

Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy, much like [infrared \(IR\) spectroscopy](#). However, *whereas IR bands arise from a change in the dipole moment of a molecule due to an interaction of light with the molecule, Raman bands arise from a change in the polarizability of the molecule due to the same interaction.* This means that these observed bands (corresponding to specific energy transitions) arise from specific molecular vibrations. When the energies of these transitions are plotted as a spectrum, they can be used to identify the molecule as they provide a “molecular fingerprint” of the molecule being observed. Certain vibrations that are allowed in Raman are forbidden in IR, whereas other vibrations may be observed by both techniques although at significantly different intensities, thus these techniques can be thought of as complementary.

Since the discovery of the Raman effect in 1928 by [C.V. Raman](#) and K.S. Krishnan, Raman spectroscopy has become an established and practical method of chemical analysis and characterization applicable to many different chemical species.

Samples may be in the form of

- *Solids (particles, pellets, powders, films, fibers)*
- *Liquids (gels, pastes)*
- *Gases*

The Raman Effect and Normal Raman Scattering

When light is scattered from a molecule, most photons are elastically scattered. The scattered photons have the same energy (frequency), and therefore wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is termed the Raman Effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a

vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a Raman spectrum.

The Scattering Process

When a beam of light is impinged upon a molecule, photons are absorbed by the material and scattered. The majority of these scattered photons have exactly the same wavelength as the incident photons and are known as *Rayleigh scatter*. In the scattering process, the incident photon excites an electron into a higher “virtual” energy level (or *virtual state*) and then the electron decays back to a lower level, emitting a scattered photon. In Rayleigh scattering, the electron decays back to the same level from which it started and thus, Rayleigh scattering is often referred to as a form of elastic scatter. The process of Rayleigh scattering is visualized in Figure 1.

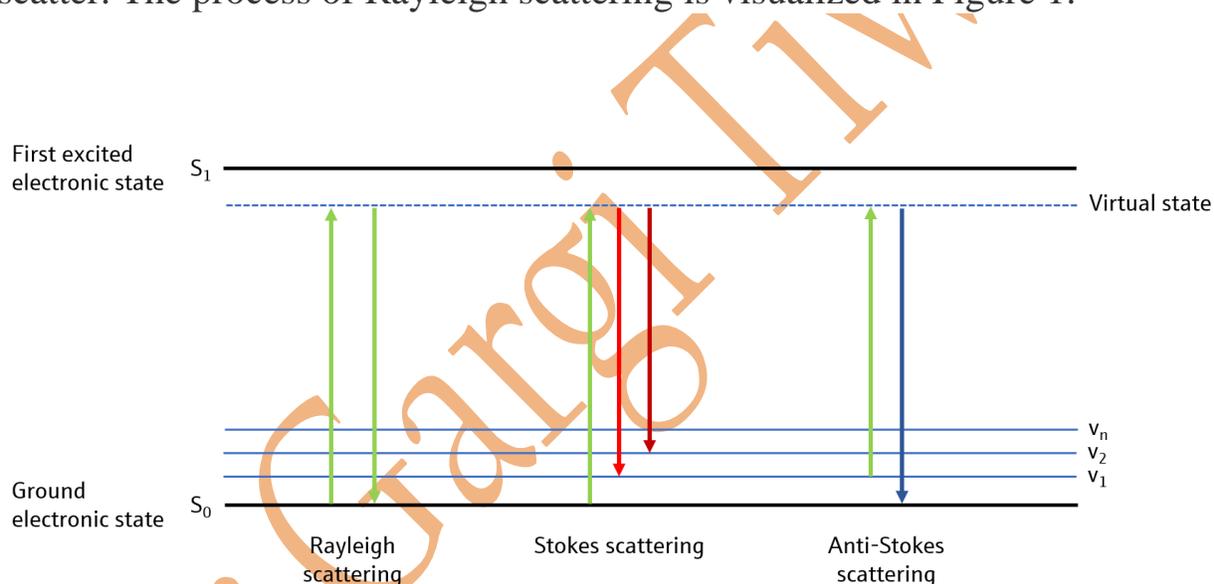


Figure 1: Energy level diagram for scattering processes. Left: Rayleigh scattering, Center: Stokes Raman scattering and Right: anti-Stokes Raman scattering.

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule’s electric field. In quantum mechanical terms,

the scattering can be described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The virtual state description of scattering is shown in Figure 1.1a. In the Raman effect, the electron excited in the scattering process decays to a different level than that where it started which is termed inelastic scattering.

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 1. Numerically, the energy difference between the initial and final vibrational levels, or Raman shift in wave numbers (cm^{-1}), is calculated through equation 1 in which $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ are the wavelengths (in nm) of the incident and Raman scattered photons, respectively.

$$\bar{\nu} = \left(\frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} \right) \times 10^7$$

The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature rise in a material.

At room temperature, the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state and the scattered photon will have lower energy (longer wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. Figure 1, (center) depicts Raman Stokes scattering.

A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the

ground state. The scattered photon appears at higher energy, as shown in Figure 1, (right). At room temperature, the Anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, and since the Stokes and anti-Stokes spectra contain the same frequency information, most Raman experiments look at Stokes-shifted scatter only.

Vibrational Energies

The energy of a vibrational mode depends on molecular structure and environment. Atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding all effect the vibrational force constant which, in turn, dictates the vibrational energy.

For example, the stretching frequency of a phosphorus-phosphorus bond ranges from 460 to 610 to 775 cm^{-1} for the single, double and triple bonded moieties, respectively. Much effort has been devoted to the estimation or measurement of force constants. For small molecules, and even for some extended structures such as peptides, reasonably accurate calculations of vibrational frequencies are possible with commercially available software.

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active. Their spectra are important in such fields as polymers and semiconductors. In the gas phase, rotational structure is resolvable on vibrational transitions. The resulting vibration/rotation spectra are widely used to study combustion and gas phase reactions generally. Vibrational Raman spectroscopy in this broad sense is an extraordinarily versatile probe into a wide range of phenomena ranging across disciplines from physical biochemistry to materials science.