

An Introduction to optical Raman scattering

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6.1 Scattering

In addition to being absorbed and emitted by atoms and molecules, photons may also be *scattered* (approx. 1 in 10^7 in a transparent medium). This is not due to defects or dust but a molecular effect which provides another way to study energy levels.

This scattering may be:

Elastic and leave the molecule in the same state (**Rayleigh Scattering**) or

Inelastic and leave the molecule in a *different* quantum state (**Raman Scattering**)



Nobel Prize 1904
(physics)



Nobel Prize 1930
(physics)

6.2 Rayleigh Scattering

Lord Rayleigh calculated that a dipole scatterer $\ll \lambda$ scatters with an intensity:

no. of scatterers ————— polarizability

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

n.b., $I \propto \frac{1}{\lambda^4}$

5 times more effective
for 400nm than 600nm
Hence the sky is blue!
(and sunsets red)

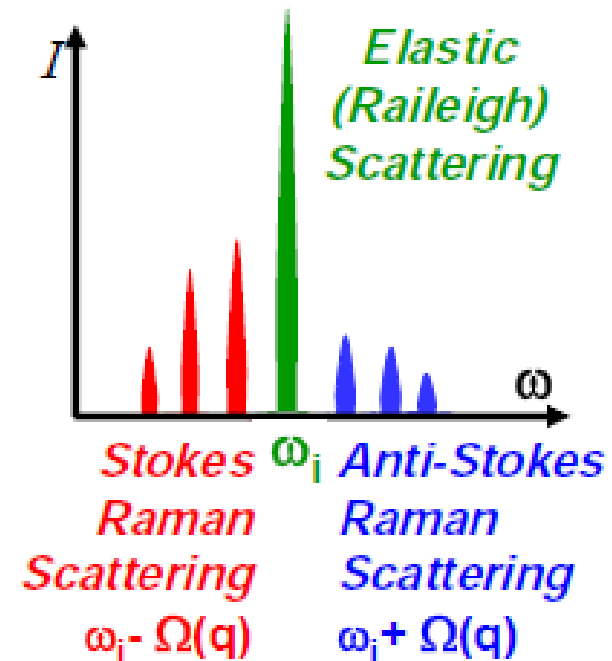
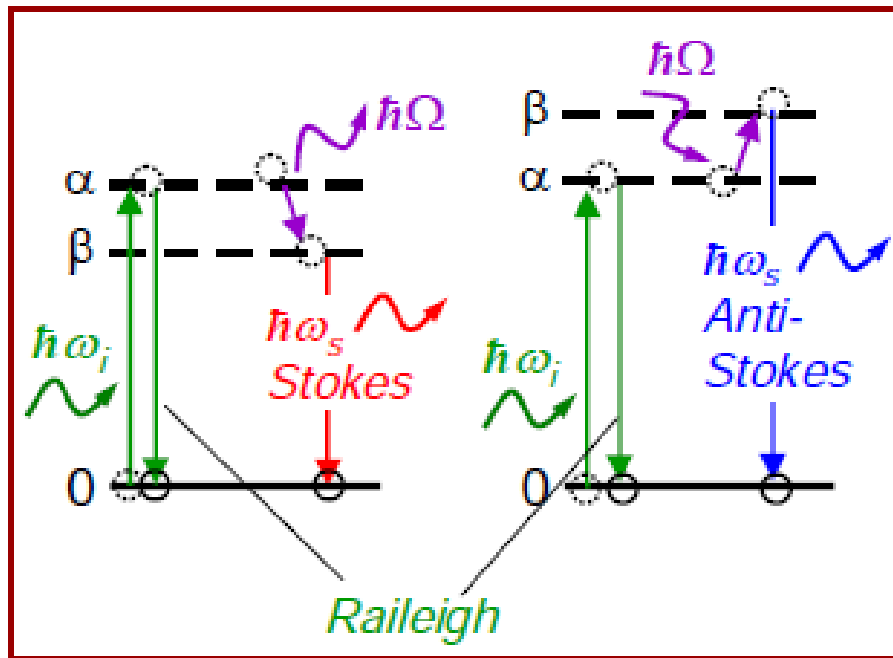
wavelength

distance

scatterer - observer

Inelastic light scattering mediated by the *electronic polarizability* of the medium

- a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or *Raileigh scattering*)
- but a small amount of light is scattered at different wavelengths (inelastic, or *Raman scattering*)



Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations²

What is Raman shift ?

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$$\text{Raman Shift} = \hbar\omega_s - \hbar\omega_i = \pm\hbar\Omega$$

Hg lamp

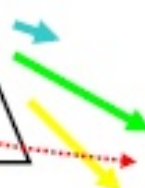
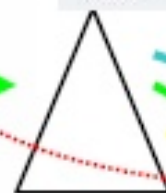
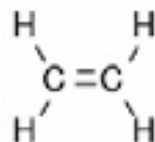
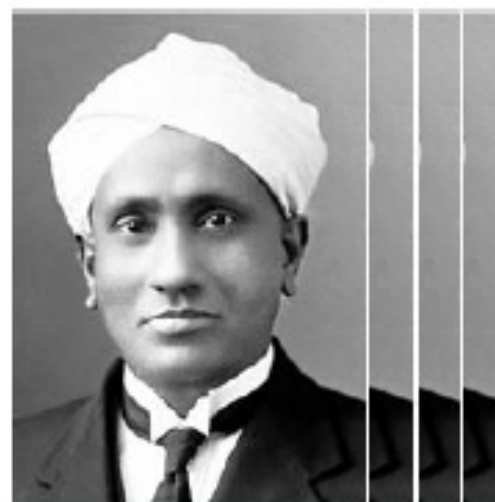


