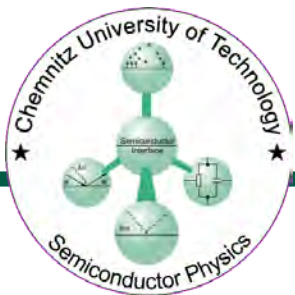
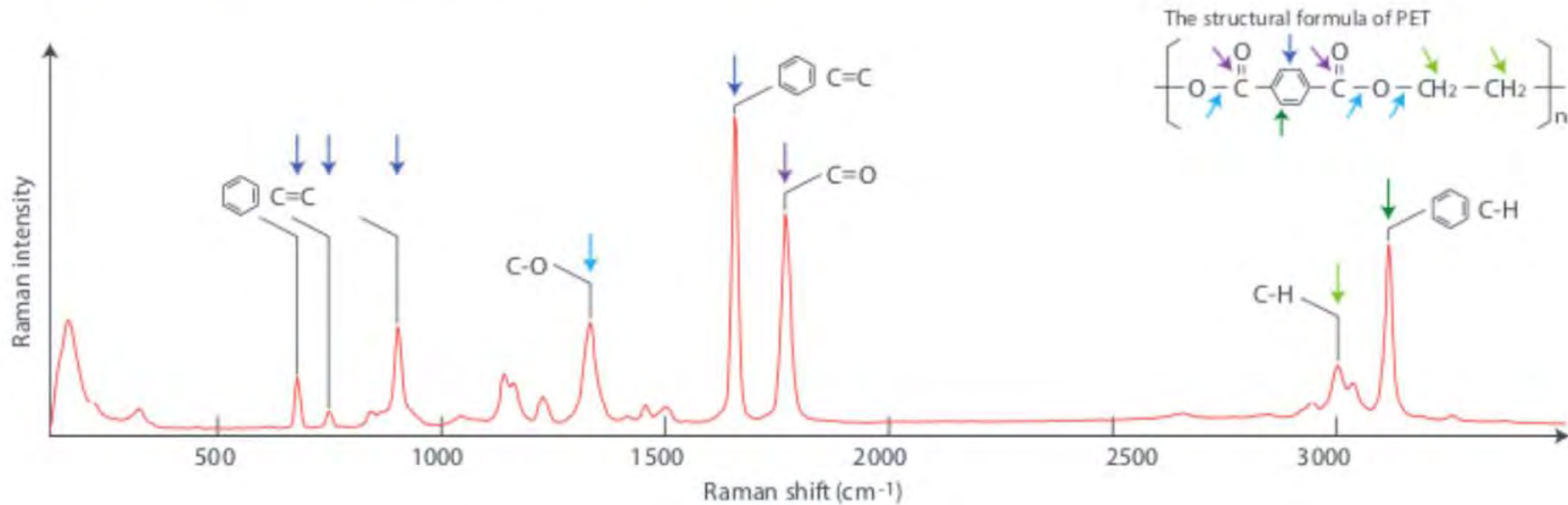
The vibrational information of the molecule can be read from the horizontal axis of the Raman spectrum, and the intensity of activity can be read from the vertical axis (right figure). Specifically, one can identify the type and quality of chemical bonds. Moreover, if it is a crystalline substance, the degree of crystallization and distortion of crystal lattice can be known.

