(REVIEW ARTICLE)

Chemical analysis by laser-based Raman spectroscopy

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Abstract

Raman was first discovered by C.V. Raman and K.F. Krishnan in 1928.It is a spectroscopic technique based on inelastic scattering of monochromatic light usually- from a laser in the visible or near infra-red part of electromagnetic spectrum. It probes vibrational, modes of the molecule and crystals of solid,liquid, and gaseous samples.

t is commonly used in chemical analysis to provide a fingerprint by which molecules can be identified. At the time of its discovery from observing sunlight, obvious challenges were posed by the lack of a good Raman source, lack of a good detector, and by interference from fluorescence, which in some cases overwhelmed the Raman signal. The advent of laser made good for the deficiency of a good Raman source, multichannel detectors like Photodiode Arrays (PDA) or Charge - Coupled Devices (CCD) for a good detector and Fourier –transform for fluorescence.

In addition, instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are now used to reduce Rayleigh scattering and obtain high-qualityRaman spectra. Thus, Raman has become the optimal technique for versatile, minimally invasive spectroscopy.

Keywords: Laser Ray Keyword; Raman Spectroscopy; Keyword Chemometric Analysis; Raman Spectrum; Label Free

1. Introduction

The typical Raman system consists of four main components namely: excitation source (laser), sample interface, spectrometer (filter or wavelength selector) and detector (4). A good Raman laser should feature several different characteristics including narrow linewidth, small form factor, low power consumption and extremely stable power output with stable wavelength output. The second component is sample interface. A commonly used interface in Raman spectrometry is the fiber-optic probe which has important feature of high optical Raman density cut-off. Due to its flexibility, it can be easily adapted into a variety of sample chambers such as liquid flow cells, gas flow cells and optical microscope.

The third component is a spectrometer such as a notch filter to select and obtain the Raman spectrum of the sample. The major performance factors are high resolution, low noise, small form factor, and low power consumption.

The fourth component, detector, is chosen to match the excitation laser employed. For ultraviolet excitation, a photomultiplier tube (PMT) or Charged Coupled Detector is normally the best choice, whereas a standard Charged Coupled Detector is typically used for visible excitation and an indium gallium arsenide array for near infrared.

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2. Mechanism of Action

It is well established that about 99.99% of all the incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for the practical purpose of molecular characterization. Only about 0.001 % of the incident photons produces inelastic Raman scattering, an amount insignificant in magnitude but significant as a basic non-destructive technique (5). Inelastic scattering means that the frequency of the photons in the monochromatic light changes upon the interaction with the sample. Therefore, the photons of the laser light are absorbed by the sample and remitted. The frequency of the remitted photons is shifted upward (antiStokes, lower energy and higher frequency) and downward (Stokes, higher energy, and lower frequency) in comparison with the laser frequency and the Raman effect is observed (6). The Raman Effect is proportional to the third third-order nonlinear susceptibility. It is based on molecular deformations in the electric field determined by molecular polarizability. The laser beam is also considered as an oscillating electromagnetic wave, as it induces dipole moment that deforms the molecule upon interaction with the sample.

On this premise, the Raman spectra are dependent on the rovibronic (rotational and vibrational energy levels of the ground electronic state) states of the sample. Moreover, Raman scattering intensity is a function of Stokes and anti-

