

BACKGROUND

Spontaneous Raman scattering is an inelastic process by which an incident photon exchanges energy with the target material, via the absorption or emission of one or more phonons (vibrational quanta) corresponding to oscillatory modes of the material structure. Raman side bands in the spectra of the scattered light provide a signature of local bonding arrangements and can be used to identify phase and composition. The information is similar to that obtained in infrared absorption experiments, but Raman measurements can be performed with visible light sources. Particular modes, called “optical” phonons, are detected in Raman spectroscopy of crystalline materials. These modes have frequencies approaching the optical range, but with vanishingly small crystal momentum.

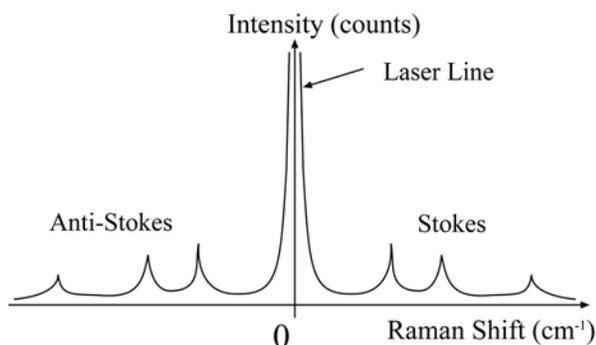


Fig.: Schematic of Raman spectrum.

Raman scattering has applications in the study of nanomaterials, such as carbon nanotubes and quantum dots. Raman modes can be related to such properties as surface functionalization and particle size.

GOAL

We will work through the basic startup and calibration of the spectrometer. We will then analyze various bulk materials and nanomaterials. Your goal is to participate in learning the operation of this equipment so that it can be used in your research.

Monochromatic radiation is needed for Raman experiments, so that discrete modes can be identified in the spectrum of scattered light. The energy of a photon is related to the frequency by $E = hf$. The photon energy can also be expressed in terms of the inverse wavelength in vacuum, with units of cm^{-1} , called “wave numbers”, using $E = hc/\lambda$. Note that $hc = 1.24 \times 10^{-4} \text{ eV} \cdot \text{cm}$.

Raman scattering causes a shift in the photon energy, i.e., $\Delta E = E_f - E_i$:

$$\Delta E = \frac{hc}{\lambda_f} - \frac{hc}{\lambda_i} = hc \cdot \Delta \left(\frac{1}{\lambda} \right) = -hc \cdot \Delta w$$

The Raman shift Δw is independent of the incident energy (wavelength). The choice of excitation wavelength is not without relevance, however; optical absorption and emission from the sample, as well as detection efficiency, generally depend on wavelength. Both Stokes and anti-Stokes processes occur, involving creation or annihilation, respectively, of phonons. So the observation of a Raman mode can often be confirmed by observation of its Stokes or anti-Stokes counterpart.

Raman active modes represent changes in polarizability of the material. The Raman spectra from crystalline materials are strongly influenced by selection rules, which relate the relative incident and scattered polarizations. Surface sensitivity can be enhanced by exposure to highly polarizable media, especially gold or silver layers, or nanoparticles.

PROCEDURE

Acquire Raman spectra from several materials, such as the following:

- 1) Silicon wafer;
- 2) Germanium wafer;
- 3) Diamond powder;
- 4) Carbon nanotubes;
- 5) TiO₂ nanopowder (anatase, rutile).

REPORT

Write a description of the spectrometer and its basic operation. Your report should include:

- 1) The laser wavelength (in nm);
- 2) All measured Raman shifts $\Delta\omega$ (in cm^{-1});
- 3) Plotted spectra.