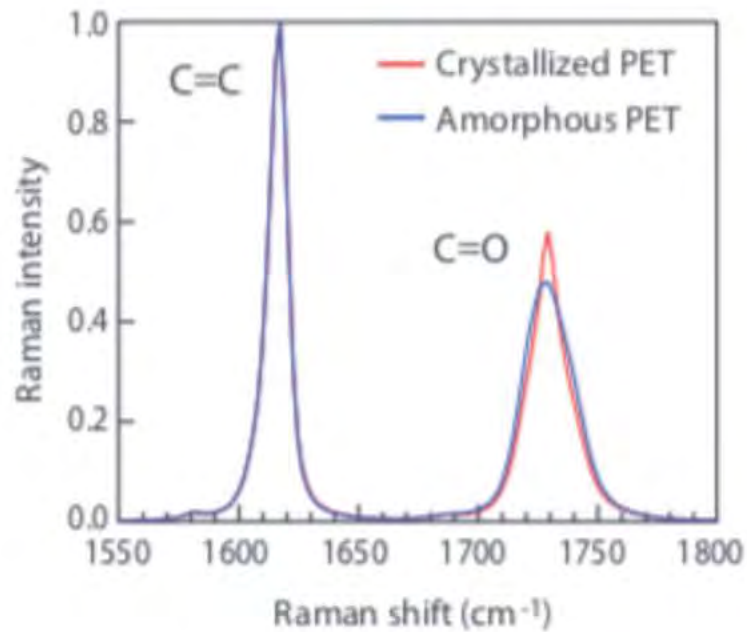


Simple guide for reading Raman peak

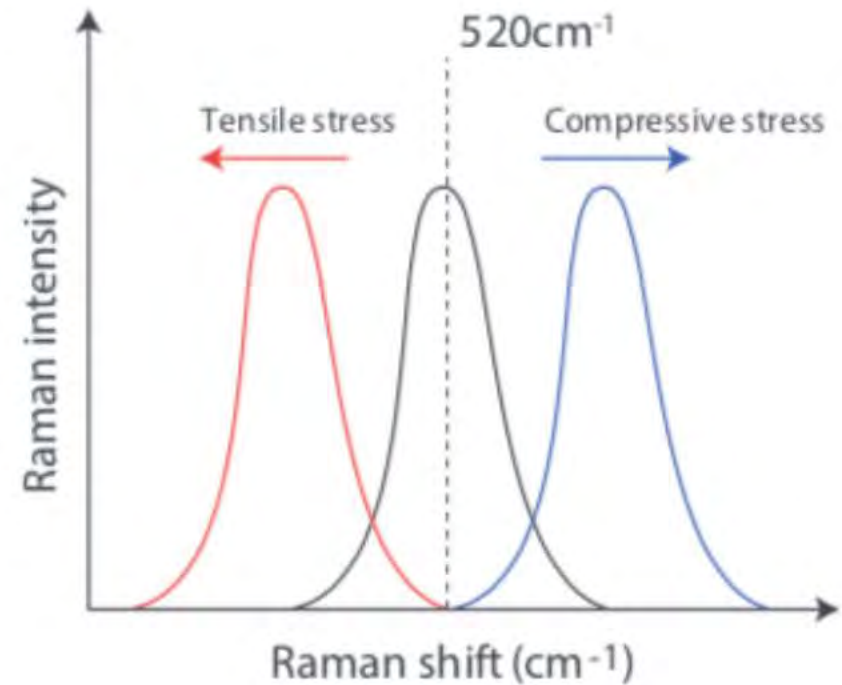


The molecular structure and Raman spectra of PET



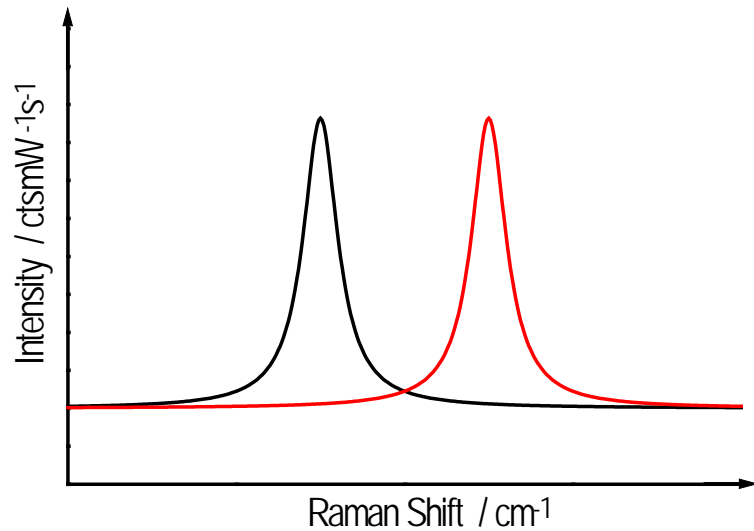


2. Crystalline evaluation

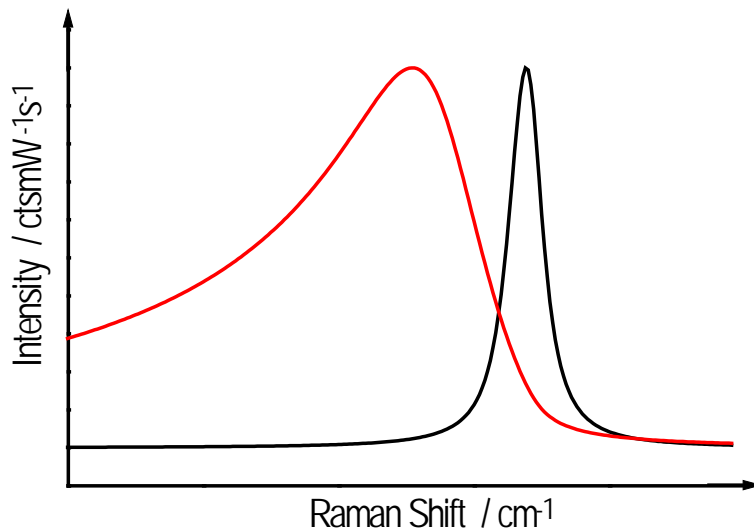


3. Strain analysis

Line shifts & Line widths: influence of various factors



frequency shift by
temperature $\approx 2\text{cm}^{-1}/100^\circ\text{C}$
pressure $\approx 1\text{cm}^{-1}/1\text{kbar}$

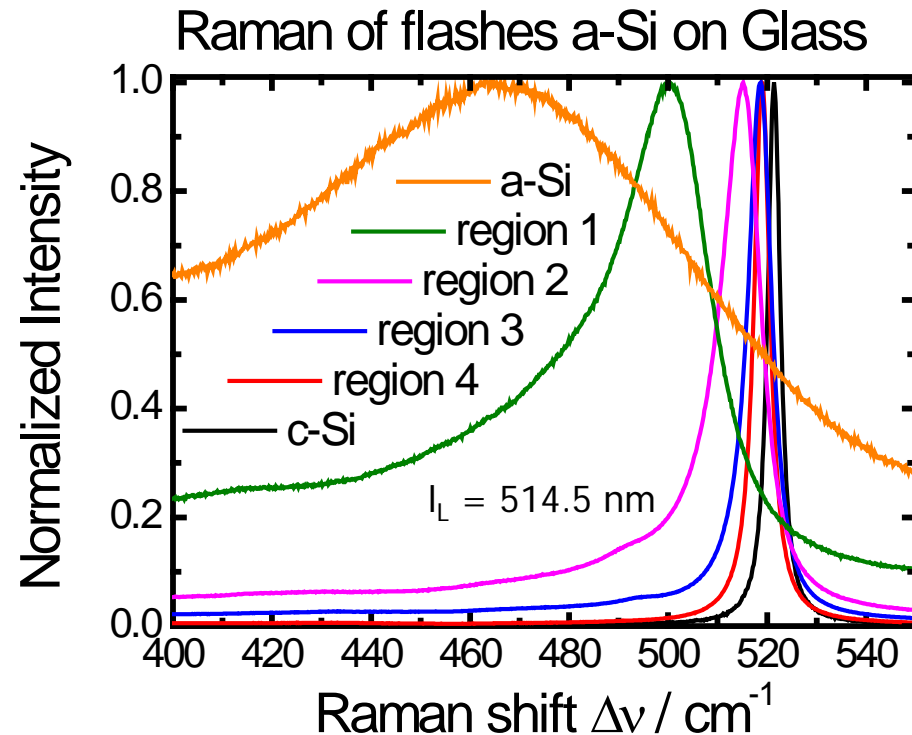
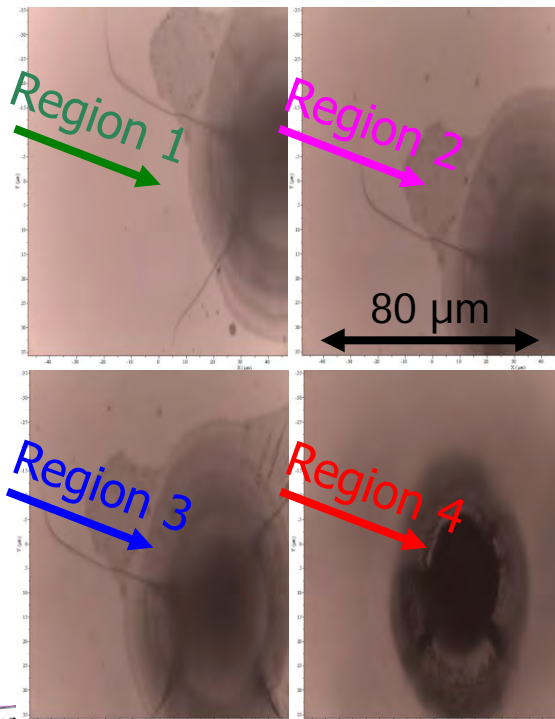


lineshape:
asymmetric broadening and shift
occurs as a result of
lattice disturbance:

Raman Shift / cm^{-1}

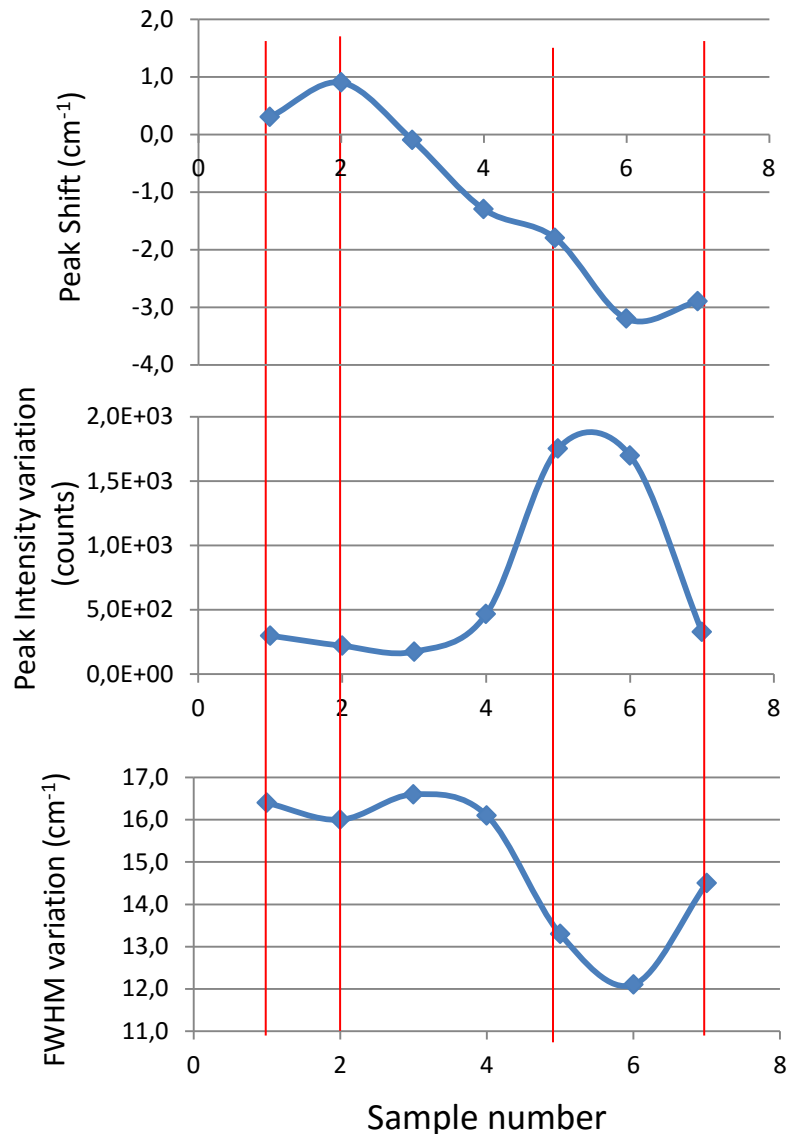
Raman spectra: lineshape change due to defects

Example: flashed amorphous Si layers



lineshape: asymmetric broadening and shift occurs as a result of lattice perturbations.

Raman Data Analysis: an example



Peak Shifts are related to strain during cooling down process (?) Upwards: compressive; downwards: tensile

highest: 2 (compressive) - lowest: 6 (tensile)

Intensity of peaks can be related to concentration of a certain species; higher concentrations result in higher peaks and vice versa (when we are not close to resonance conditions).

highest: 5 & 6 - lowest: 1, 2, 3

FWHM variations are related to crystallinity; to the phonon lifetime so that for the "perfect crystal" lines are typically narrow and their width is determined by the phonon anharmonicity (phonon decay processes). The presence of defects of any kind will shorten the phonon lifetime and, correspondingly, broaden the linewidth.

highest: 1, 2, 3, 4 - lowest: 5&6

Temperature dependence

$$\frac{I_{Anti-Stokes}}{I_{Stokes}} = \frac{n(\nu = 1)}{n(\nu = 0)} = e^{-\frac{h\bar{\nu}_{vib}}{k_B T}}$$

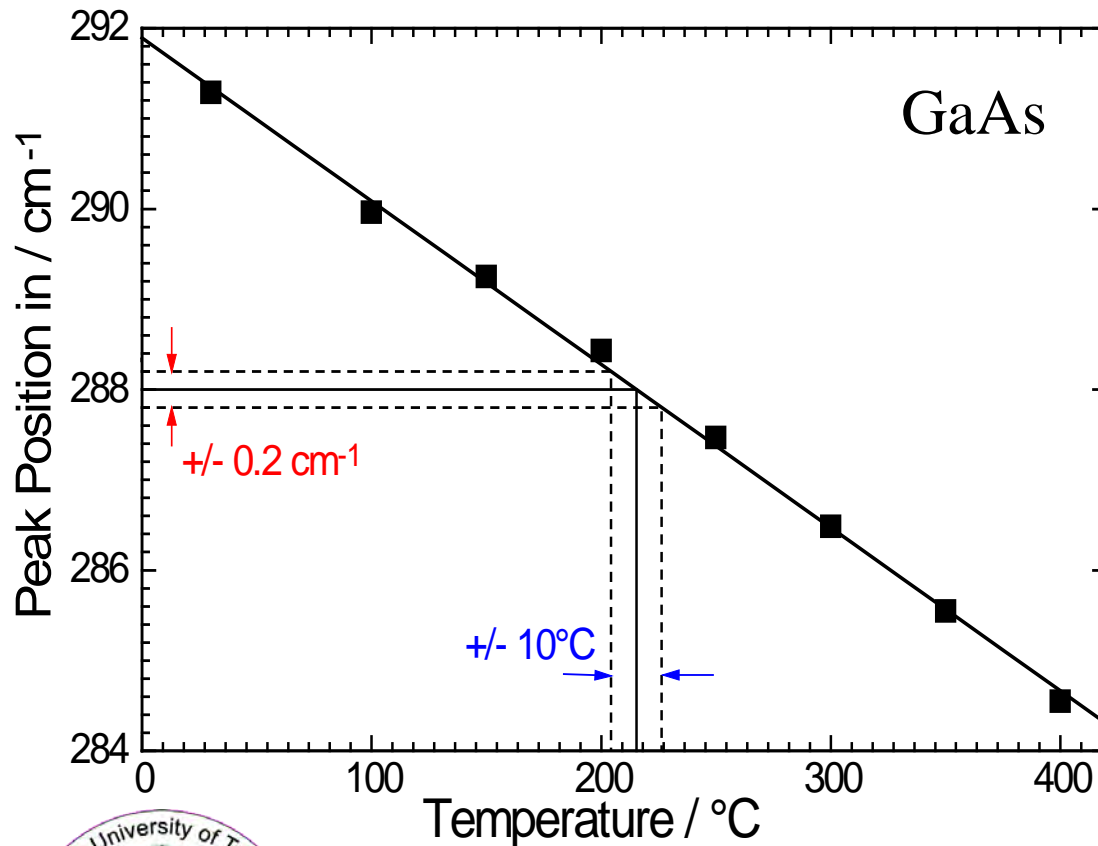
Information on the population of a phonon mode is given by the ratio of the Stokes and anti-Stokes intensity of the spontaneous Raman signal.

