

## Discovery of the Raman Effect

In 1928, Sir C.V. Raman and his colleague K.S. Krishnan made their discovery of what came to be called Raman scattering while searching for an optical analog to the Compton Effect. It was nearly simultaneously discovered by G.S. Landsberg and L.I. Mandelstam, two Russian physicists, during the course of their studies on specific heats of solids. Raman and Krishnan observed the inelastic scattering of light first by focusing filtered sunlight, and later by focusing a quartz mercury arc lamp through a photographic filter to remove all lines of greater wavelength than 4356 Å, and directing it into samples of common solvents. The resultant spectra were collected on photographic plates, and showed modified lines that indicated a change of wavelength in the outgoing light. The first Raman spectra acquired of benzene are presented in Figure 2.1 Because the efficiency of Raman scattering is so low, extremely long acquisition times were needed in this early work (2-100 hours for liquids and more than 180 hours for vapors have been reported). In total, Raman and Krishnan observed scattered secondary radiation in 60 liquids and vapors.

Due to the inefficient nature of the scattering, several technological advances were necessary before Raman spectroscopy became a common laboratory technique. As discussed in the previous section, only 1 in 10<sup>6</sup> to 10<sup>8</sup> incident photons are returned shifted by the interaction with the molecules. The development of the laser, then, permitted much more effective measurements because of the dramatic increase in the amount of incident light. Improvements in monochromator systems, both to resolve the Raman spectrum and limit the amount of Rayleigh scattering present in spectral data, also encouraged use of Raman spectroscopy to study molecular structure and chemical systems. Miniaturized Raman systems in current use, including those in the TSI product line, became possible with the advent of frequency-stabilized solid state lasers and small monolithic spectrometers.

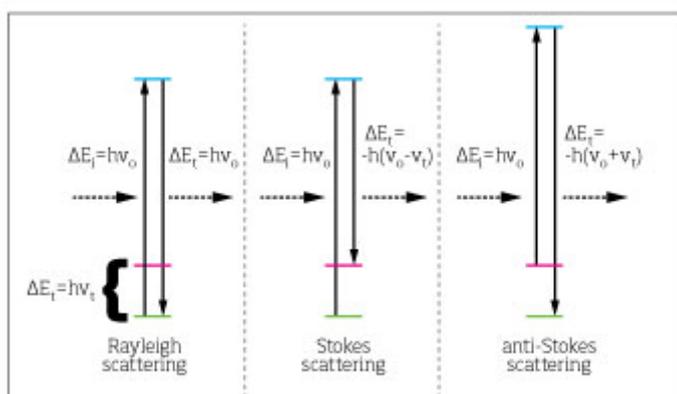
Further, narrow notch filters are also available for the removal of the excitation light in the spectra and sophisticated software solutions exist for background elimination and in support of end-user purposes.

## Basics of Raman Spectroscopy

When a sample is illuminated with a laser and the scattered light is dispersed with a spectrograph, the output of the spectrograph will show a strong line at the excitation wavelength, and weaker lines appearing on both lower and higher frequencies of the strong line. Light scattered at the incident wavelength is called Rayleigh scattering. The shifted features are called Stokes and anti-Stokes lines, respectively, and have their origin in the interchange of energy between the light and the molecules causing the scattering. Because actual electronic or vibrational states are not accessed in this process, the frequency shifts observed in Raman spectroscopy are independent of excitation wavelength.

