

Raman Spectroscopy for Materials Science

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Outline, Lecture 1

- Introduction to the Raman process
- Vibration-modulated susceptibility
- Polarisation-resolved measurements
- Stokes/Anti-stokes scattering
- Phonons, dispersion, zone centre modes
- Second order scattering

The potential

- Raman spectroscopy is easy and fast.
- It usually shows discontinuous changes across structural phase transitions.
- Composition can be determined if there are reference data on well-characterised material.
- Crystal orientation can usually be determined.
- All that with a spatial resolution of better than 1 μm .
- But the spectra are complicated functions of structure; some analysis might be required and there are traps.

Raman (inelastic) scattering

Before scattering



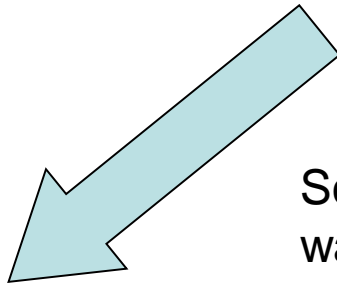
Incident photon

$$E = \hbar\omega$$

After scattering

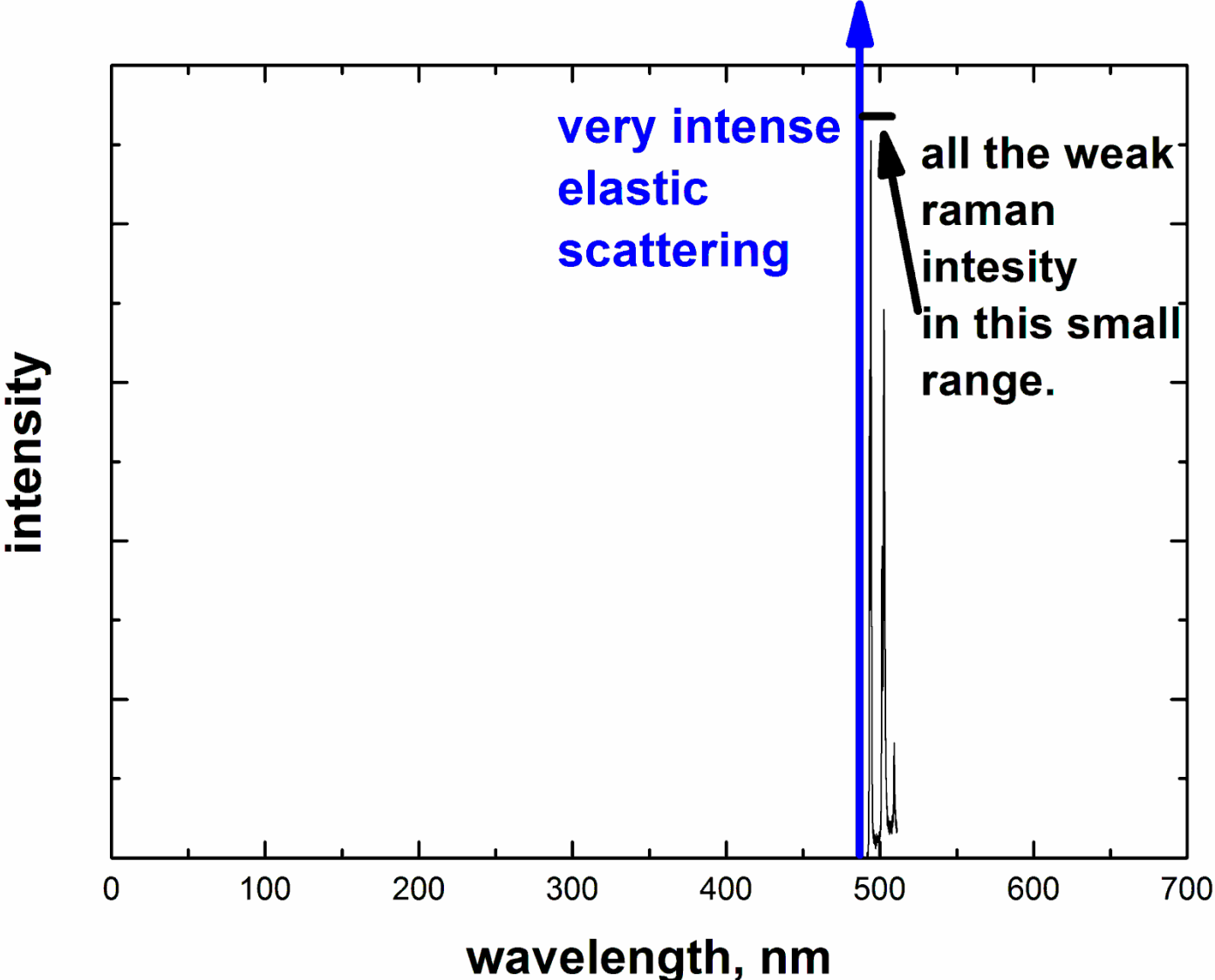


Emitted vibrational
wave, $E = \hbar\Omega$



Scattered photon, $E = \hbar\omega' = \hbar(\omega - \Omega)$, at a longer wavelength than incident photon. The spectrum at this shifted wavelength gives the frequencies of vibrations, in turn related to the material's structure.

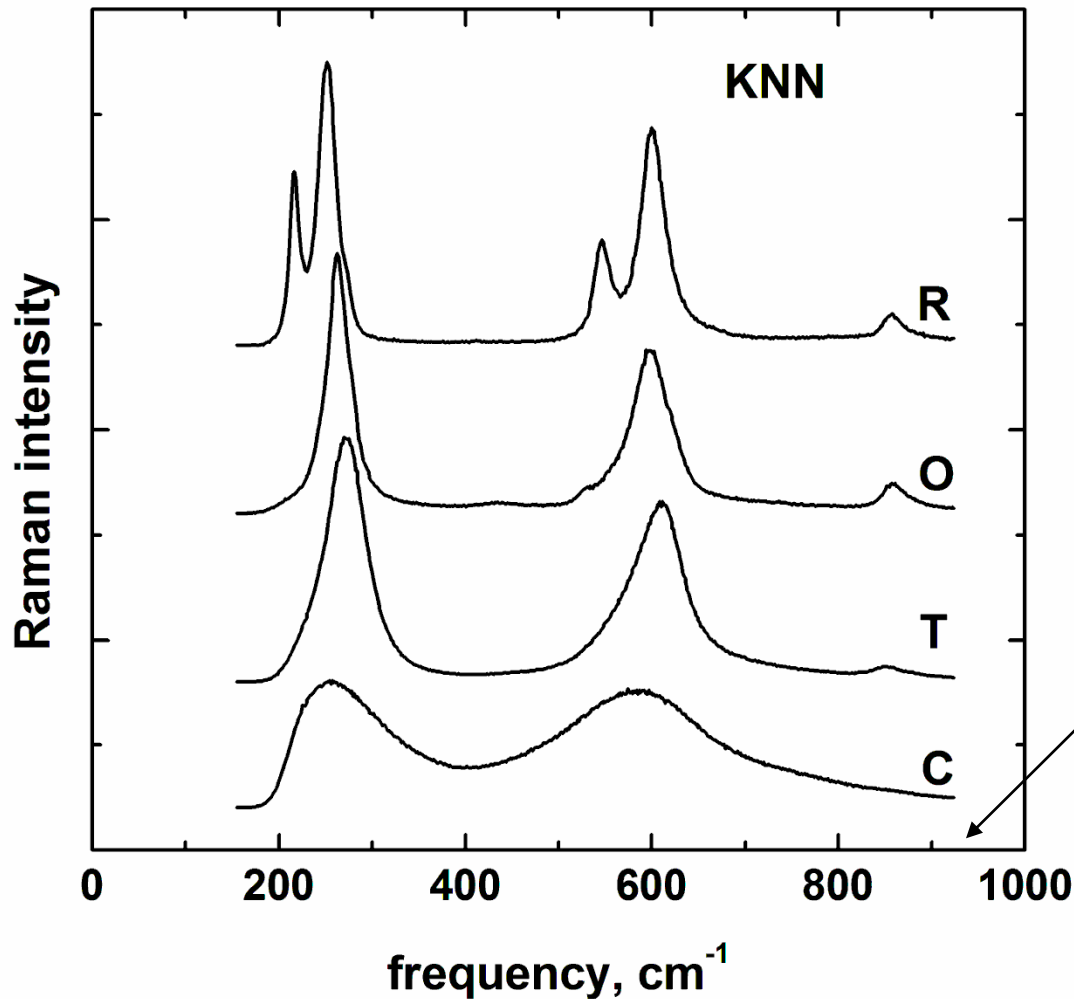
Scattered light intensity plotted vs the wavelength of the scattered light