Example: $\left. \begin{array}{l} \bar{\nu}_{vib} = 1000 \text{ cm}^{-1} \\ T = 300 \text{ K} \end{array} \right\} \Rightarrow \frac{I_{Anti-Stokes}}{I_{Stokes}} = e^{-5} = 7 \text{ ‰}$




- Temperature determination by means of Raman spectroscopy

Raman spectra: shift with temperature



Using temperature induced shift of **Raman** phonon peak:

	$\text{cm}^{-1}/100^{\circ}\text{C}$
InSb:	2.1
InP:	2.0
GaAs:	1.8
Si:	2.2
ZnSe:	2.4



Several variations of Raman spectroscopy have been developed.
The usual purpose is to enhance the sensitivity, to improve the spatial resolution or to acquire very specific information.

Spontaneous Raman spectroscopy

Hyper Raman

Surface-enhanced Raman spectroscopy (SERS)

Resonance Raman spectroscopy

Surface-enhanced resonance Raman spectroscopy (SERRS)

Angle-resolved Raman spectroscopy

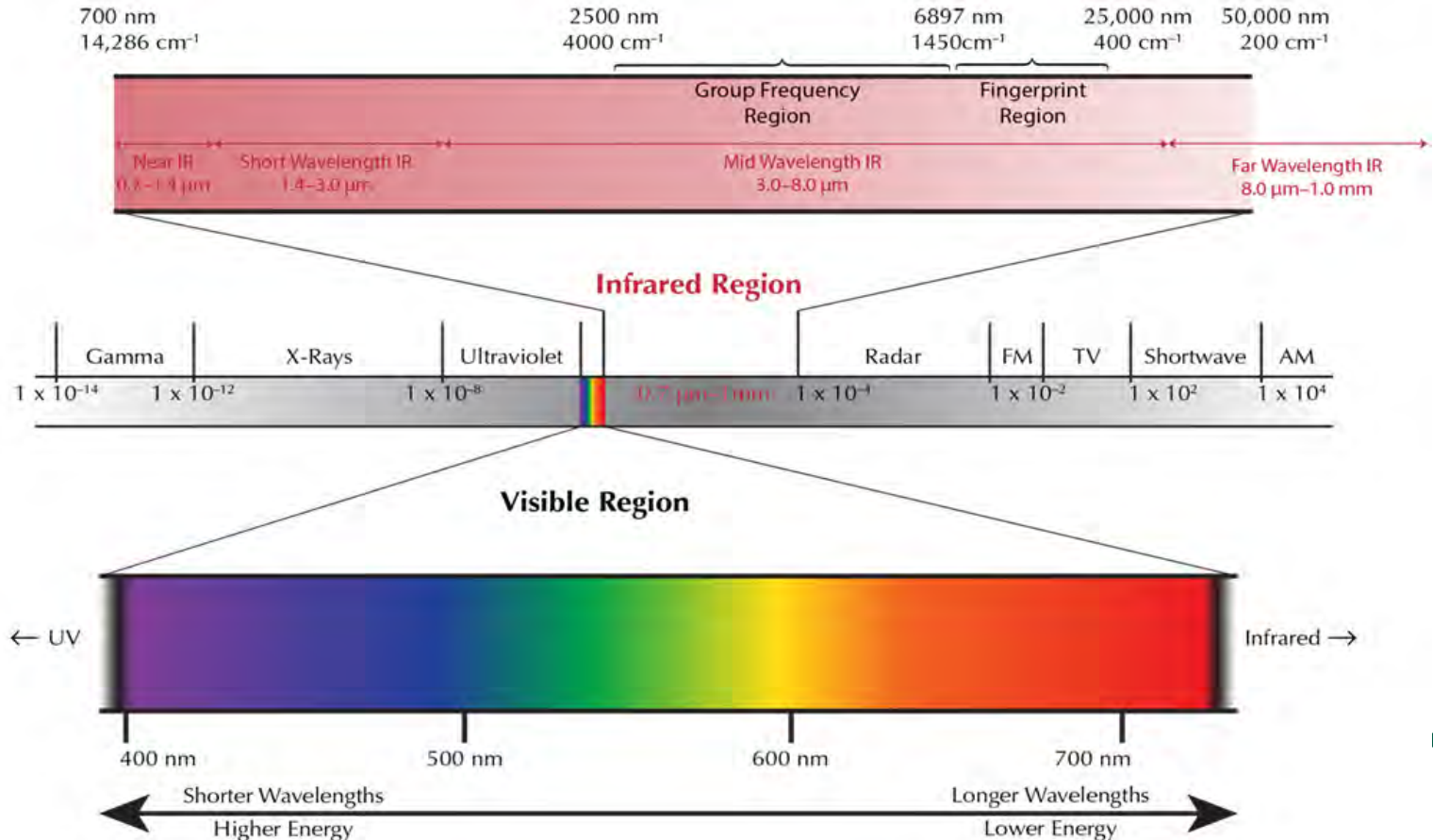
Optical tweezers Raman spectroscopy (OTRS)


Tip-enhanced Raman spectroscopy (TERS)

Etc....



- Infrared spectroscopy involves the interaction of infrared radiation with matter.
- The infrared portion of the electromagnetic spectrum is usually divided into 3 regions: near-, mid- and far- infrared, named for their relation to the visible spectrum.



- 
- ❑ Infrared spectroscopy exploits the fact that **molecules absorb frequencies that are characteristic of their structure.**
 - ❑ These absorptions occur at **resonant frequencies**, i.e. the frequency of the absorbed radiation **matches the vibrational frequency.**
 - ❑ The **resonant frequencies** are associated with the **normal modes** corresponding to the molecular electronic ground state potential energy surface.
 - ❑ The **resonant frequencies** are also related to the **strength of the bond** and the **mass of the atoms** involved.

➤ Thus, the **frequency of the vibrations** are associated with a particular **normal mode** of motion and a **particular bond type.**

In order for a vibrational mode in a sample to be **"IR active"**, it must be associated with **changes in the dipole moment**.