Photo plate

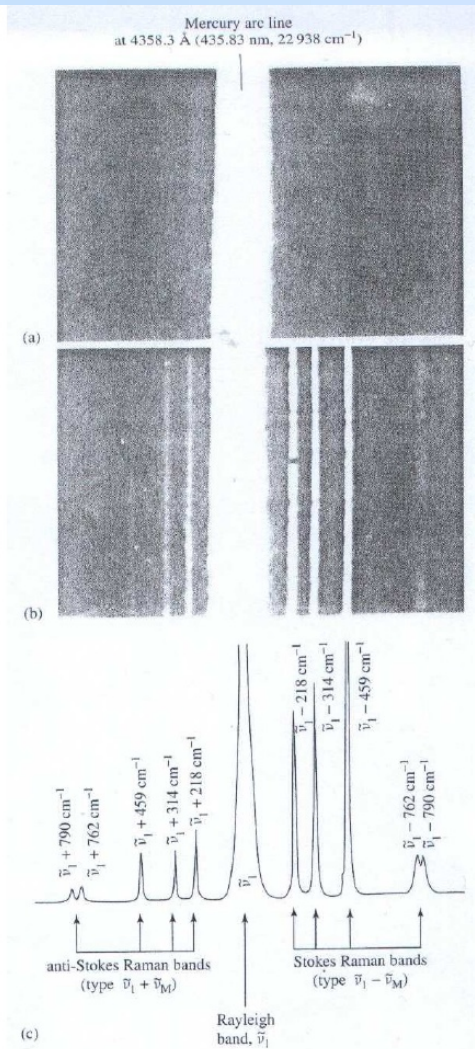
- Stretching: a change in the length of a bond, such as C-H or C-C
- Bending: a change in the angle between two bonds, such as the HCH angle in a methylene group
- Rocking: a change in angle between a group of atoms, such as a methylene group and the rest of the molecule.
- Wagging: a change in angle between the plane of a group of atoms, such as a methylene group and a plane through the rest of the molecule,
- Twisting: a change in the angle between the planes of two groups of atoms, such as a change in the angle between the two methylene groups.



Sir
Chandrasekhara
Venkata Raman

India

Molecular vibrations:



3 Presentation of Raman Spectra

The use of the angular frequency $\omega = 2\pi\nu = 2\pi\frac{c_0}{\lambda}$ is very convenient for theoretical treatments but uncommon in the representation of spectra. Spectra are usually displayed on a wavenumber scale ($\tilde{\nu}_M$ unit cm^{-1}) which is related to ω_M by $\tilde{\nu}_M = \omega_M/2\pi c_0$. Figures 3a) and b) show facsimiles of photographically recorded spectra of CCl_4 reported by Raman and Krishnan [6] using a mercury arc as excitation source (435.83 nm, $\tilde{\nu}_1 = 22938 cm^{-1}$) and Figure 3c) shows the spectrum excited by an Ar^+ laser (487.99 nm, $\tilde{\nu}_1 = 20487 cm^{-1}$) and recorded directly. A Raman spectrum of CCl_4 presented according to the recommendations of the IUPAC is shown in Figure 4.

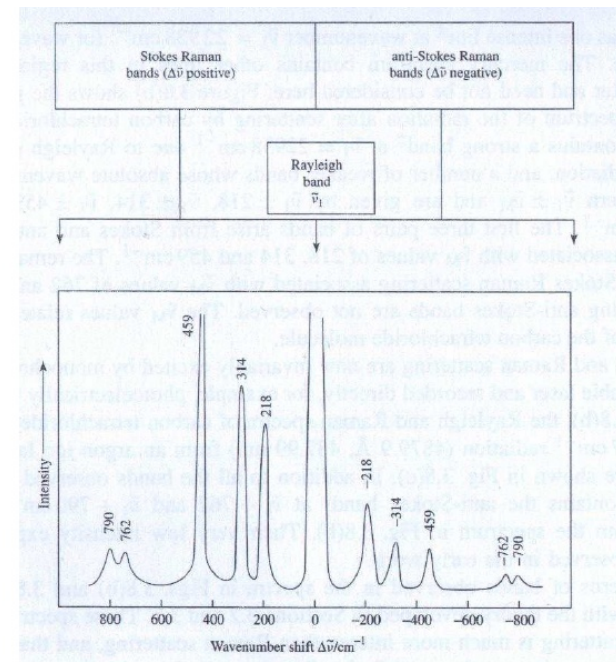


Figure 4: Presentation of the Raman spectrum of CCl_4 according to IUPAC recommendation

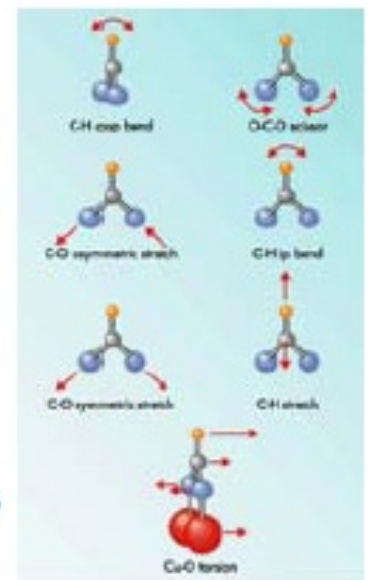
Figure 3: (a) Spectrum of a mercury arc in the region of 4358.3 Å (435.83 nm, $\tilde{\nu}_1 = 22938 cm^{-1}$). (b) Rayleigh and Raman Spectra of CCl_4 excited by mercury arc radiation at $\tilde{\nu}_1 = 22938 cm^{-1}$. (c) Rayleigh and Raman spectra of CCl_4 excited by an Ar^+ laser $\tilde{\nu}_1 = 20487 cm^{-1}$ (487.99 nm). Adopted from [1]

For example, 1 cm^{-1} implies 1.23984×10^{-4} eV and 8065.54 cm^{-1} implies 1 eV.[1]

