

1 Raman Spectroscopy

On interaction of matter with a beam of radiation, the radiation may be transmitted, absorbed, polarized, reflected, refracted, diffracted, scattered, or it may excite fluorescence (Fig. 1). Transmission is the interaction of radiation with matter without loss of energy while absorption involves attenuation of radiation energy. Polarization takes place when one of the radiation components is filtered. Emission of lower energy radiation compared with incident radiation is referred to as fluorescence. Radiation is said to undergo reflection when it is deflected in the direction of the radiation source, refraction when it bends on passing into different media, and diffraction when radiation bends around obstacles and spread out of small openings. Deflection of radiation in random directions is called scattering.

Scattering of radiation by particles in a medium (e.g., fog or smoke in air; colloidal solution) is called the Tyndall effect. Molecules in the medium/sample can also affect scattering. There are two types of molecular scattering—Rayleigh and Raman scattering. In Rayleigh scattering (as well as Tyndall scattering), the

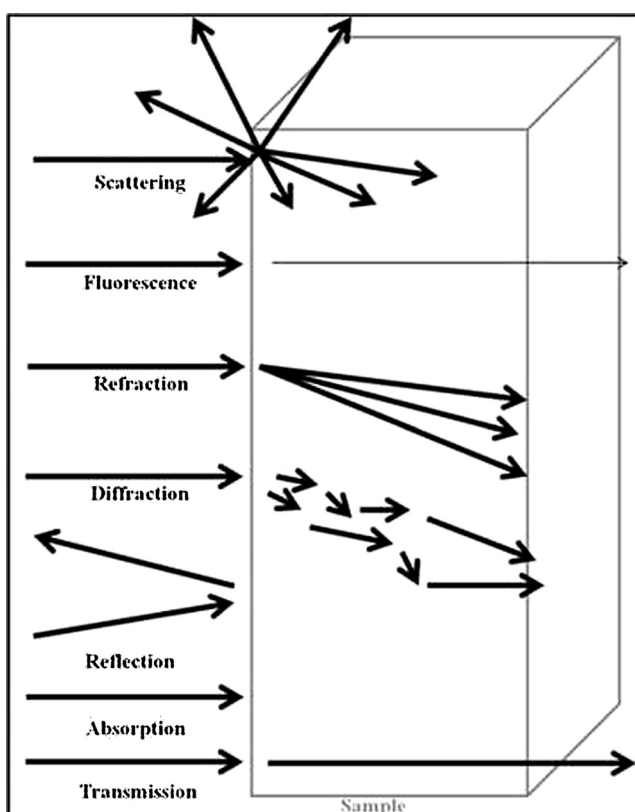


Figure 1 Ray diagram of transmission, absorption, reflection, diffraction, refraction, fluorescence, and scattering occurring on interaction of matter with a beam of radiation.

energy of the scattered photon is the same as that of the incident photon, hence Rayleigh scattering is also called elastic scattering. As opposed to this, in Raman scattering or inelastic scattering, the energy of the scattered photon is different from that of the incident photon. When the energy of the scattered photon is less than the incident photon, the scattering is called Stokes Raman scattering, whereas when the energy of the scattered photon is greater than the incident photon, the scattering is referred to as anti-Stokes Raman scattering.

1.1 History

The phenomenon of inelastic scattering was first experimentally proven by and named after Sir C. V. Raman (Fig. 2).¹ The effect was predicted by Smekal,² Kramers and Heisenberg,³ Schrödinger,⁴ and Dirac⁵ before Raman while developing the theory of quantum mechanics. Sir Raman provided the first experimental proof in his letter to *Nature* entitled “A new type of secondary radiation” in 1928. The experiment consisted of a telescope to converge a beam of sunlight and complementary light filters—blue-violet and yellow-green filters (Fig. 3). When the complementary filters were placed between the source of light and the scattering material such as a purified liquid or its dust-free vapor, the track of light through the scattering material was extinguished. However, upon placing the scattering material between the filters—such that the order is light source, blue-violet filter, sample, and yellow-green filter—the track of light through the scattering material reemerges (Fig. 3). This shows the phenomenon of scattered light having energy different from that of the incident light, confirming the Raman effect.⁶ Sir Raman showed the existence of inelastic scattering in 60 different samples and declared the phenomenon to be of universal nature.⁷ With the help of a mercury arc lamp as the excitation source instead of sunlight and a quartz



Figure 2 Sir C. V. Raman.¹