A molecule can vibrate in many ways, and each way is called a *vibrational mode*. Molecules with N number of atoms:




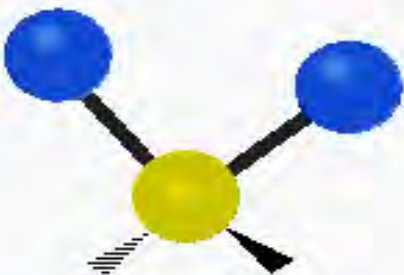


- linear molecules have $3N - 5$ degrees of vibrational modes,
- nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom).

Symmetrical molecules don't absorb in the IR spectrum.

Asymmetrical diatomic molecules absorb in the IR spectrum.

The complexity of the spectra depends on the nr. of bonds and IR vibrational active modes.

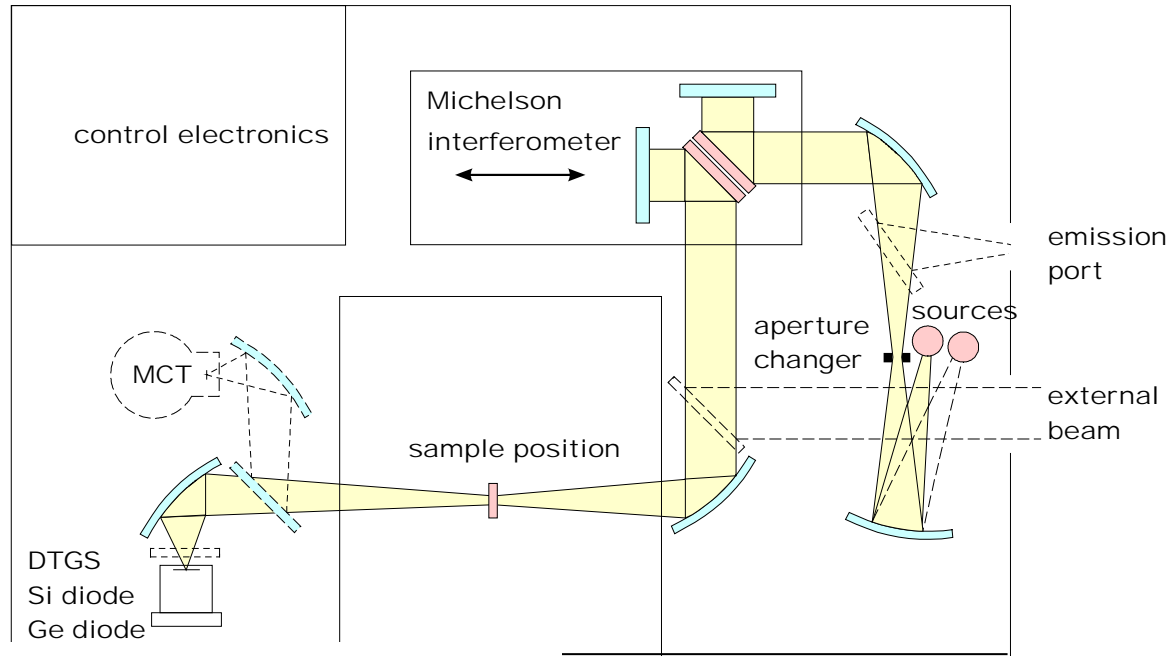


Symmetry Direction	Symmetric	Antisymmetric
Radial	 <p>Symmetric stretching</p>	 <p>Antisymmetric stretching</p>
Latitudinal	 <p>Scissoring</p>	 <p>Rocking</p>
Longitudinal	 <p>Wagging</p>	 <p>Twisting</p>

Applications (just for reference, not restrictive)

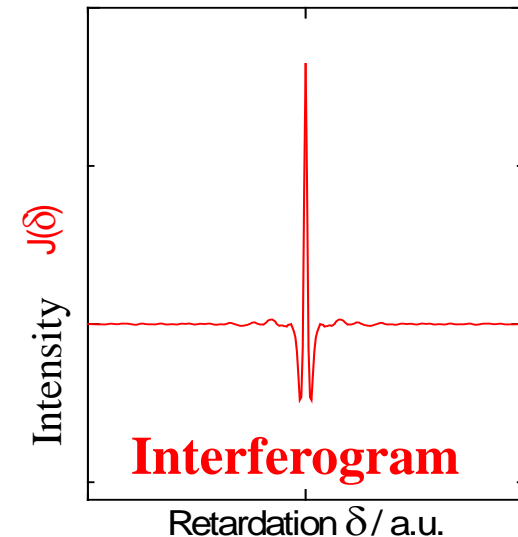
- The higher-energy **near-IR**, approximately $14000\text{--}4000\text{ cm}^{-1}$ ($0.8\text{--}2.5\text{ }\mu\text{m}$ wavelength) can excite **harmonic vibrations**.
- The **mid-infrared**, approximately $4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) may be used to study the **fundamental vibrations** and associated **rotational-vibrational structure**.
- The **far-infrared**, approximately $400\text{--}10\text{ cm}^{-1}$ ($25\text{--}1000\text{ }\mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for **rotational spectroscopy**.

IR Spectroscopy Measurement Technique



Michelson Interferometer:

- Beam splitter
- Moving mirror

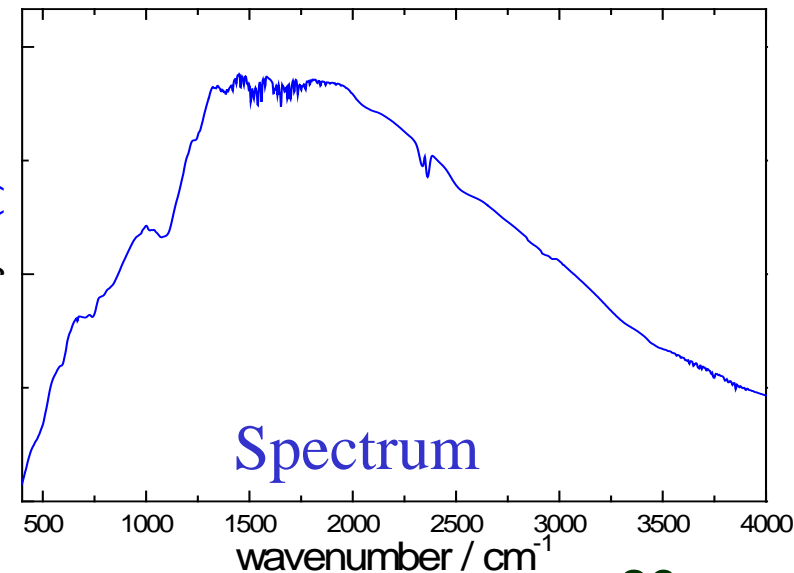


FOURIER TRANSFORMATION:

$$I(\bar{\nu}) = \int_{-\infty}^{\infty} I(\delta) \exp(-2\pi i \bar{\nu} \delta) d\delta$$

$$J(\delta) = \int_{-\infty}^{\infty} I(\bar{\nu}) \exp(2\pi i \bar{\nu} \delta) d\bar{\nu}$$