Some frequency units

- The vibrational frequencies are most useful
- So the spectra are routinely plotted vs $\omega - \omega' = \Omega$
- And those are usually shown as $\Omega/(2\pi c)$, named the “wave number”, units cm^{-1} .
- It is the inverse of the wavelength (λ) of *light* that has the same frequency as the vibration; the number of EM wave lengths per unit length for a photon of frequency Ω .
- But note that neither photons **NOR** the vibration here has that wavelength; it is merely a convenient unit for frequency; $(1/\lambda) = 2\pi\omega/c$.

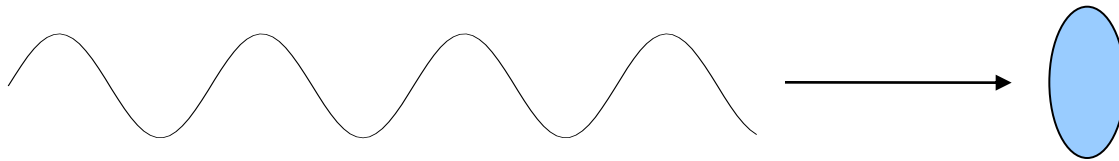
**Plotted vs the frequency difference, equivalent to
the frequency of the lattice vibration**



Intensity plotted vs
 $(\omega - \omega')[1/(2\pi c)]$
 $= [1/\lambda' - 1/\lambda]$

A little algebra (1)

E-M wave tickles a molecule:



\mathbf{E} (on molecule) = $\mathbf{E}_0 e^{-i\omega t}$ (\mathbf{E} = electric field)

(dipole moment) $\mathbf{P} = \chi \mathbf{E}$ (χ = susceptibility)

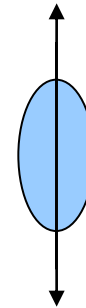
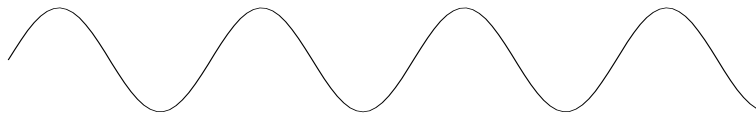
The dipole moment oscillates with \mathbf{E} and it's a tiny antenna that re-radiates at the same frequency ω .

That's scattered light, in this case at the same frequency as the incident EM wave.

(It may also absorb light via electronic transitions, but that's another story.)

A little algebra (2)

E-M wave tickles a *vibrating* molecule:



Vibrating at
frequency Ω

Vibrations modulate the susceptibility:

$$\chi = \chi_0 + \chi_1 e^{i\Omega t}$$

$$\text{So now } \mathbf{P} = \chi_0 \mathbf{E}_0 e^{-i\omega t} + \chi_1 \mathbf{E}_0 e^{-i(\omega-\Omega)t}$$

And the second term re-radiates at
frequency $\omega' = \omega - \Omega$.

We name that after its discoverer,
Chandrasekhara Venkata Raman

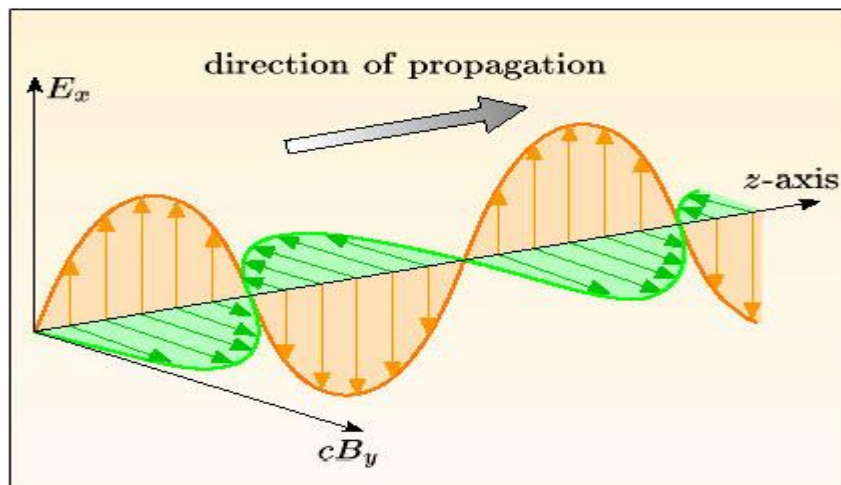


A note about polarisation

The amplitude of the re-radiated (Raman) EM wave is proportional to χ_1 , and its intensity to χ_1^2 .