Wavelength in nm = 10,000,000/ cm^{-1} so 20,000 cm^{-1} => 500 nm

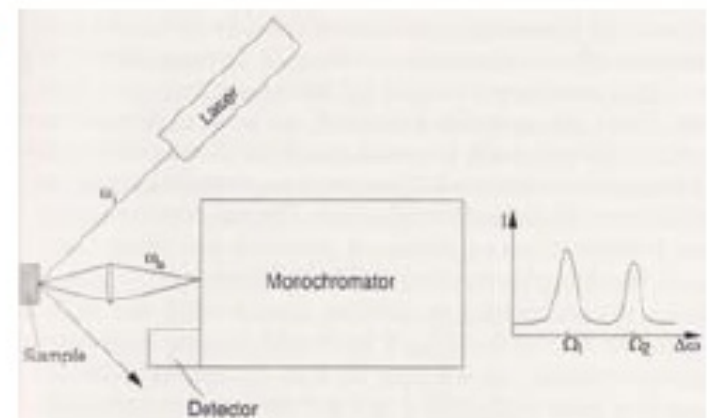
Excitations

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



Experimental setups

1. **Excitation source: Lasers or Synchrotron radiation**
2. **Sample: optical cryostats, magnets, pressure cells, etc**
3. **Polarizers for selection rules analysis**
4. **Spectrometers**
5. **Detectors**



Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain *Selection rules*:

1. Energy conservation:

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$\hbar\Omega$ Excitation energy

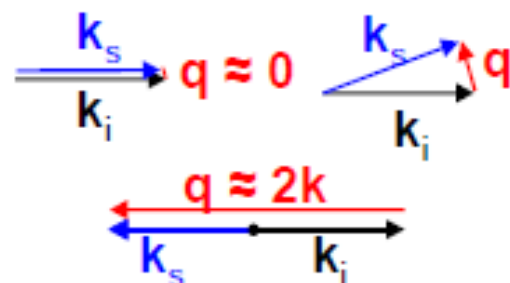
2. Momentum conservation in crystals:

$$\mathbf{k}_i = \mathbf{k}_s \pm \mathbf{q} \Rightarrow 0 \leq |\mathbf{q}| \leq 2|\mathbf{k}| \Rightarrow 0 \leq |q| \leq \frac{4\pi n}{\lambda_i}$$

$$\lambda_i \sim 5000 \text{ \AA}, \quad a_0 \sim 4\text{-}5 \text{ \AA} \Rightarrow \lambda_{\text{phonon}} \gg a_0$$

Phonons

\Rightarrow only small wavevector (close to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals



3. Selection rules determined by crystal symmetry and by symmetry of excitations

Phonons

- Quantum mechanics: energy levels of the harmonic oscillator are quantized
- Similarly the energy levels of lattice vibrations are quantized.
- The quantum of vibration is called a *phonon*
(in analogy with the photon - the quantum of the electromagnetic wave)

Allowed energy levels of the harmonic oscillator: $E = (n + 1/2)\hbar\omega$

where n is the quantum number

A normal vibration mode of frequency ω is given by $\mathbf{u} = \mathbf{A}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$

mode is occupied by n *phonons* of energy $\hbar\omega$; momentum $\mathbf{p} = \hbar\mathbf{q}$

Number of phonons is given by :
(T – temperature)

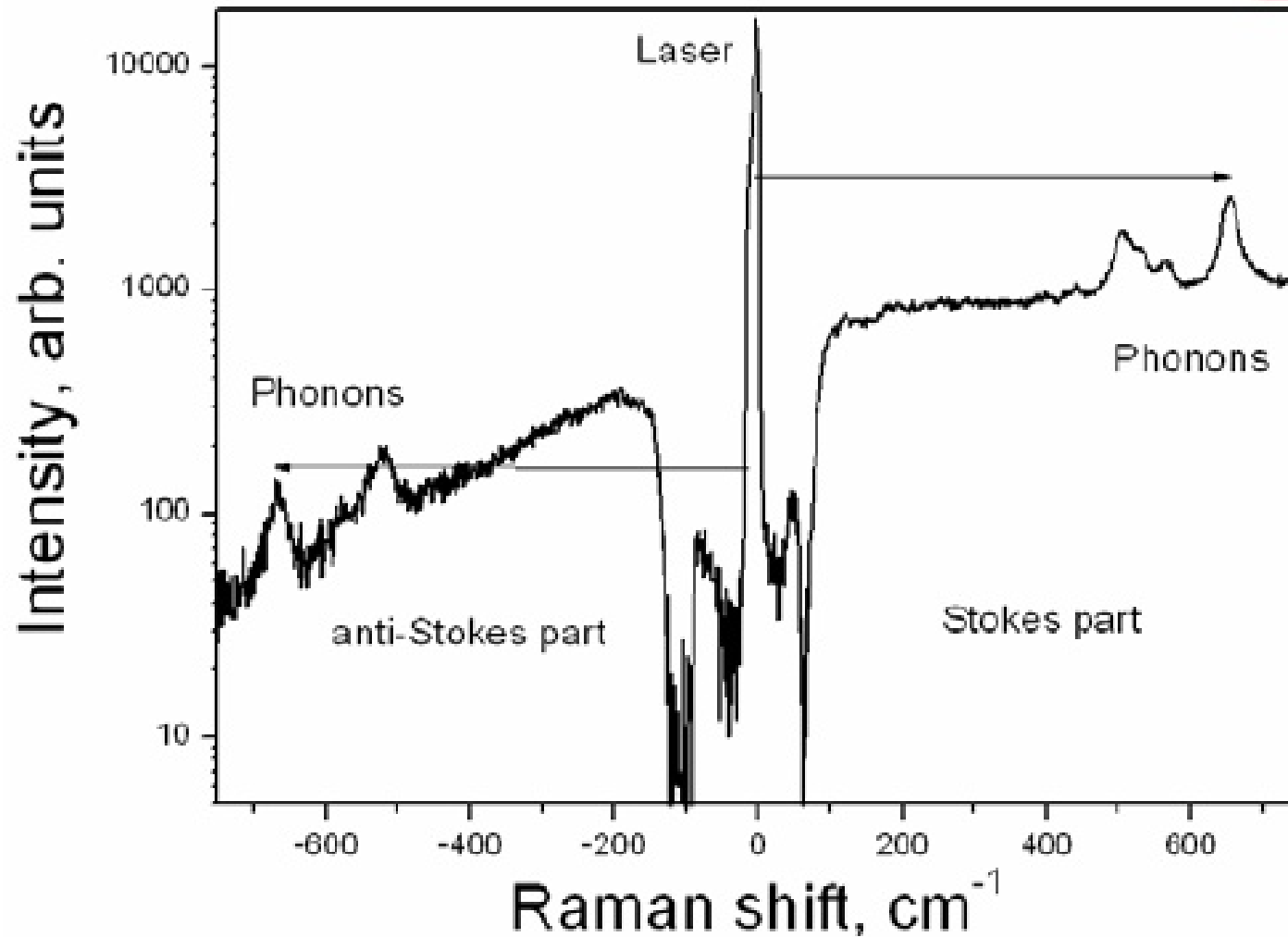
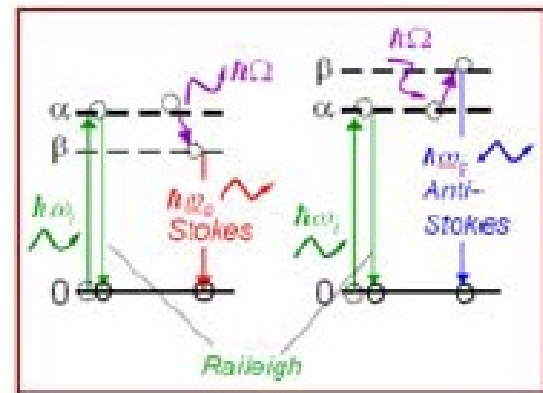
$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

