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A BRIEF ILLUSTRATION OF RAMAN SPECTROSCOPY

ASSIGNMENT-MATERIALS & STRUCTURE PROPERTY CORELATION

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Introduction

While Raman spectroscopy has long been recognized as a valuable research technique in the years since the phenomenon was first observed by Dr. C. V. Raman in 1928, it is only fairly recently that Raman has emerged as an important analytical tool across a number of industries and applications. No longer designed to appeal only to highly specialized and trained experts, the best of today's Raman instruments are fully integrated and come with built-in system intelligence that frees the user to focus on results and not on having to become an expert in the technology itself. Busy analytical laboratories are now able to adopt Raman spectroscopy without having to devote time to developing the expertise that used to be essential in order to be able to collect high quality data.

Due to its sensitivity, high information content, and non-destructive nature, Raman is now used in many applications across the fields of chemistry, biology, geology, pharmacology, forensics, pharmaceuticals, materials science, and failure analysis. Spectral libraries in excess of 16,000 compounds are now available for direct compound identification.

In many laboratories, infrared and Raman spectroscopy are used as complementary techniques, because each method looks at different aspects of a given sample. While IR is sensitive to functional groups and to highly polar bonds, Raman is more sensitive to backbone structures and symmetric bonds. Using both techniques provides twice the information about the vibrational structure than can be obtained by using either alone.

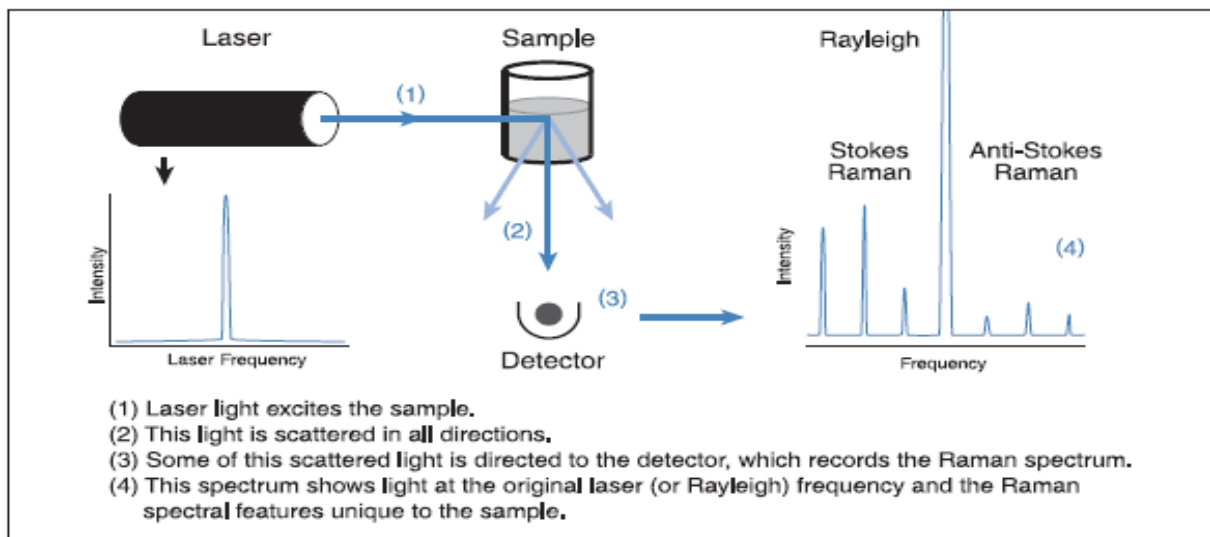
In addition to providing unique information about a sample, Raman offers several additional benefits, including:

- Minimal or no sample preparation
- Sampling directly through glass containers
- Non-destructive analysis, so the same sample can be used in other analyses
- Non-intrusive analysis, permitting study of more labile sample features, such as crystal structure
- Minimal water interference
- No interference from atmospheric CO₂ or H₂O