Its polarisation is parallel to $\chi_1 \mathbf{E}_0$, which depends on the polarisation (i.e the electric field direction) of the EM wave, and need not even be parallel to that polarisation.

The **scattered polarisation** will in general have components both parallel and perpendicular to the incident polarisation.



The polarisation of an EM wave is by convention regarded as parallel to the electric field (\mathbf{E}) of the wave. The magnetic field (\mathbf{B}) is at all points perpendicular to \mathbf{E} .

Stokes/Antistokes

So far has been no mention that the EM wave can **gain** energy from the vibration (an **Antistokes** event), only the **loss** to a vibration (the **Stokes** process) is included above.

Both are possible, and their intensities are linked.

The Antistokes process requires that there is initially some energy in the vibrational mode, so it must be absent if the oscillator is in the ground (lowest energy) state; it must be at zero temperature.

In general the two signals are related by

$AS/S = \exp(-\hbar\Omega/k_B T)$; (k_B = Boltzmann constant, T on an absolute (e.g. Kelvin) scale.)

In a crystal

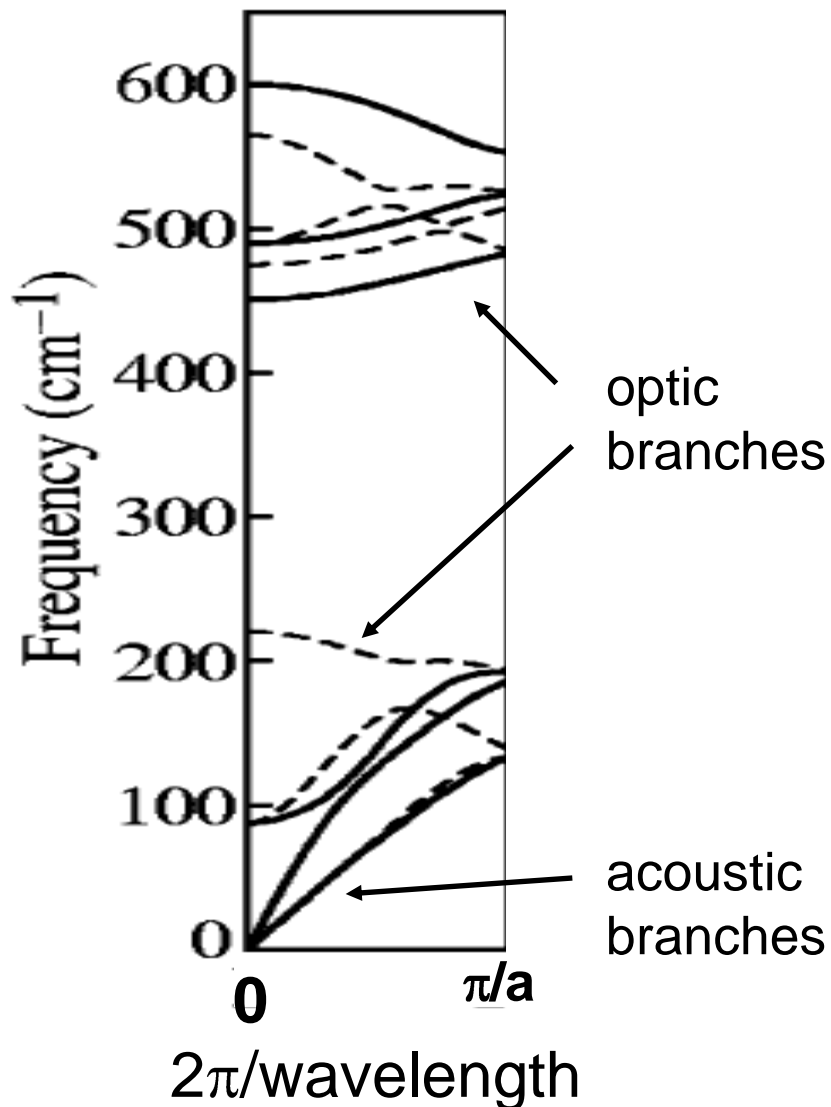
The vibrations are waves, labelled phonons, with wave vector