Intensity $I(\bar{\nu})$



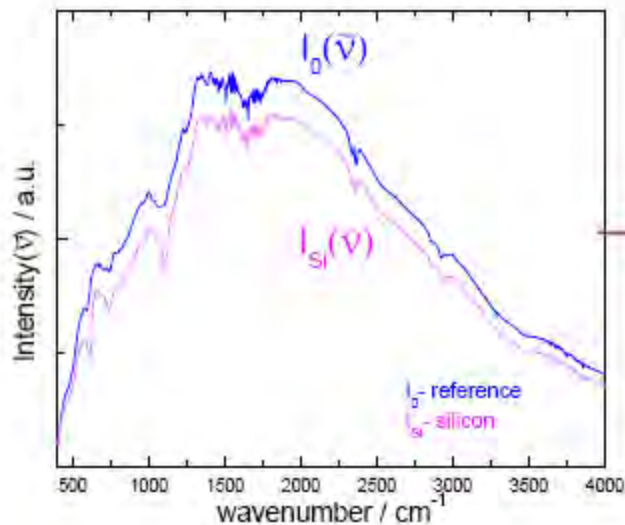


- ✓ The infrared spectrometer consists principally of a source, detector, beam splitter, interferometer and a user interface for Fourier transformation.
- ✓ The detection mechanism of the spectrometer is based on the Michelson principle which records the intensity with respect to the optical path.
- ✓ a beam splitter reflects part of the projected energy to a fixed mirror and another part to a moving mirror.
- ✓ A time sampling of the path length difference is done.
- ✓ a detector records the intensity of energy modulated to produce an interferogram.

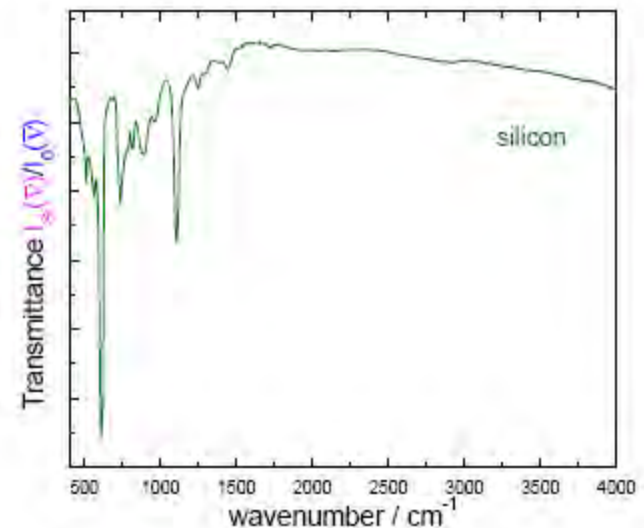
Measurement procedure

- Spectra of reference $I_0(\nu)$ and sample $I_{Si}(\nu)$ are measured (single channel spectra)
- The spectrum of the sample $I_{Si}(\nu)/I_0(\nu)$ is the divided spectrum : sample/reference

→ identification of different vibrations in sample

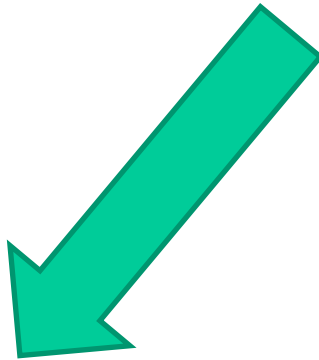


Single channel spectra



Resulting transmittance spectrum

2 primary techniques



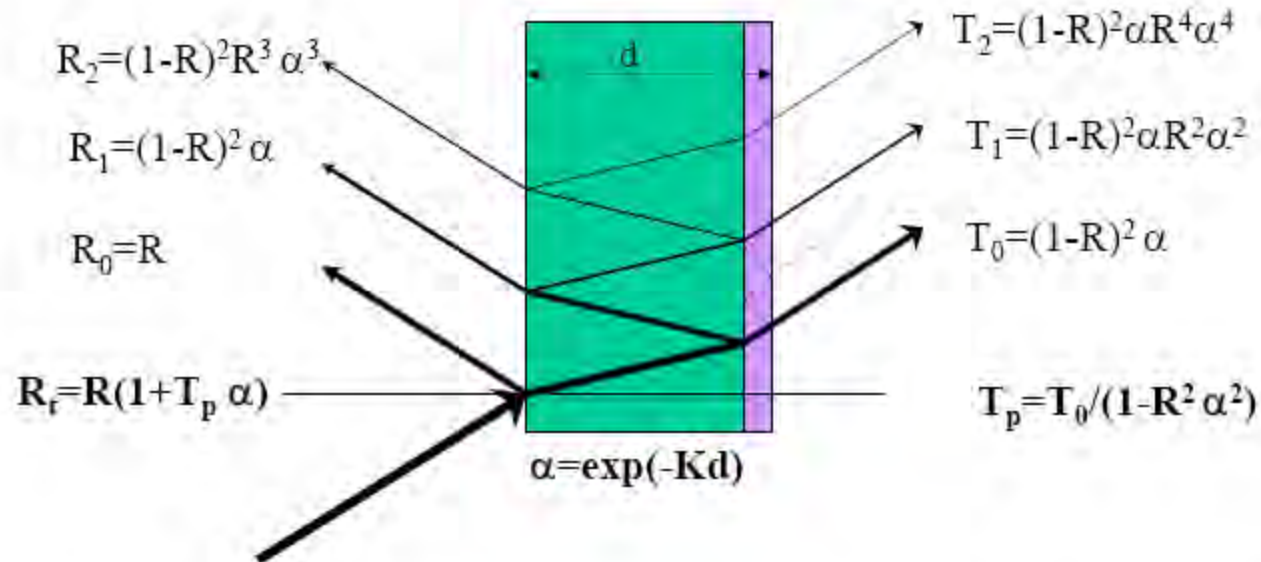
transmission

reflection

- specular reflection
- infrared reflection-absorption spectroscopy (IRAS)
- attenuated total reflection (ATR)
- Multiple Internal reflection (MIR)

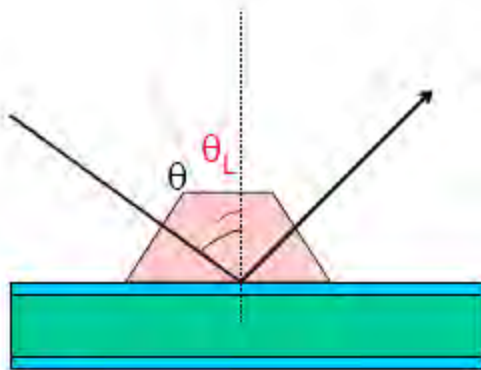
Absorption

Reflection and Transmission IR spectroscopy



- If the thickness of the sample or the film has the same order of magnitude with the wavelength of IR radiation, interference can occur