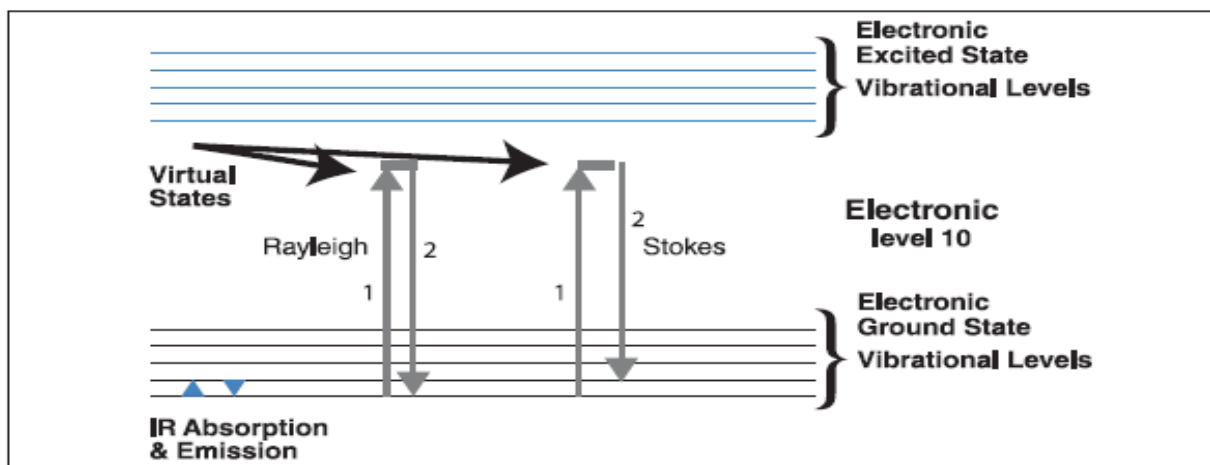
The objective of this booklet is to provide an introduction to the technique of Raman spectroscopy and its relevance as an analytical tool. The first section contains a simple description of the theory behind the Raman effect, followed by a discussion of the relevance of Raman spectroscopy and its complementarity with other vibrational techniques. This is followed by an overview of the two major Raman instrument designs: dispersive Raman and Fourier transform Raman (FT-Raman). Advantages and key applications are discussed for each of these instruments, followed by a list of desirable features in modern instruments.

Theory: The Raman Effect

When a sample is irradiated with an intense monochromatic light source (usually a laser), most of the radiation is scattered by the sample at the same wavelength as that of the incoming laser radiation in a process known as **Rayleigh** scattering. However, a small proportion of the incoming light – approximately one photon out of a million – is scattered at a wavelength that is shifted from the original laser wavelength.



As illustrated in the simplified energy level diagram, a molecule at rest resides in the ground vibrational and electronic states. The electric field of the laser beam raises the energy of the system for an instant by inducing a polarization in the chemical species. The polarized condition is not a true energy state and is referred to as a "virtual state". Relaxation from the virtual state occurs almost instantaneously and is predominantly to the initial ground state. This process results in Rayleigh scatter, which is scattered light of the same wavelength as the excitation laser. Relaxation to the first excited vibrational level results in a Stokes-Raman shift. Stokes-Raman shift scattered light is of lower energy (longer wavelength) than that of the laser light. In addition, most systems have at least a small population of molecules that are initially in an excited vibrational state. When the Raman process initiates from the excited vibrational level, relaxation to the ground state is possible, producing scatter of higher energy (shorter wavelength) than that of the laser light. This type of scatter is called anti-Stokes Raman scatter and is not illustrated.



The vibrational states probed by Raman spectroscopy are similar to those involved in infrared spectroscopy. However, the two **vibrational spectroscopy** techniques are complementary, in that vibrations that are strong in an infrared spectrum (those involving strong dipole moments) are typically weak in a Raman spectrum. Likewise, non-polar functional group vibrations that give very strong Raman bands usually result in weak infrared signals. As an example, hydroxyl- or amine-stretching vibrations and the vibrations of carbonyl groups are usually very strong in an FT-IR spectrum and are weak in a Raman spectrum. The stretching vibrations of carbon double and triple bonds and the symmetric vibrations of aromatic groups give a very strong Raman signal.

