

PERSPECTIVES ON THE HISTORY OF THE RAMAN EFFECT AND ITS IMPLEMENTATION

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INTRODUCTION

Chandrasekhara Venkata Raman (1888–1970) reported the light scattering phenomenon that has become known as the Raman effect in 1928 (Raman and Krishnan 1928). This followed theoretical predictions by Smekal (1923) that such a phenomenon should exist. Raman initially used sunlight, and then the light from a mercury lamp, to excite the spectrum presumably produced when a photon of light lost a small amount of its energy to a molecular vibration.

The idea that molecular vibrations can provide chemical information on materials came originally from the infrared absorption work of William Coblentz (Coblentz 1905-1908) when he was at the National Bureau of Standards (now the National Institute of Standards and Technology) in Washington, DC (USA). As differentiated from an infrared (IR) absorption process, the Raman process involves two photons and is a scattering phenomenon. Because both Raman and Coblentz were physicists, some analytical chemists have said that vibrational spectroscopy is a gift from the physicists to the chemistry community.

INSTRUMENTATION

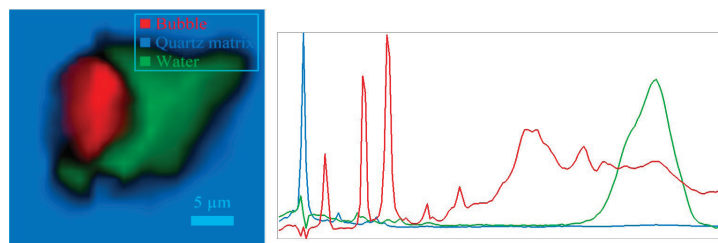
Raman's first measurements were made on a small prism-based instrument with a photographic plate, all encased in a wooden box (FIG. 1). After preparation (synthesis) of the desired sample, it was extensively purified, and spectra of it were recorded over a period of days (today in a few seconds!). Raman line shifts were calculated manually.



FIGURE 1 (LEFT) Picture of Sir Chandrasekhara Venkata Raman (1888–1970), winner of the 1930 Nobel Prize for Physics. (RIGHT) The first Raman instrument as built by Raman himself. IMAGE BY D. MUKHERJEE (INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE IN JADAVPUR, KOLKATA), WITH PERMISSION.

From about 1930 to 1990, Raman instruments were quite large. They included a premonochromator to eliminate the nonshifted (laser) excitation light, which has an intensity at least six orders of magnitude greater than that of the Raman-shifted light, and they had to be long enough to disperse the light sufficiently. Early instruments had a drive system that rotated the grating so that the signal, including the Raman-shifted radiation, would arrive wavelength by wavelength at the detector (single-channel photomultiplier tube for high sensitivity). During the 1960s and even later, the data output was from a strip-chart recorder (if your pen went dry, you lost your experimental results!).

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DEVELOPMENT OF LASERS AND MICROPROBES

During the 1960s, one of the most important innovations for Raman spectroscopy was the introduction of a laser (the laser celebrates its 60th birthday in 2020), which was both monochromatic and produced a coherent, parallel beam of small diameter. These properties made the laser easy to manage optically and, ultimately, to design into a microscope system. The first reported use of the He–Ne laser to excite Raman spectra was by Weber and Porto (1965). Subsequently, Ar and Kr gas lasers were introduced with wavelengths between 799.3 nm and 401.6 nm, and ultraviolet (UV) lines in the 350 nm range. These lasers also could be “frequency doubled” to yield wavelengths as short as 244 nm. Continuously tunable lasers (dye and Ti-sapphire) were developed, pumped with high-power Ar lasers. Most recently, solid-state diode lasers with *significantly* lower utility requirements have become those most used for analytical applications, and this category includes the frequency-doubled Nd:YAG laser with a strong output at 532 nm. There are also pulsed lasers, whose use is restricted to more specific applications, such as time-resolved spectroscopy.

By 1990, instruments were redesigned to accommodate a 1” multichannel detector from which the signals were collected and treated on desktop computers. Efficient notch filters or edge filters were developed to remove the unshifted laser light before it entered the monochromator, thereby preventing the desired signal from being obscured by “stray light.” Consequently, instruments could be single stage rather than triple stage in design, making them more compact and more efficient in detecting the Raman signal. With the availability of desktop computers, sophisticated software evolved, providing analytical and interpretational capabilities at nominal cost.