Attenuated Total Reflection (ATR)



$$n_{\text{prism}} > n_{\text{layer}}$$

$$\sin \theta_L = n_{\text{layer}} / n_{\text{prism}}$$

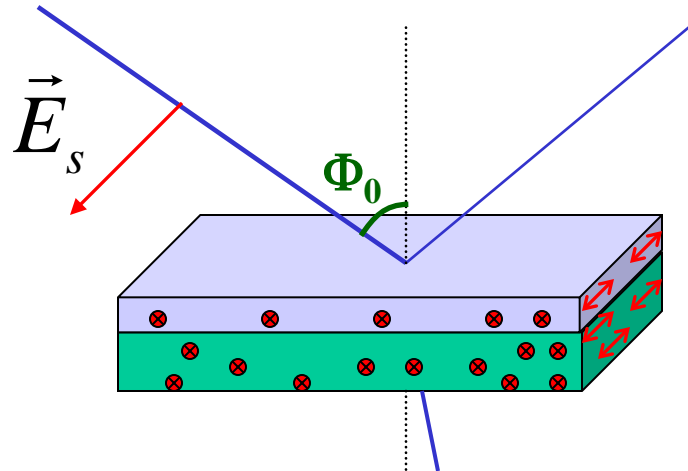
θ_L -critical reflection angle

- **ATR** is a single reflection technique used for the study of surfaces
- *Intimate optical contact* is necessary (press of the prism)
- Very *slight penetration* occurs (few nm)
- The evanescent wave totally reflected in prism may be absorbed by surface species

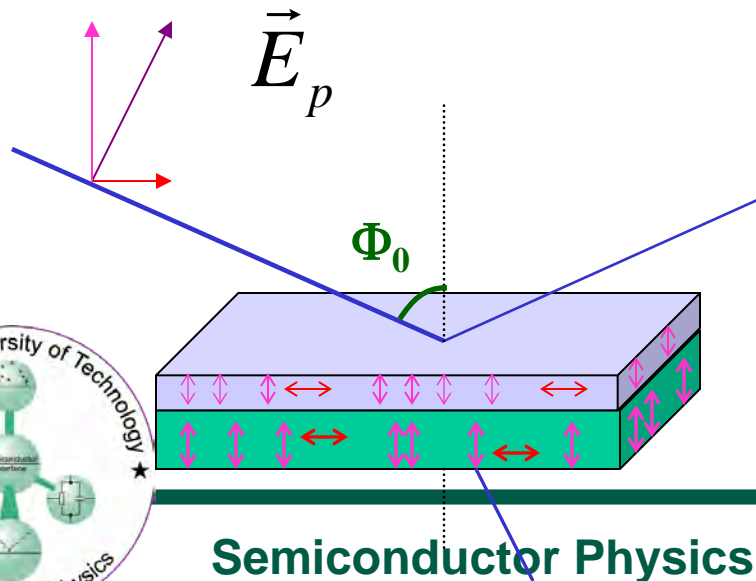
Multiple Internal Reflection (MIR)



In MIR geometry the signal from surface is enhanced, because the light interacts with the surface for *several times*



- s – Polarisation:
Electric field vector perpendicular
(senkrecht) to incidence plane

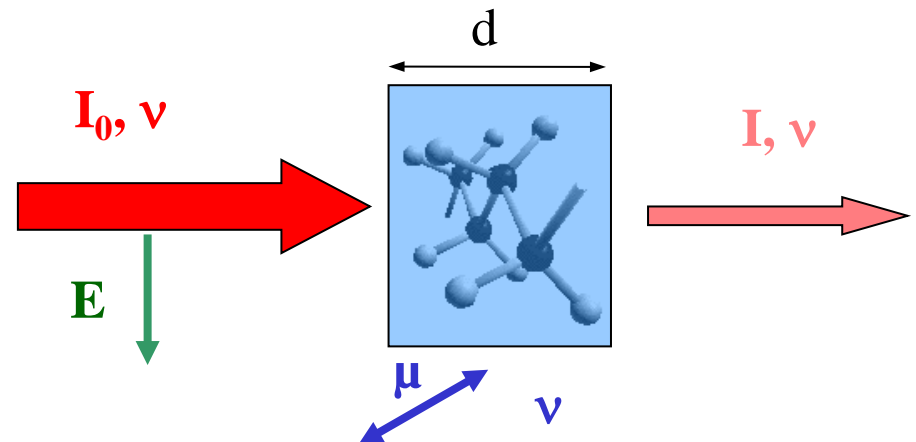


- p – Polarisation:
electric field vector parallel to
the incidence plane

Infrared Absorption

Factors which influence the absorption of IR radiation in a layer :

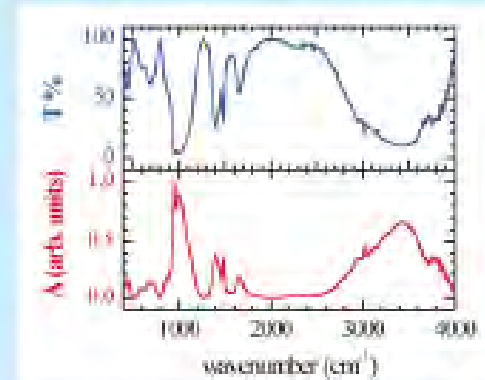
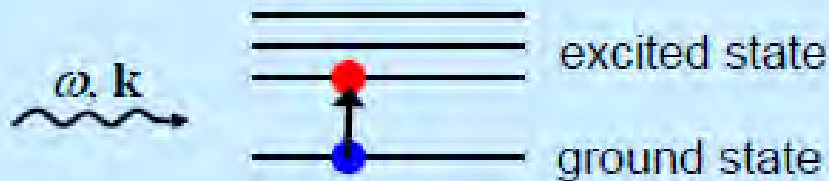
- amplitude of electric field , E
- Modulus of the (dynamic) electric dipole of the vibration, μ
- relative orientation of E and μ
- optical thickness $n \cdot d$