Raman spectroscopy provides key information about the structure of molecules. The position and intensity of features in the spectrum reflect the molecular structure and can be used to determine the chemical identity of the sample. Spectra may also show subtle changes depending on the crystalline form. With the extensive spectral libraries that are now available, it is very straightforward to identify compounds by spectral library searching.

Why Raman Spectroscopy?

Raman spectroscopy offers some major advantages in comparison with other analytical techniques. Raman is a light scattering technique, so all that is required for the collection of a spectrum is to place the sample into the excitation beam and collect the scattered light. There are few concerns with sample thickness and little interference from the ambient atmosphere, so there is no need for high-vacuum or desiccated sample holders. Glass, water and plastic packaging have weak Raman spectra, making the technique even easier to use. Samples usually can be analyzed directly inside a glass bottle or plastic bag without having to open the package and risk contamination. Aqueous samples are readily analyzed without having to remove water, and because there is no interference from ambient humidity, there is no need to purge the instrument.

No two molecules give exactly the same Raman spectrum, and the intensity of the scattered light is proportional to the amount of material present. Thus Raman provides both qualitative and quantitative information about the sample, allowing for spectral interpretation, library searching, data manipulation and the application of chemometric methods.

Raman spectroscopy is non-destructive. There is no need to dissolve solids, press pellets, compress the sample or otherwise alter its physical or chemical structure. This makes Raman spectroscopy ideal for investigating physical properties such as crystallinity, phase transitions and polymorphs. The lack of sample preparation also minimizes cleanup and the possibility of cross-contamination.

Raman spectroscopy also has several additional advantages. Unlike other vibrational techniques, its operational wavelength range is usually independent of the vibrational modes being studied. Since Raman spectroscopy measures the shift in frequency from that of the excitation laser, it can be performed using any operating range from UV to NIR. It thus permits access to vibrational mode information normally associated with wavelengths ranging from 2 – 200 μm . This makes Raman ideal for the study of inorganic materials that have vibrational frequencies in the far-infrared that are otherwise difficult to reach. Dispersive Raman microscopy using visible excitation wavelengths delivers 1 μm spatial resolution, and is widely used in the analysis of micron-level sample contaminants.

Raman spectrometers are based on one of two technologies: **dispersive Raman** and **Fourier transform Raman**. Each technique has its unique advantages and each is ideally suited to specific types of analysis.

Selecting an Instrument

Since most modern Raman instruments are purchased to be used as analytical tools, instrument design should focus on making Raman easy to use without compromising performance.

A well-designed instrument lets its user focus on results and not on having to become a Raman expert. The following list includes some of the things to look for:

Easy to Use

- Features such as autoexposure, smart backgrounds and autofocus rely on the instrument and software intelligence to optimize data collection parameters. This is analogous to the way that the expertise required to achieve professional-level photography has been embedded into digital cameras.
- Components such as lasers, gratings, Rayleigh filters and sampling accessories should be easy to exchange, either through automation and a mouse-click, or by employing SmartLock technology to ensure reproducible results. Smart components are readily recognized by the system software, their identities recorded for full traceability and the user is alerted if components are incompatible with each other.

Laser Safe

- Instruments where the user cannot be exposed to a direct laser beam are classified as Class I laser safe and can be used in open laboratories. Class IIIb laser-safe instruments have to be used in restricted environments in order to prevent inadvertent exposure to the laser beam and are therefore much less convenient to use.

High Performance

- High spatial resolution: one of the key reasons for purchasing a dispersive Raman microscope is to take advantage of its micron-level spatial resolution. In order to achieve this performance consistently, the instrument design must make it easy to maintain optimal alignment. The Thermo Scientific Nicolet™ Almega™ XR and Thermo Scientific DXR Raman microscope spectrometers employ a rapid, patented, software-driven alignment method that makes it easy to incorporate instrument alignment into routine laboratory maintenance procedures.
- Full spectral range: in order to take full advantage of the power and information content of Raman spectroscopy, spectrometers should cover the full spectral range; from 50 cm^{-1} at the low end to 3500 cm^{-1} at the high end of the spectrum.