$q = 2\pi/\text{wavelength}$ (of the *phonon*)

That can range from $-p/a$ to $+p/a$, a the lattice constant ≈ 0.5 nm. If there are N ions in a unit cell then there are $3N$ different vibrational modes, each with its own frequency, for each value of wave vector.

So we can draw a “dispersion curve”.

Dispersion for InN



The phonon “dispersion”, meaning the frequency as a function of wavelength, is usually plotted as frequency vs $(\text{wavelength})^{-1}$, across the Brillouin zone. Then infinite wavelength is at zero, the zone centre, commonly labeled the Γ (gamma) point. It’s the frequencies along the left-hand edge that have infinite wavelength.

In a perfect crystal only the zone centre phonons can be Raman active, and usually not even all of those are.

Infrared absorption spectroscopy (an aside)

IR spectroscopy is also limited to zone-centre phonons, but often from branches that are not Raman active.

In fact if the crystal has a centre of inversion symmetry then **NO** modes are simultaneously IR and Raman active.

Second order Raman scattering

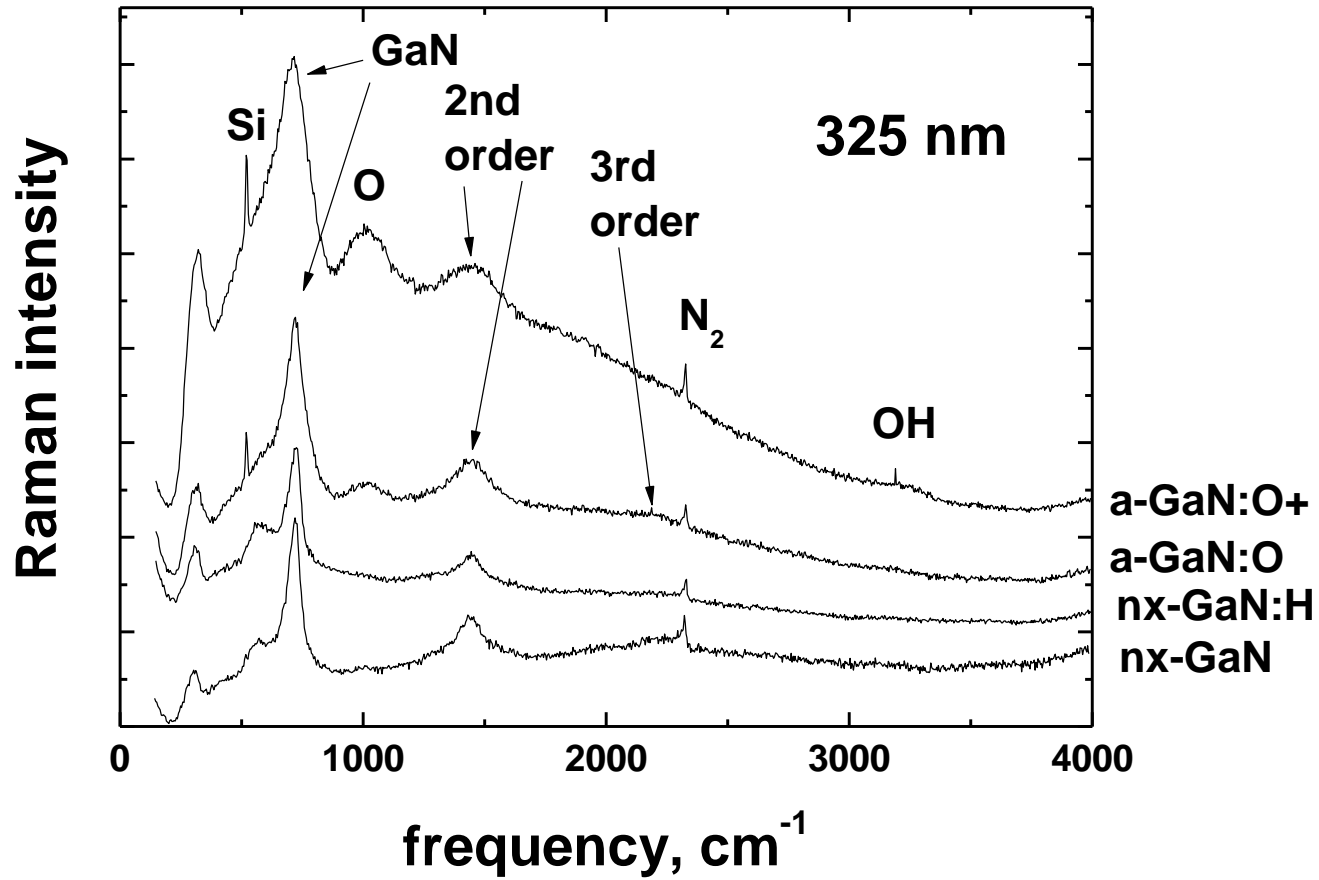
All above is “first order” scattering, the excitation of only one phonon.