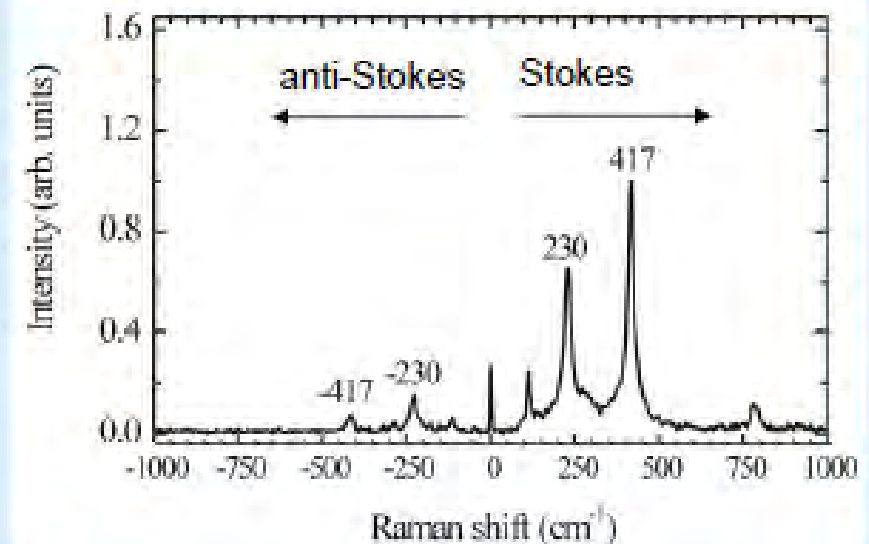
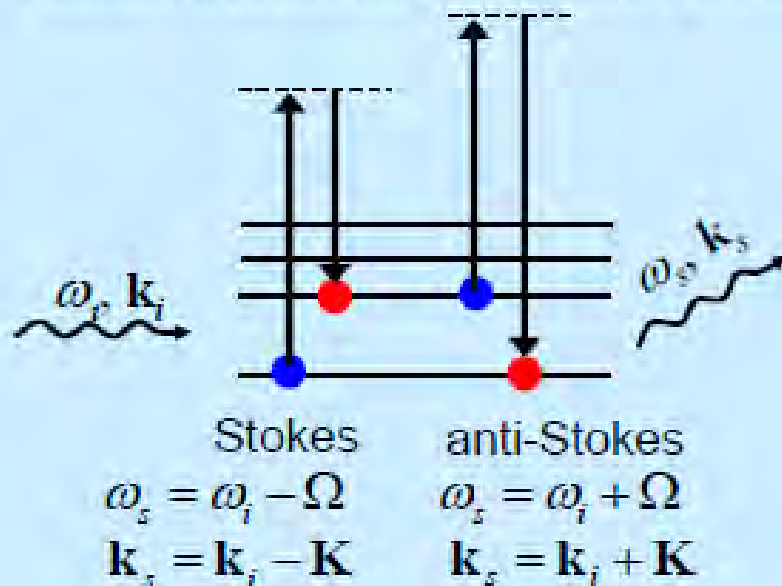


electromagnetic wave as a probe radiation (**photon – opt. phonon interaction**):

Infrared absorption: $\hbar\omega_{\text{photon}} = E_{ES}^{(\text{phonon})} - E_{GS}^{(\text{phonon})}$



Raman scattering \equiv inelastic light scattering from optical phonons

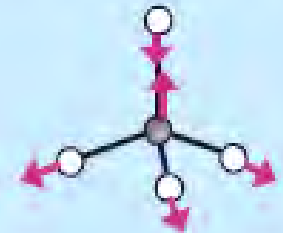


IR activity: induced dipole moment due to the change in the atomic positions

$$\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$$

$$\boldsymbol{\mu}(Q) = \boldsymbol{\mu}_0 + \sum \frac{\partial \boldsymbol{\mu}}{\partial Q_k} Q_k + \dots \quad Q_k - \text{configurational coordinate}$$

\nwarrow
 $\neq 0$, IR activity



IR: “asymmetrical”, “one-directional”

Raman activity: induced dipole moment due to deformation of the e⁻ shell

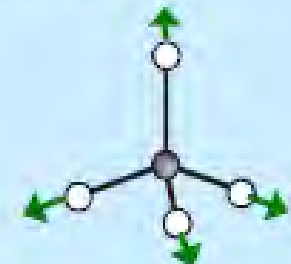
Polarizability tensor: $\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix}$

$$\alpha(Q) = \alpha_0 + \sum \frac{\partial \alpha}{\partial Q_k} Q_k + \dots$$

\nwarrow
 $\neq 0$, Raman activity

$$\mathbf{P} = \alpha \cdot \mathbf{E}$$

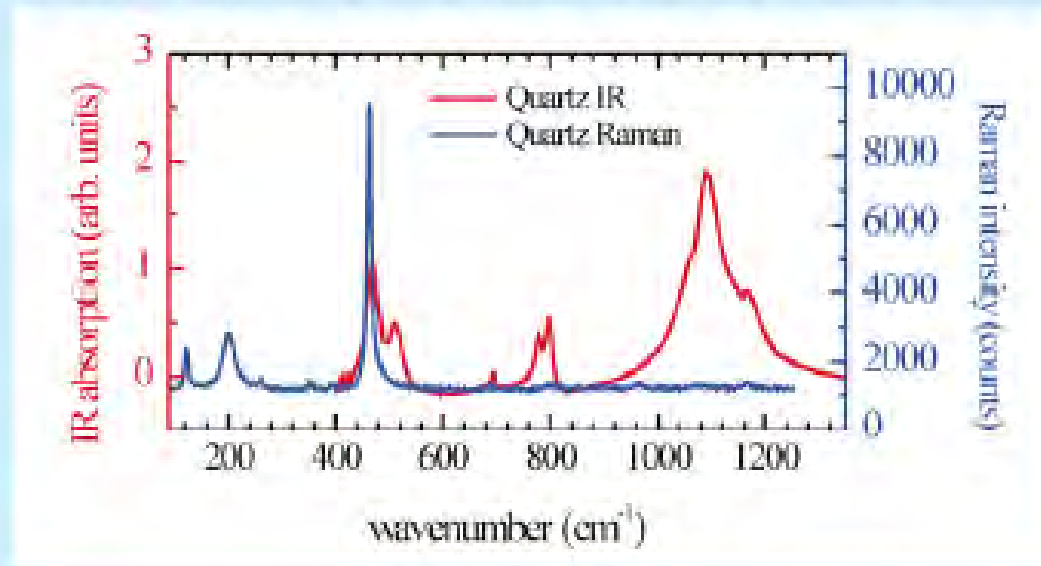
\uparrow
induced polarization
(dipole moment per unit cell)



Raman: “symmetrical”, “two-directional”

N.B.! simultaneous IR and Raman activity – only in non-centrosymmetric structures

- IR and Raman spectra are different for the same crystal



different interaction phenomena \Rightarrow different selection rules !



Next lecture

Atomic Structure & Chemical Bonding