Reproducibility: In the Past Raman had a Reputation for Poor Reproducibility, However this can be Addressed by Careful Design

- The excitation laser power can vary considerably from one laser to the next and from one instrument to the next. Incorporation of a laser power regulator that permits the user to specify and regulate the laser power at the sample eliminates this cause for non-reproducible Raman scattering intensity.
- Automatic intensity correction compensates for the wavelength dependence of the silicon CCD detector response and results in reproducible peak intensities whatever the excitation wavelength.
- X-axis non-reproducibility is the result of inadequate spectrograph and laser calibration. Automated, software-driven multipoint laser and spectrograph calibrations are essential for reliable instrument-to-instrument comparisons. This is particularly important for successful sample identification using library searching.
- Heterogeneous samples, such as tablets or powders will give non-reproducible results if the excitation laser spot size is smaller than the heterogeneous components. Sampling devices for these applications should be designed to raster over the surface of the sample so that the excitation beam and the Raman scatter are collected over a representative portion of the sample surface. The Thermo Scientific DXR SmartRaman employs VDPS (Variable Dynamic Point Sampling) technology to automate this.

Application scope of Raman spectroscopy

- Pharmaceutical industry
- Petrochemistry, industrial chemistry, polymers
- Material science
- Semiconductors, photovoltaic materials
- Life science (human, animal and plants : biology, biochemistry, biophysic, virus, tumour...)
- Geology and mineralogy, gemmology
- Nuclear science, isotopic effects
- Forensics sciences, forensic science laboratories : [see dedicated page](#)
- Art, archeology, paints, pigment, stained-glass windows, earthenwares, potteries, inks and many more.

Detailed data informations obtained from a Raman spectrum

- Lines position give informs about compound nature, by comparition with databases.
 - Variations of force constant

Strains induce a frequency shift from the standard value. If the material or the molécule is compressed, the frequency shift is positive. The force constant and the frequency increase, and vice versa.

- Isotopic effects

The isotopic effects concern the nucleus of atoms that make up the compound. Two atoms are called isotopes they have the same number of protons. The number of protons in the nucleus of an atom is designated by the atomic number. Two isotopes have the same atomic number. What distinguishes them is that they have a different atomic mass. The atomic mass of an atom is the number of nucleons that contains the nucleus of the atom. The atomic mass difference is due to a different number of neutrons N.

One can cite the example of the widespread natural carbon-12 ^{12}C and carbon-13 ^{13}C .

Raman spectroscopy can reveal the relative proportion of isotopes using the mass of each of them as has been shown a section of the harmonic oscillator. For the same vibration mode, there are as many lines in the Raman spectrum of the compound as there are isotopic combinations (2 isotopes = 3 combinations).

- Ratio between the various peaks intensity informs about the relative composition of the compound sample. With organized structures (like crystals), the ratio informs about directionnal effects (polarised measurements).
- Wide at half-maximum informs in general about the disorder factor, composition homogeneity or crystalline quality of a structured material.

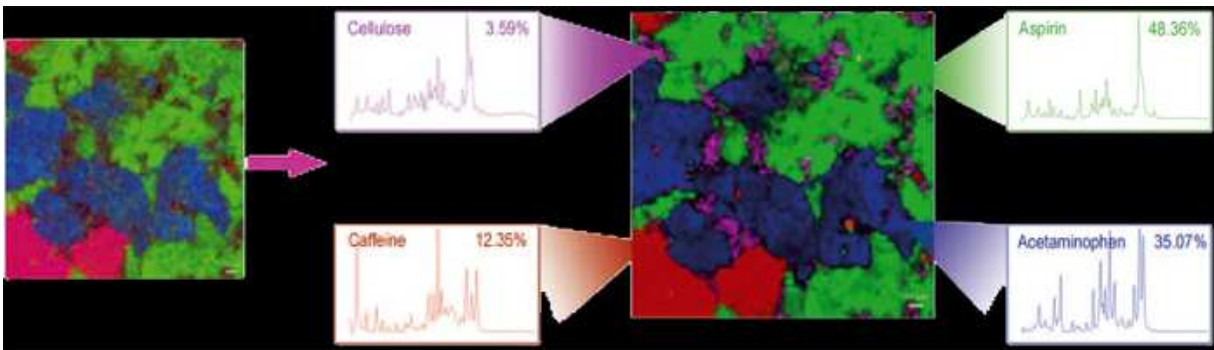
Mapping informations from Raman imaging

The new generation of confocal Raman microscopes offers a non-destructive and non-contact method of sample analysis at the sub-micron level.