It can be that two phonons can be excited, “second order” scattering.

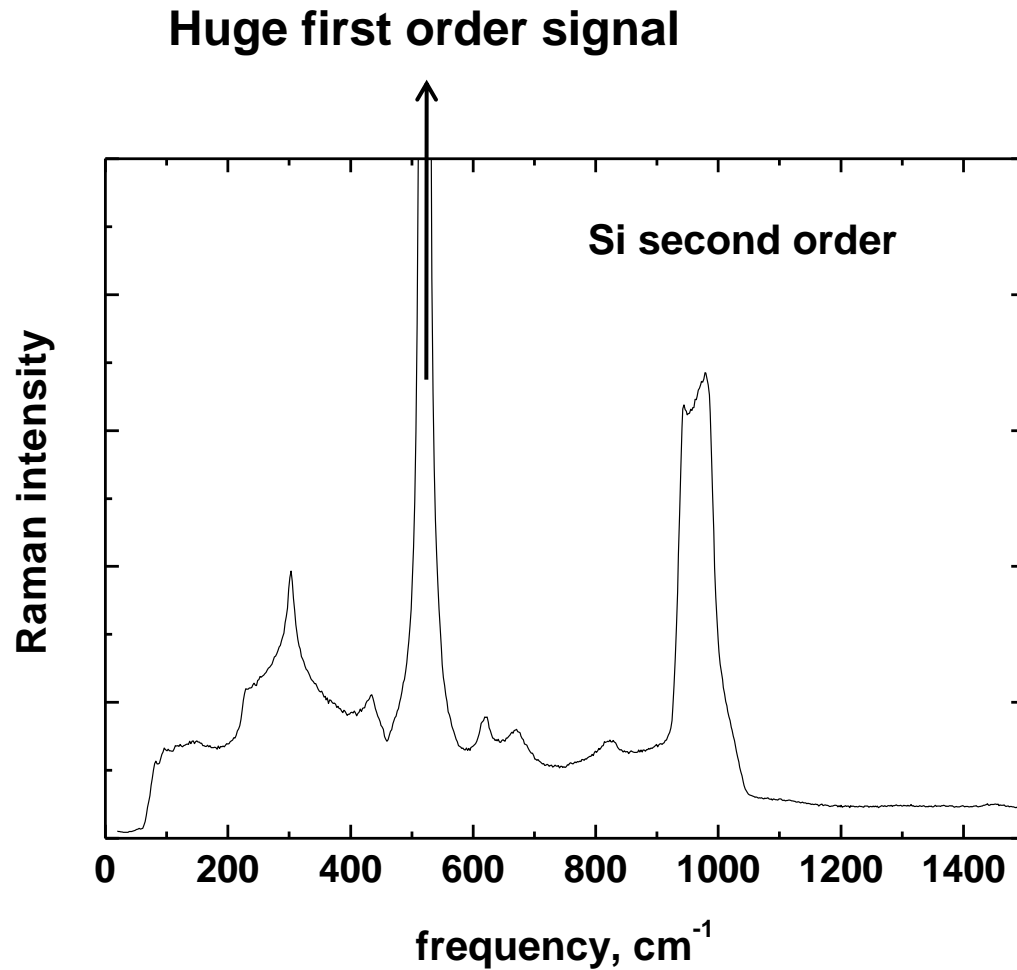
The wavelength selection rule in this case is that the two phonons must have equal wave vectors (or wavelength) but must be travelling in opposite directions.