The total vibrational energy of the crystal is the sum of the energies of the individual phonons:

(p denotes particular
phonon branch)

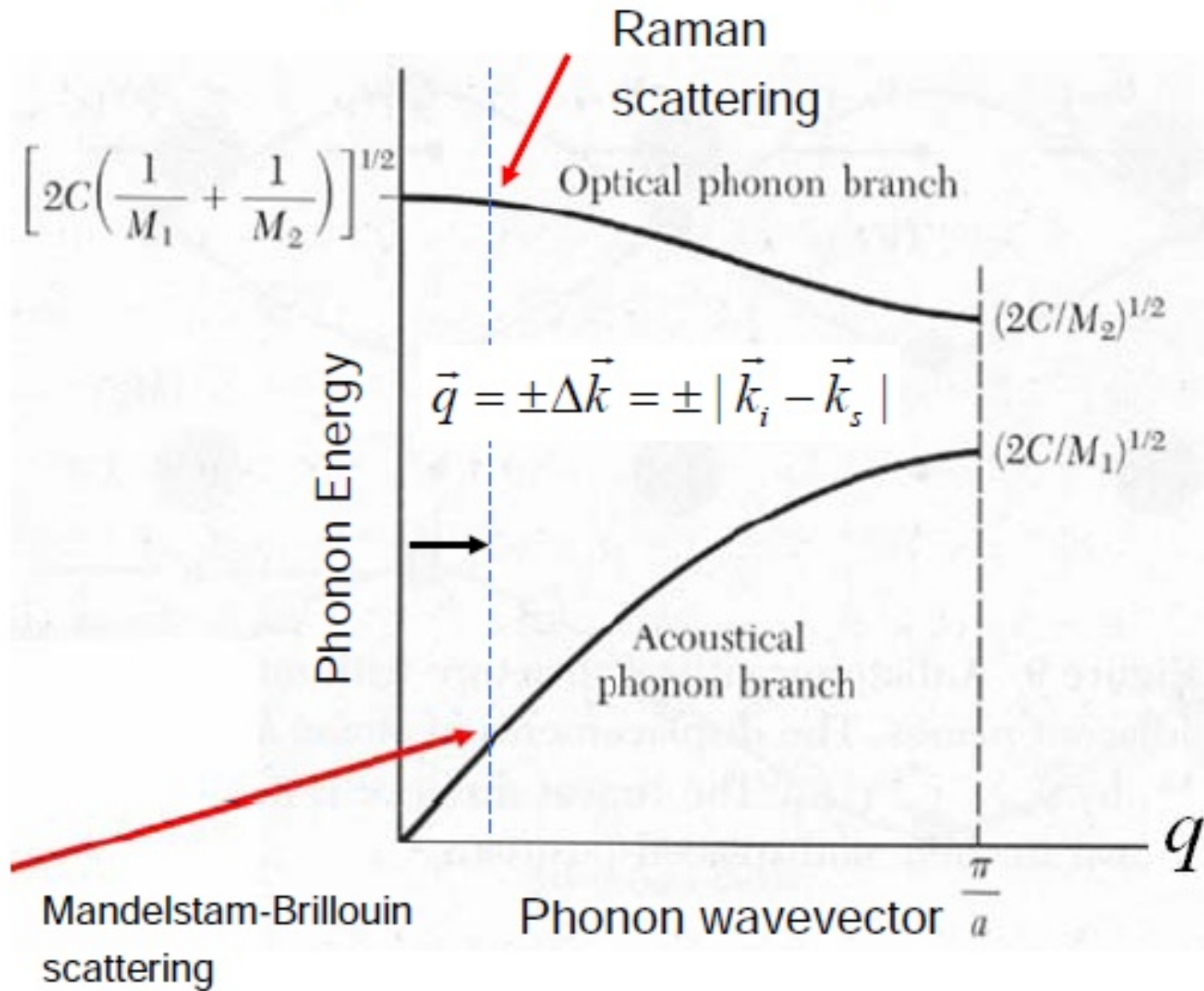
$$E = \sum_{\mathbf{qp}} E_{\mathbf{qp}} = \sum_{\mathbf{qp}} (n_{\mathbf{qp}} + 1/2)\hbar\omega_p(\mathbf{q})$$

Raman scattering: how does it look like?