A huge technical and application step forward came from the nontrivial coupling of the optics of a microscope with those of a spectrometer. The period from the mid to late 1970s saw the introduction of the commercially available Raman microscope (FIG. 2, LEFT) in France (Delhaye and Dhamelincourt 1974, 1975), as well as a specialized system developed at the National Bureau of Standards (Rosasco et al. 1975). FIGURE 2 (RIGHT) is an example of a contemporary Raman microprobe with a footprint the size of a standard research-grade microscope. More details on current and past Raman instrumentation can be found in Adar (2001, 2007) and Dubessy et al. (2012).

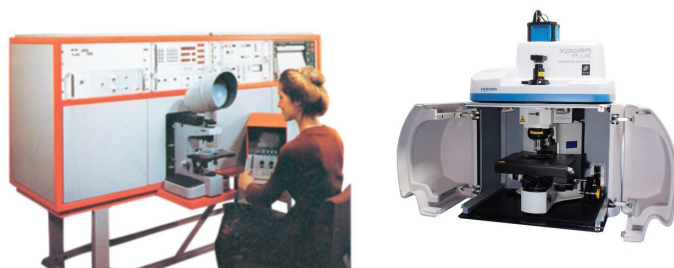


FIGURE 2 (LEFT) The MOLE™ (Molecular Optical Laser Examiner) of 1977. IMAGE: HORIBA SCIENTIFIC, WITH PERMISSION. (RIGHT) The XploRA™ a contemporary Raman microprobe with a 200 mm spectrograph that accommodates four interchangeable gratings, up to three internal lasers, and a motorized XY stage. IMAGE: HORIBA SCIENTIFIC, WITH PERMISSION.

INFRARED (IR) MICROSCOPY COMPARED TO RAMAN MICROSCOPY

Some materials have vibrations that are either IR or Raman active, however, most materials have both vibration types. The two vibrational spectroscopies of Raman and IR are complementary in many ways. For example, bands that are strong in Raman spectra may be weak or absent in IR, and vice versa. Nevertheless, the methods for generating and collecting their signals are quite different. Compared to IR microscopes, Raman systems offer several advantages. Working at visible wavelengths enables a Raman instrument to provide better spatial resolution than an IR microscope, because the resolution is physically constrained by the working wavelength. The Raman spectrum can be typically recorded down to a few tens of cm^{-1} from the laser line, whereas an IR instrument typically cuts off at about 650 cm^{-1} which is determined by the instrument's optical elements. Raman spectroscopy, therefore, provides much more information on mineralogical samples, which have multiple vibrational lines below 650 cm^{-1} . Raman signals can be gathered *below* the surface of a mineral (giving access to solid and fluid inclusions), in contrast to infrared spectra which can only be detected from a surface or a very thin section, and then with no depth information. Raman spectra also tend to exhibit bands that are narrower than those in infrared spectra, thus providing more detailed information.

EVOLUTION OF ACCEPTANCE AND APPLICATION OF THE RAMAN MICROPROBE

Acceptance of the Raman microscope as an analytical tool was slow in coming for a variety of reasons. For one thing, during the middle of the 20th century, exposure to Raman spectroscopy in an analytical chemistry course demonstrated the weakness of the Raman signal and the difficulty of dealing with samples carrying fluorescent impurities, which can obscure the Raman signal. Until the availability of lasers with multiple wavelengths (enhancing Raman signal strength and enabling optimization of a measurement for a particular sample), inexpensive desktop computers (enabling access to state-of-the-art software), notch filters and multichannel detectors (reducing the instrument footprint by a factor of ~5 and the time to record a spectrum by orders of magnitude), and of course, sampling via a research-grade microscope (for easy sample set-up and microanalysis), acquisition of Raman spectra was quite difficult.

Progress in opening this technology to new fields *always* involved someone demonstrating its usefulness in that field. The earliest area was contaminant analysis, especially for the semiconductor industry, which was experiencing exponential growth as the Raman microscope was evolving. The first measurements for proof-of-principal in contaminant analysis and for application in the geosciences (especially for fluid inclusions) were made in France by the group that had introduced the technology. In the US, convincing workers of the usefulness was more difficult because most Raman users at the time were physicists who seemed oblivious to microanalytical needs. Chemists were not able to fully utilize the technology until the ready availability of red lasers, which avoid the excitation of luminescence. Microanalysis, however, was exactly what the geoscience (especially mineralogical, petrological, and geochemical) community wanted. Electron probe microanalysis was developing rapidly to provide micrometer-scale elemental information.

The Raman microprobe, operating at a comparable spatial scale, provided structural–chemical information, e.g., phase identification (including distinguishing polymorphs), as well as the ability to analyze liquids and gases and to access phases while they were still embedded within their host matrix. This issue of *Elements* illustrates the explosion in geoscience applications that followed.

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