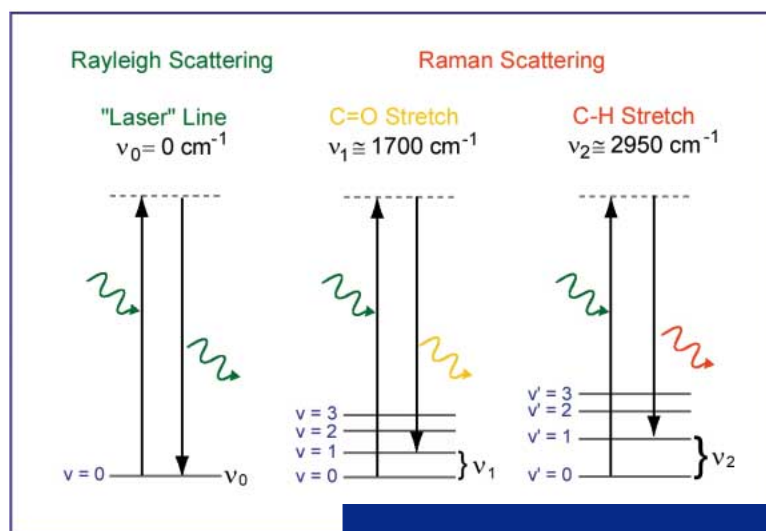


An Introduction to Raman for the Infrared Spectroscopist

What is Raman?

Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and quantitation. The technique involves shining a monochromatic light source (i.e. laser) on a sample and detecting the scattered light. The majority of the scattered light is of the same frequency as the excitation source; this is known as Rayleigh or elastic scattering. A very small amount of the scattered light (ca. 10^{-6} times the incident light intensity) is shifted in energy from the laser frequency due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample. Plotting the intensity of this “shifted” light versus frequency results in a Raman spectrum of the sample.



Vibrational energy level diagram showing Rayleigh and Raman (Stokes) scattering.

Generally, Raman spectra are plotted with respect to the laser frequency such that the Rayleigh band lies at 0 cm^{-1} . On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations. The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.

How Do Raman and Infrared Differ?

The spectrum obtained from Raman scattering is complementary to an infrared absorption spectrum. Raman offers several advantages over mid-IR and near-IR spectroscopy, including:

- Little or no sample preparation is required.
- Water is a weak scatterer – no special accessories are needed for measuring aqueous solutions.
- Water and CO_2 vapors are very weak scatterers – purging is unnecessary.
- Inexpensive glass sample holders are ideal in most cases.
- Fiber optics (up to 100's of meters in length) can be used for remote analyses.
- Since fundamental modes are measured, Raman bands can be easily related to chemical structure.
- Raman spectra are “cleaner” than mid-IR spectra – Raman bands are narrower, and overtone and combination bands are generally weak.
- The standard spectral range reaches well below 400 cm^{-1} , making the technique ideal for both organic and inorganic species.
- Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum (e.g. $-\text{S}-\text{S}-$, $-\text{C}-\text{S}-$, $-\text{C}=\text{C}-$).

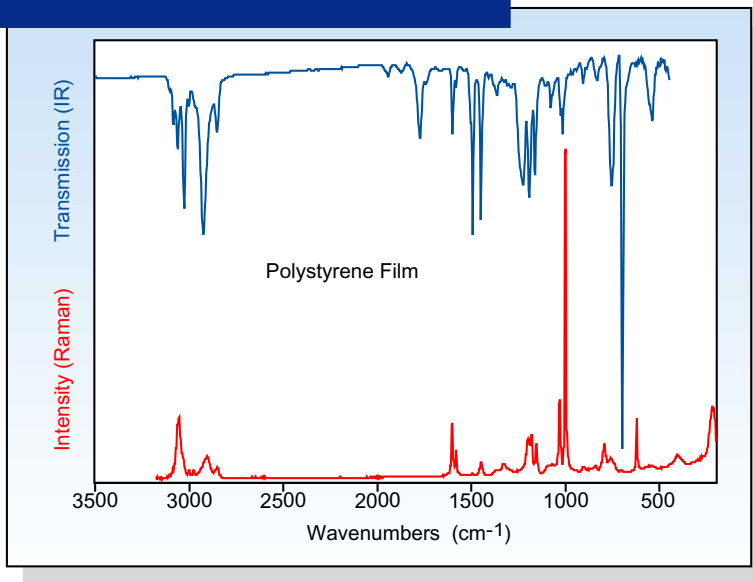
When Should I Use Raman?

Raman can be used for both qualitative and quantitative applications. Raman spectra are very specific, and chemical identifications can be performed by using search algorithms against digital databases. As in infrared spectroscopy, band areas are proportional to concen-

tration, making Raman amenable to quantitative analysis. In fact, because Raman bands are inherently sharper than their infrared counterparts, isolated bands are often present in the spectrum for more straightforward quantitative analysis.

Infrared absorption and Raman scattering are governed by completely different selection rules. Infrared bands arise from an interaction between light and the oscillating dipole moment of a vibrating molecule. Raman bands arise from an oscillating induced dipole caused by light waves interacting with the polarizability ellipsoid of a vibrating molecule. (It is common to describe the polarizability ellipsoid as the shape of the electron cloud around the molecule). Thus, symmetric stretches, vibrations involving multiple bonds, and vibrations of heavier atoms typically give rise to strong bands in the Raman spectrum. Asymmetric molecules will have bands at similar frequencies in both the infrared and Raman spectra, but their relative intensities will be very different. In most cases, a chemical species will have strong, indicative bands in both its Raman and IR spectra but they may not coincide. Which technique is superior depends upon the molecule of interest, the concentration level, the matrix or solution, other interfering species present, and the desired sampling method. For many applications, Raman may be the better answer to your spectroscopic identification or monitoring needs.

A comparison of the infrared absorption and Raman spectra of polystyrene. Note the complementary nature of the two data sets.



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111 Downey Street
Norwood, MA 02062
Tel. (781)440-0202
Fax (781)551-0283

www.inphotonics.com
info@inphotonics.com