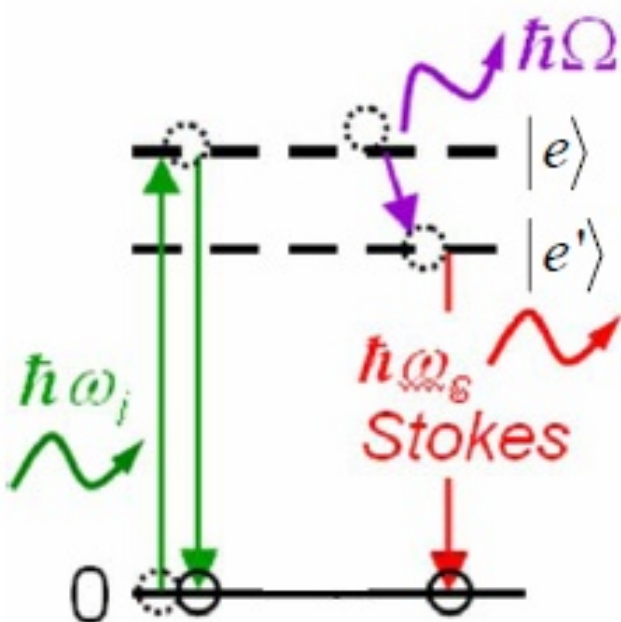


Mandelstam-Brillouin vs. Raman scattering

Examples of Phonons in Crystals



Quantum Theory of Raman Scattering



$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega$$

$$\vec{k}_i = \vec{k}_s \pm \vec{q}$$

- the electronic transition from the ground state $|0\rangle$ to an excited state $|e\rangle$: creation of an electron-hole pair due to the absorption of a photon with the energy $\hbar\omega_i$.
- the electron-lattice interaction, i.e. the electronic transition from $|e\rangle$ to $|e'\rangle$ under creation or annihilation of a phonon with $\hbar\Omega$.
- the transition from $|e'\rangle$ to the ground state $|0\rangle$: recombination of the electron-hole pair under emission of a photon $\hbar\omega_s$.

$$\chi_{\alpha,\beta}(\omega_i, \omega_s) = \frac{e^2}{m_0^2 \cdot \omega_s^2 \cdot V} \sum_{e,e'} \frac{\langle 0|p_\alpha|e'\rangle \langle e'|H_{E-L}|e\rangle \langle e|p_\beta|0\rangle}{(E_{e'} - \hbar\omega_s)(E_e - \hbar\omega_i)}$$

Here m_0 is the electron mass and V the scattering volume, p_α and p_β are vector components of the dipole operators of the scattered and incident light, and H_{E-L} is the electron-phonon interaction Hamiltonian. E_e and $E_{e'}$ are the energies of the excited electronic states.

Selection rules for Raman Scattering by phonons

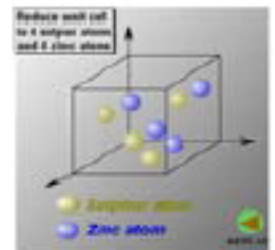
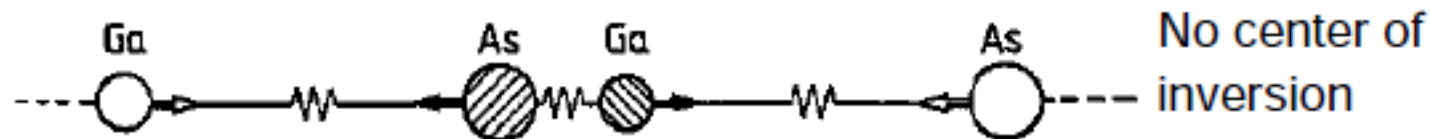
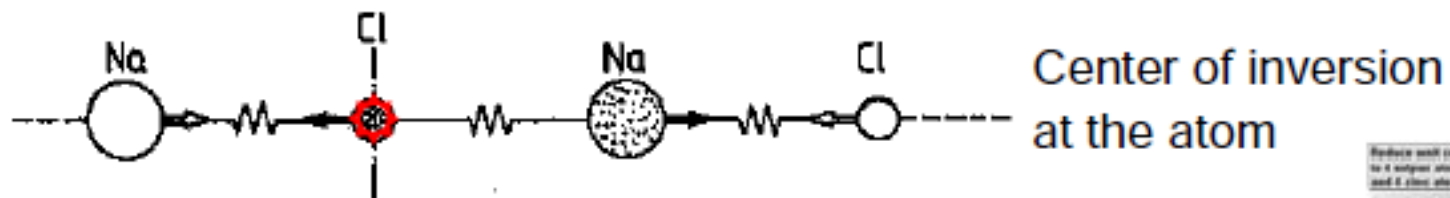
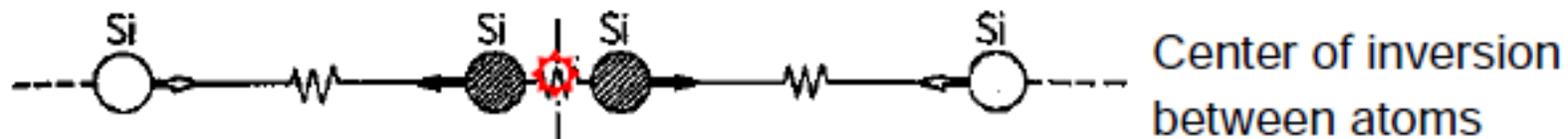
$$\bar{Q} = \bar{Q}_0 \cdot e^{i(\vec{k} \cdot \vec{r} - \omega_0 t)}$$

$$\hat{I} \cdot (\bar{Q}) = -\bar{Q} \quad \text{"odd"}$$

$$\hat{I} \cdot (\bar{Q}) = \bar{Q} \quad \text{"even"}$$

A_{1g} B_{2g} Symmetry of Raman-active modes, "g" – gerade (*de.*) = even

A_{2u} F_u Symmetry of IR-active modes, "u" – ungerade (*de.*) = odd



Phonon symmetry for different crystal lattices: The dashed circles are the diatomic base of an elementary cell, open circles are atoms of neighbouring cells. The dash-dotted vertical lines mark the centre of inversion. (a) Si (O_h^7 -structure) has a g-mode (even symmetry), which is Raman-active. (b) NaCl (O_h^5 -structure) has a u-mode (odd symmetry), which is IR-active. (c) GaAs (T_d -structure) shows both Raman and IR-activity