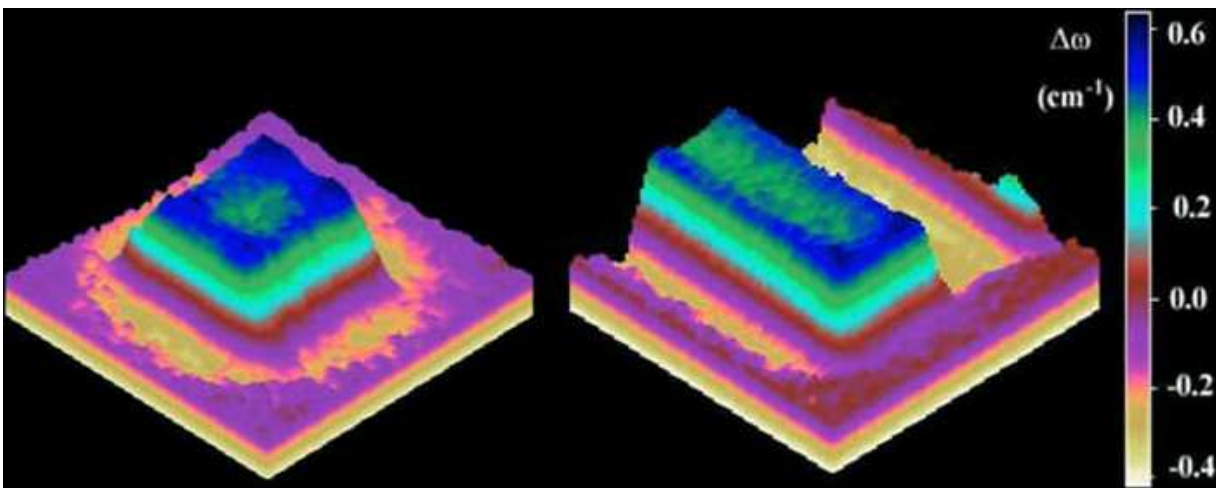
More particularly, Raman imaging provides the spatial distribution of the various molecular species within the sample, making it possible to produce fast and accurate chemical images.

- Chemical component distribution
- Phase mapping and polymorph identification
- Micro-analysis of stress and molecular orientation
- Identification of functional groups in organic and biological samples

According to the reported parameter : peak position, integrated intensities, width at half-maximum, Raman imaging informs about composition, stress, relative abundance or crystalline quality.



Raman image of a pharmaceutical tablet showing the spatial distribution of the different components and their corresponding Raman spectra.