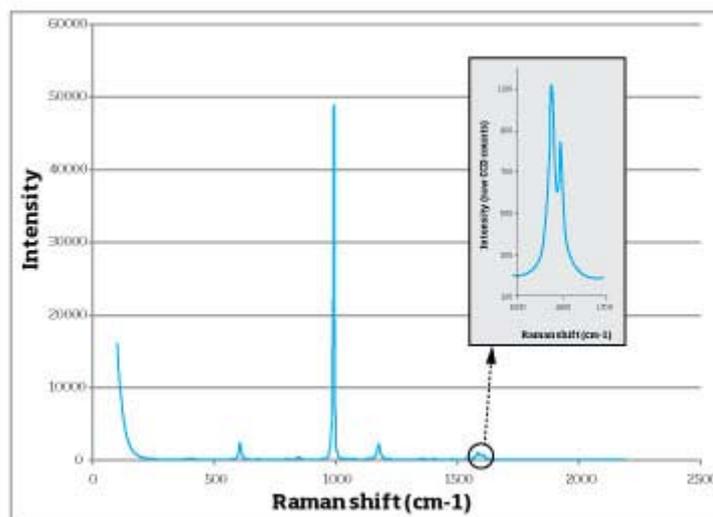
In accounting for the origin of the observed shifts, both classical and quantum explanations are useful, but both descriptions rely on the property of polarizability. Polarizability is the relative tendency of a charge distribution to be distorted from its normal shape by an external electric field. It increases as the volume occupied by the bond electrons increases.

In the classical explanation of Raman spectroscopy, the electric vector of the incident illumination induces an oscillating electrical dipole, by virtue of the bond's native polarizability, which subsequently emits radiation. If the atoms in the molecule are not moving with respect to one another, the induced dipole, and therefore the scattered light, has the same frequency as the excitation laser. If the molecule is in motion, vibrating or rotating, the amplitude of the dipole will depend on the positions of the atoms within the sample molecule. In this case, the rotational and vibrational frequencies of the molecule will influence the scattered light such that the outgoing radiation consists of light of frequencies equal to the sum and difference between the incident beam and anti-Stokes and Stokes features. The quantum explanation is also related to a change in polarizability.



**Figure 1. Quantum description of Raman and Rayleigh scattering processes**

In both the classical and quantum descriptions of Raman scattering, actual scattering of light by molecules is governed by the relative polarizability of the electron distribution associated with the molecule. The Raman intensity is proportional to the square of the induced dipole moment (i.e. the square of the polarizability derivative). If the vibration does not appreciably change the polarizability, the induced dipole moment will be small, and the Raman emission feature weak. Vibrations involving bonds that are already polar. In this description, the incoming photons promote the molecule into a higher lying energy state (usually a virtual state). The transition moment between the lower and higher states is the polarizability tensor. Energy available to the emitted, or scattered, photon is the energy of the excitation beam ( $\nu_0$ ) plus or minus the vibrational state of the molecule prior to excitation ( $\nu_{vib}$ ). The scattered photons therefore have frequency of  $\nu_0 \pm \nu_{vib}$ . These processes are shown in Figure 1. The efficiency of Raman scattering is usually quite low; only about 1 out of every 106-108 incident photons is frequency shifted. Because near room temperature, most molecules are near their vibrational ground states, the signal intensity in the Stokes features is normally much larger than in the anti-Stokes. Indeed, for most applications, the anti-Stokes features are not even collected. (i.e. the electrons are shared unevenly between the atoms of the bond) before the arrival of the photon, such as C-O, N-O and O-H, are weak scatterers. Bonds that are relatively neutral, however, such as C-C, C-H and C=C, undergo large changes in polarizability during a vibration. These bonds have very active Raman features. This explains the strong Raman features of molecules with large pi bonds and ring structures, as well. Illustrative of this principle, a spectrum of benzene is presented in Figure 2. The feature at 992  $\text{cm}^{-1}$  is the ring breathing vibrational mode.



Molecular fluorescence is sometimes competitive with Raman scattering. If the material under test has a component with a real electronic energy level accessible by the Raman excitation beam, a portion of the excitation beam will be absorbed. The electronic energy level will, like the ground state, have a plethora of vibrational/rotational energy levels. A gradual descent through the vibrationally excited levels of the upper electronic state will occur (intra-system crossing), and then a photon will be emitted as the molecule relaxes into the ground state. Because of the large number of vibrational states in both the excited and ground states, the outgoing photons will be emitted in a wide array of frequencies, and therefore a broad band. The tail of this broad band can overlap the Raman shifts of interest, making strategies to deal with sample fluorescence of extreme importance in Raman spectroscopy.