Induced dipole $\mathbf{p} = \alpha \mathbf{E}$; polarizability tensor α dependent on displacements Q

RAMAN SETUP

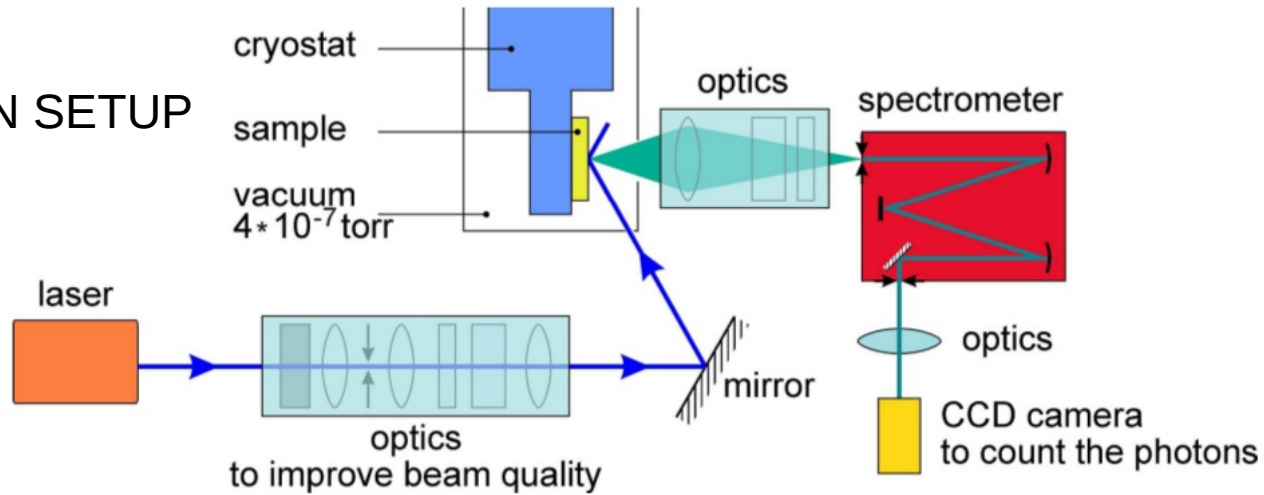


Figure 7: Typical experimental set-up for Raman spectroscopy in solids (schematic).

LASERS

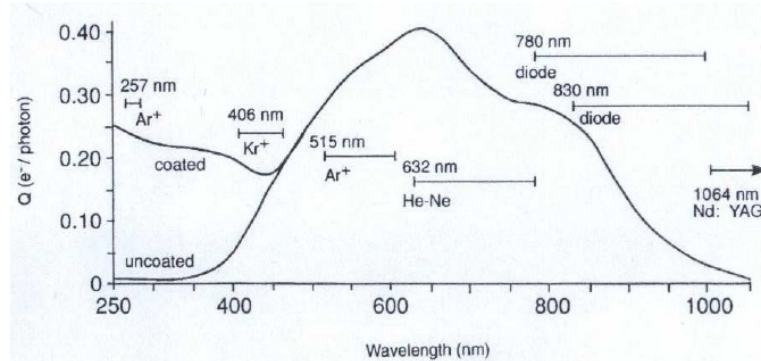
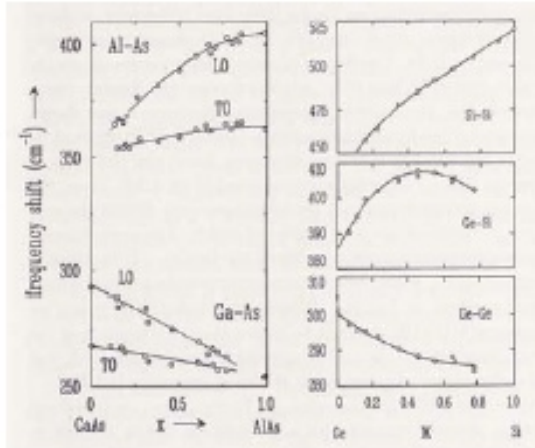


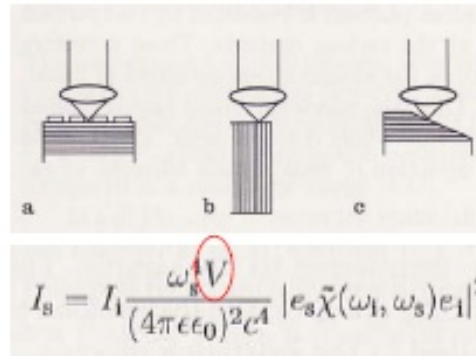
Figure 18: Wavelengths covered by a Raman range of $0 - 3000 \text{ cm}^{-1}$ for several common laser wavelengths. Additionally shown are typical quantum efficiencies of silicon-based CCD detectors. The left end of the bar is the relevant laser wavelength and zero Raman shift. Adopted from [10]

Composition analysis in microstructures



Multi-mode phonon behaviour in mixed crystals. Two-mode phonon behaviour in Al_xGa_{1-x}As: Ga-As and Al-As TO and LO modes (a) three-mode phonon behaviour in Si_xGe_{1-x}: Si-Si, Si-Ge, and Ge-Ge mode (b)