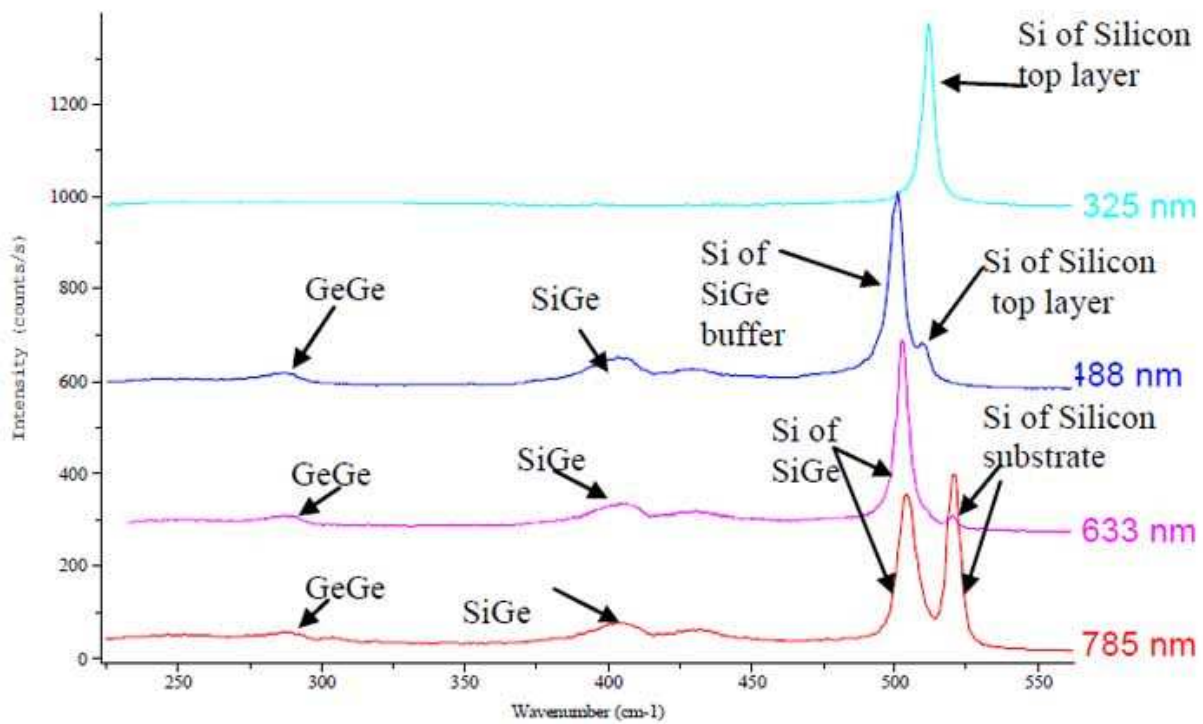


Shift of the silicon Raman peak, $\Delta\omega$, from the stress free frequency as a function of the position on 3 μm wide active square Si region (left) and line (right) isolated by PBLOCOS.

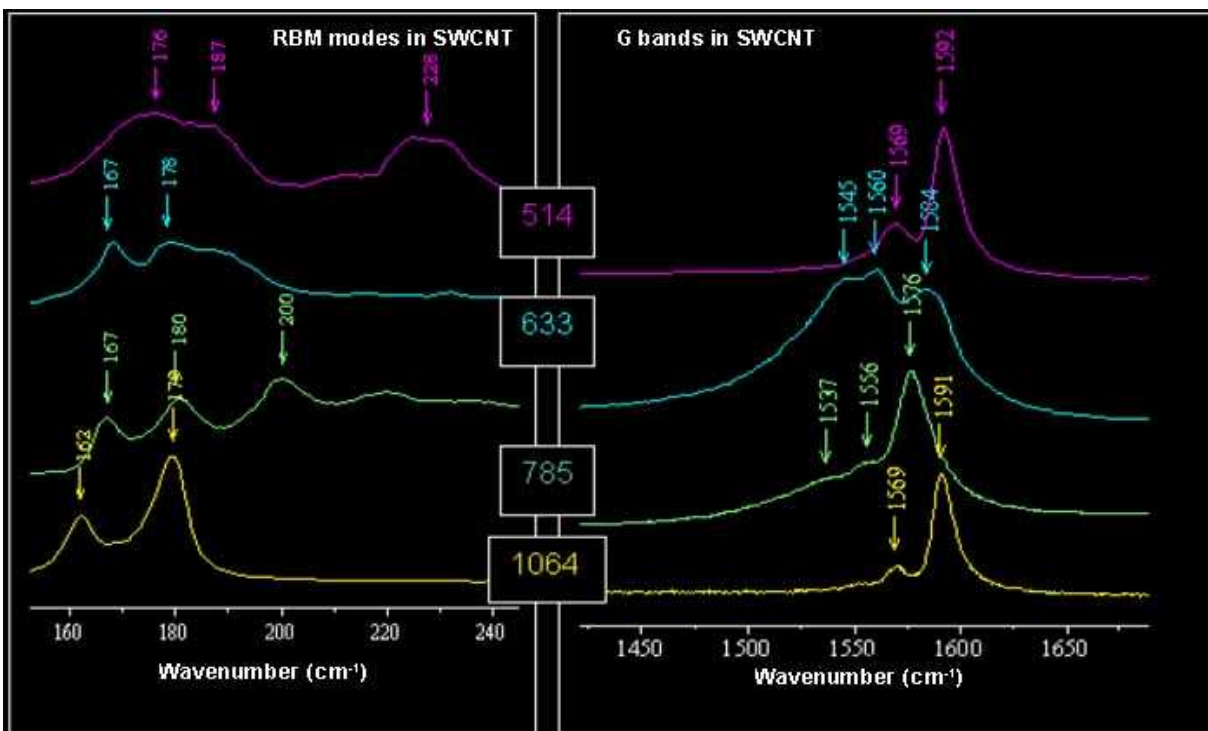
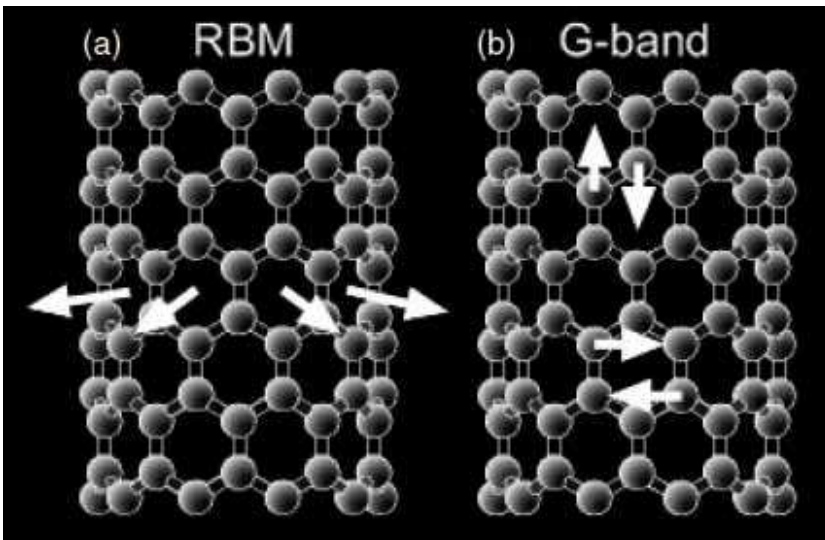
Combination with multiple laser wavelengths