Second order scattering is usually weak, but can be enhanced by various things.

Raman spectra of nanocrystalline GaN



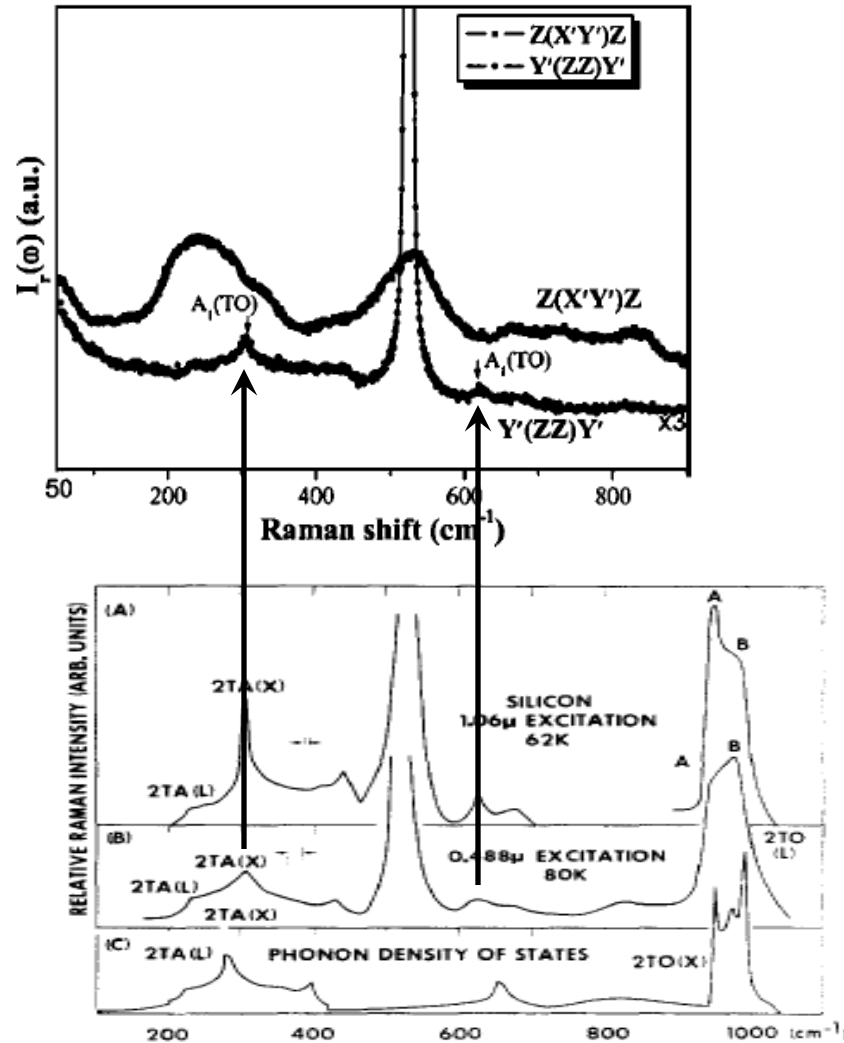
The second order signal in Si



Many traps for the unwary.

A report of Raman spectra from PZT films on Si showed weak lines assigned to PZT modes.

They were in reality second-order scattering from Si.



Raman Spectroscopy for Materials Science

Lecture 1 Summary

- Raman scattering is an *inelastic* process, photons lose (gain for Anti-stokes) energy to excitations in the material; for this course that means vibrational excitations.
- The weak scattered light is shifted little from the incident (laser) light, so the spectrometer must reject the intense elastically scattered light.
- The scattered *amplitude* is proportional to the vibration's modulation of the susceptibility.
- In crystals it is the infinite-wavelength, zero wave vector waves that can be Raman active.
- Second order, exciting two vibrational waves of equal but opposite wave vector, can be strong, with implications for studies of small or thin samples on a substrate.