Micro-Raman scattering

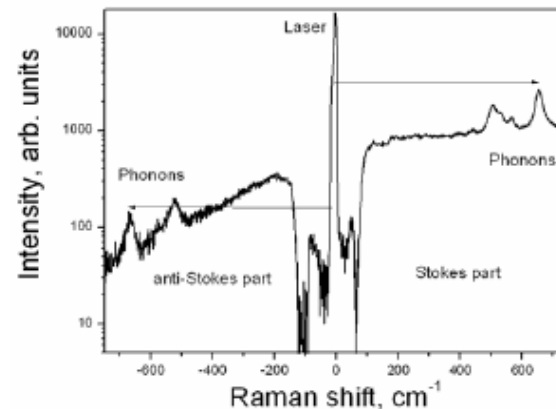


Possible realisations of micro-Raman spectroscopy from heterostructures: a locally resolved analysis of structured surfaces, b scan on a cleaved side-face, c scan on surface after bevel etching

MICRO-RAMAN

Raman thermometer

$$I_s = I_i \frac{\omega_s^4 V}{(4\pi\epsilon\epsilon_0)^2 c^4} |e_s \tilde{\chi}(\omega_i, \omega_s) e_i|^2$$



Number of phonons is given by :
(T – temperature)

$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

Classical formula is not complete!

You need to take Planck's statistics for phonons into account to calculate the scattering intensity

HW:

What is St/aSt ratio ???

Stokes ~ n + 1

anti - Stokes ~ n

Stokes Anstistokes ratio

Atomic displacement and Raman / IR-activity of optical phonons in crystals with the center of inversion

Phonons in Ge, Si, Diamond are Raman active

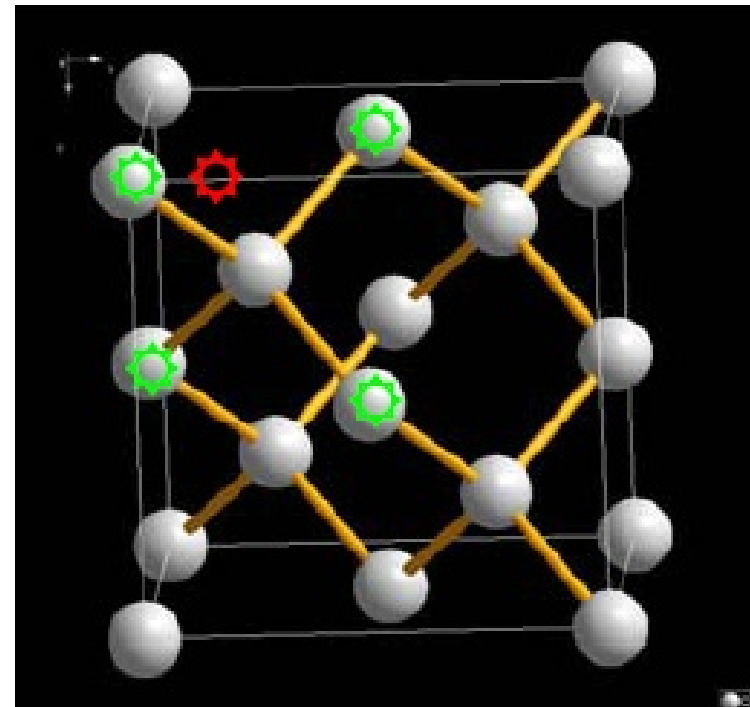
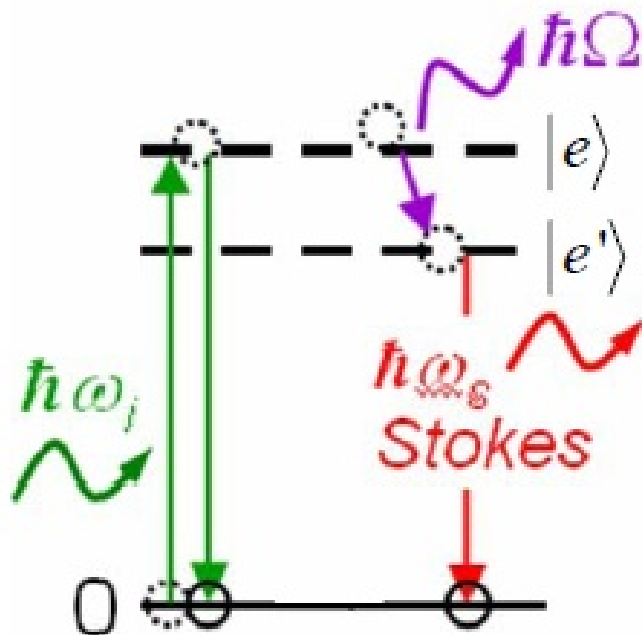
$$\chi_{\alpha,\beta}(\omega_i, \omega_s) = \frac{e^2}{m_0^2 \cdot \omega_s^2 \cdot V} \sum_{e,e'} \frac{\langle 0 | p_\alpha | e' \rangle \langle e' | H_{E-L} | e \rangle \langle e | p_\beta | 0 \rangle}{(E_{e'} - \hbar\omega_s)(E_e - \hbar\omega_i)}$$

$$\vec{Q} = \vec{Q}_0 \cdot e^{i(\vec{k} \cdot \vec{r} - \omega_0 t)}$$

$$\vec{E} = \vec{E}_0 \cdot e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\hat{I}^- \cdot (\vec{Q}) = \vec{Q}$$

$$\hat{I}^- \cdot (\vec{E}) = -\vec{E}$$



Multiple-order Raman scattering in crystalline and amorphous silicon

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(Received 5 January 1993; revised manuscript received 26 April 1993)

Raman-scattering measurements have been performed on *c*-Si and *a*-Si over a wide range of frequencies, including Stokes and anti-Stokes sides, and up to fourth order. All the features are accounted for by using the same physical parameters in both phases. In particular, it is shown that multiple-order scattering processes are not negligible, but rather of the same order of magnitude as first-order processes. In amorphous materials, light-scattering excess, spurious background, Boson-peak or hot-luminescence processes, which have been recently put forward, turn out to be mainly caused by high-order Raman-scattering processes.