Depth profiles and surface isolation are best resolved using the true confocal Raman microscope and multiple laser wavelengths.

Laser wavelength (nm)	Penetration depth in Si (nm)	Penetration depth in Ge (nm)
633	3000	32
514	762	19.2
488	569	19
457	313	18.7
325	~10	~9
244	~6	~7



Spectra recorded at 325, 488, 633 and 785 nm on structure of Si/SiGe/ on Si wafer. The relative Ge content in the constant $Si_{1-x}Ge_x$ layer is calculated from the visible Raman spectrum and the strain of the cap Si layer is derived from the UV Raman spectrum.



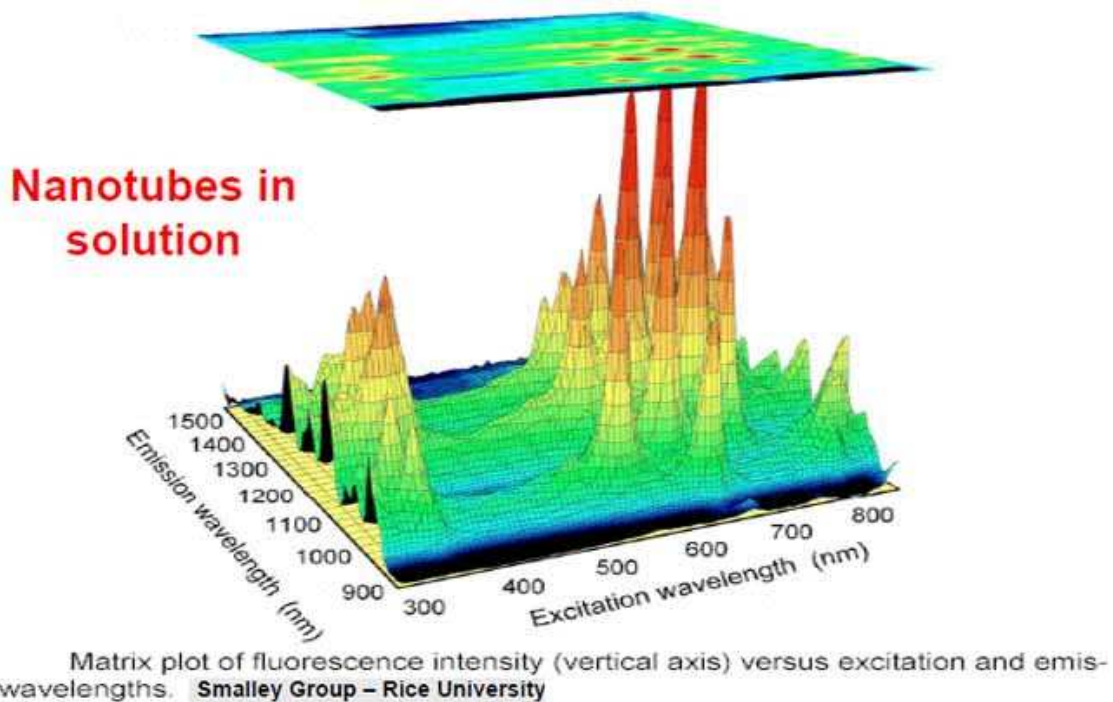
Carbon nanotube (SWCNT and MWCNT) characterisation by exciting at different wavelengths allows us sweep several resonance conditions to probe the range and distribution of SWCNT's diameters. Illustrated here are Radial Breathing modes and G bands of a SWCNT.