Test case:
Raman
spectra of
crystalline Si,
first and
second order
contributions

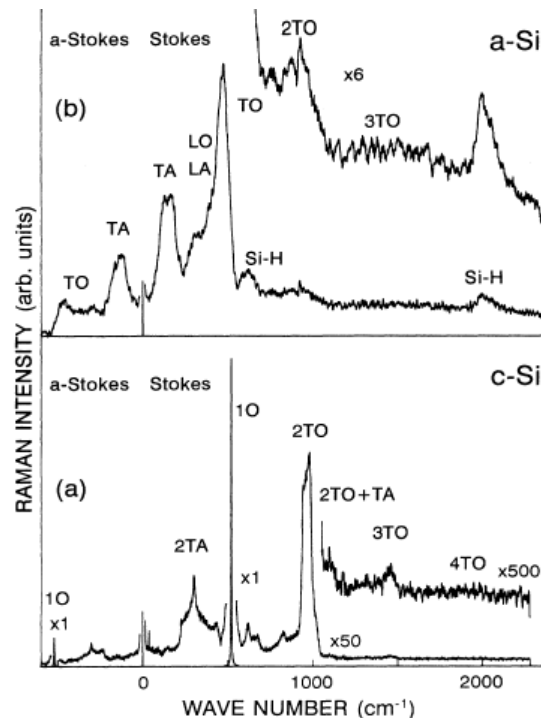


FIG. 1. Experimental Stokes and anti-Stokes Raman spectra of (a) (111) crystalline silicon and (b) hydrogenated amorphous silicon, obtained with the 488 nm exciting line at room temperature.

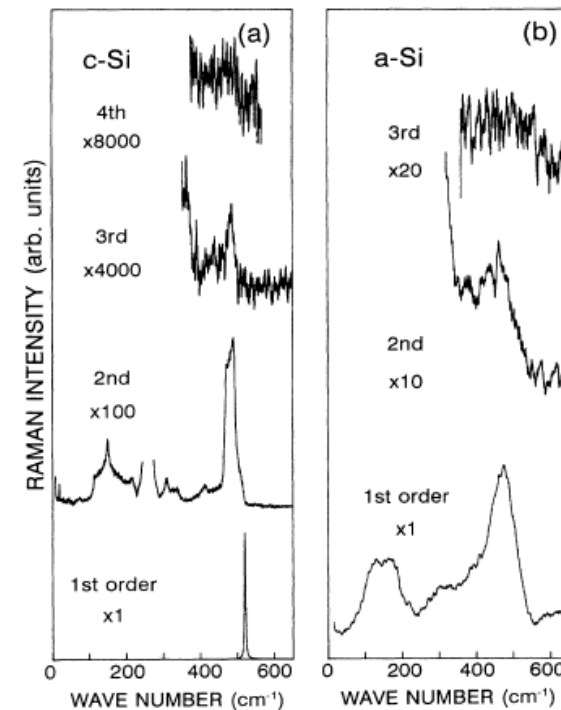
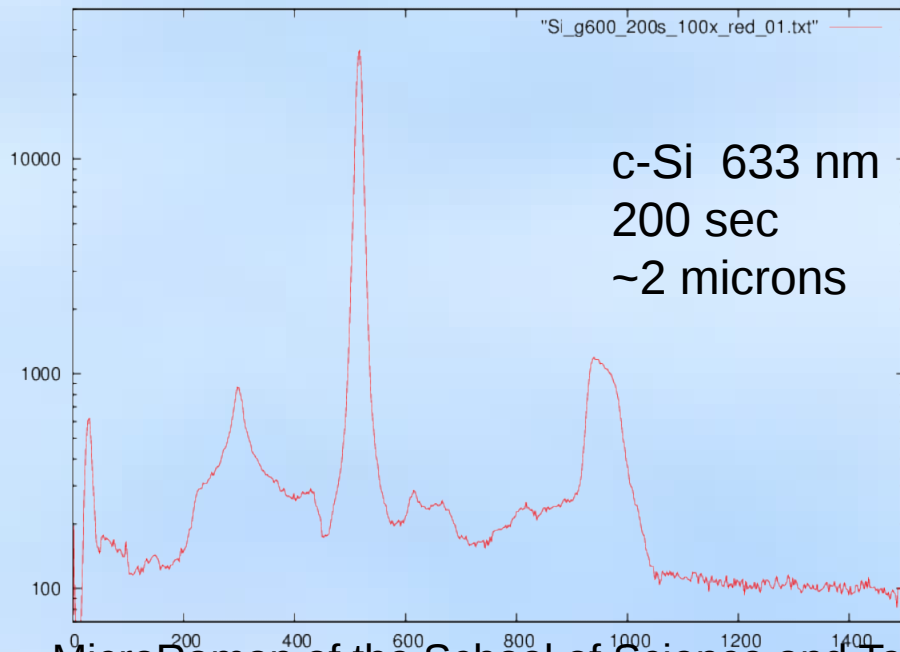


FIG. 2. Multiple-order Raman scattering in (a) *c*-Si and (b) *a*-Si. Frequency scales have been multiplied by the scattering order.



MicroRaman of the School of Science and Technology: 633 nm and 532 nm laser sources, fiber optics, Olympus microscope (up to 100x) with typical laser spot of 2-5 microns, Horiba iHR320 spectrometer with 2 gratings 1800/600 and Sincerity CCD, mapping XY (micrometer resolution). Presently under commissioning (April 2016).

Specification at Laser Wavelength	532 nm	633 nm	785 nm
Recommended Gratings	1800 g/mm 600 g/mm 150 g/mm	1800 g/mm 600 g/mm 300 g/mm	1800 g/mm 600 g/mm 300 g/mm
Spectral Range ^a (cm ⁻¹)	100 – 9700	100 – 6700	200 – 3400
Resolution (cm ⁻¹ /pixel)	1.2	0.79	0.57