MicroRaman and microphotoluminescence laser induced

By the nature of the process, laser excitation induces not only Raman effect, but also photoluminescence characterized by lines, bands or continuum.

It is verified experimentally and theoretically that laser excitation by IR or red light induces less photoluminescence than visible or UV light.

Visible photoluminescence measured with a confocal Raman microprobe have similar advantages for spatial and spectral resolution as for microRaman.



The result of all this is that Raman effect and photoluminescence can be recorded simultaneously during the same laser shoot.

Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified. For instance, the vibrational frequencies of SiO , Si_2O_2 , and Si_3O_3 were identified and assigned on the basis of normal coordinate analyses using infrared and Raman spectra. The fingerprint region of organic molecules is in the (wavenumber) range $500\text{--}2000\text{ cm}^{-1}$. Another way that the technique is used is to study changes in chemical bonding, as when a substrate is added to an enzyme.

Raman gas analyzers have many practical applications. For instance, they are used in medicine for real-time monitoring of anaesthetic and respiratory gas mixtures during surgery.

In solid-state physics, spontaneous Raman spectroscopy is used to, among other things, characterize materials, measure temperature, and find the crystallographic orientation of a sample. As with single molecules, a given solid material has characteristic phonon modes that can help an experimenter identify it. In addition, Raman spectroscopy can be used to observe other low frequency excitations of the solid, such as plasmons, magnons, and superconducting gap excitations. The spontaneous Raman signal gives information on the population of a given phonon mode in the ratio between the Stokes (downshifted) intensity and anti-Stokes (upshifted) intensity.

Raman scattering by an anisotropic crystal gives information on the crystal orientation. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal, if the crystal structure (to be specific, its point group) is known.

Raman active fibers, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibers also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes. In nanotechnology, a Raman microscope can be used to analyze nanowires to better understand the composition of the structures.

Spatially offset Raman spectroscopy (SORS), which is less sensitive to surface layers than conventional Raman, can be used to discover counterfeit drugs without opening their packaging, and for non-invasive monitoring of biological tissue. Raman spectroscopy can be used to investigate the chemical composition of historical documents such as the Book of Kells and contribute to knowledge of the social and economic conditions at the time the documents were produced. This is especially helpful because Raman spectroscopy offers a non-invasive way to determine the best course of preservation or conservation treatment for such materials.

Raman spectroscopy is being investigated as a means to detect explosives for airport security.

Raman spectroscopy has also been used to confirm the prediction of existence of low-frequency phonons in proteins and DNA greatly stimulating the studies of low-frequency collective motion in proteins and DNA and their biological functions.

Raman reporter molecules with olefin or alkyne moieties are being developed to allow for tissue imaging with SERS-labeled antibodies.

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