Stokes frequency shifts. Subsequently, the shift in energy provides information about the vibrational, rotational, and other low low-frequency transitions of the molecule. Of the two Raman active modes, Stokes is more commonly used as Raman measurement since electrons are in their ground vibrational state at room temperature.
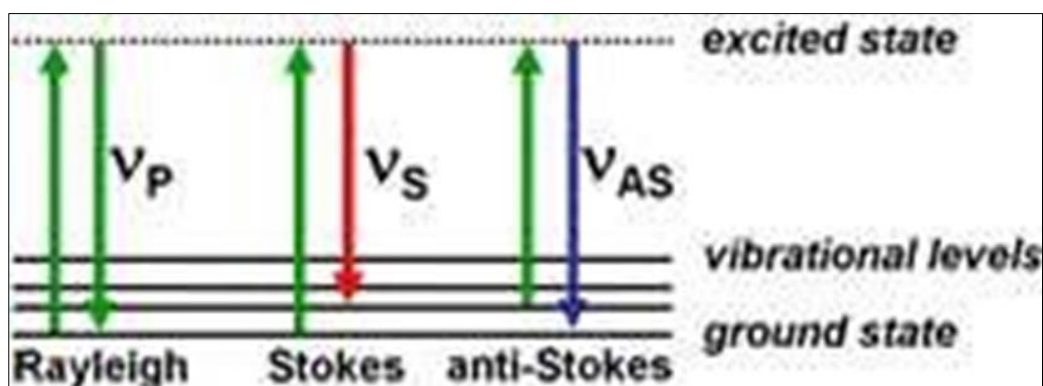

Figure 1 Raman process: light scatter with either no change in frequency (Rayleigh) or an increase (anti Stokes) or decrease (Stokes).

3. Drawback

Spontaneous Raman scattering is typically very weak (7). The main difficulty of Raman spectroscopy lies in separating the weak in elastically scattered light from the intense Rayleigh scattered laser light. More precisely, the major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect.

Commercially available interference (notch) filters are used which cut- off the spectral range of ± 80-120 cm-1 from the laser line (8). This method is efficient in stray light elimination. But it does not allow detection of low-frequency Raman modes in the range below 100 cm-1.

Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. Raman spectrometers typically use holographic gratings, which generally have a few manufacturing defects in their structure than the ruled ones. Stray light produced by holographic gratings is about one order of magnitude less intense than from the ruled gratings of the same groove density. Using multiple dispersion stage is another way of reducing stray light. Double and triple spectrometers allow Raman spectra to be taken without using notch filters. In such system Raman-active modes with frequencies as low as 3-5 cm-1 can efficiently detected.

Furthermore, several methods have been devised to enhance the intensity of the Raman scattered light. The main purpose is to enhance the sensitivity such as surface-enhanced Raman; to improve the spatial resolution, Raman microscopy; to acquire highly specific information, resonance Raman. There are also combinations of these techniques such as Surface-enhanced Resonance Raman spectroscopy , Hyper Resonance ,Tip- enhanced Raman Spectroscopy , Surface Plasmon Polarition Enhanced Raman Scattering Spectroscopy , Coherent antiStoke Raman Spectroscopy , Angle-Resolved Raman Spectroscopy , Spatially Offset Raman Spectroscopy , Stimulated Raman Spectroscopy (similar to Stimulated Emission) , Optical Tweezers Raman spectroscopy, Raman Optical Activity , Micro- cavity Substrate , Stand Off Remote Raman , Transmission Raman , Polarized Raman , Inverse Raman Spectroscopy and many more methods that are just emerging . All these make Raman to be a viable technique for a variety of different fields and applications.
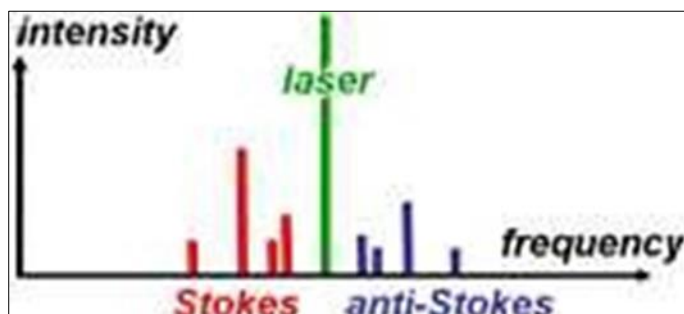

Figure 2 Raman Intensity

4. Potential Use

Chemical analysis by laser-based Raman spectroscopy provides every molecule or chemical species with its own characteristics Raman spectrum.

Therefore, it provides fingerprint by which the molecule can be identified. For instance, the vibrational frequencies of SiO, Si2O2, and Si3O3 were identified and assigned based on normal coordinate analyses using infrared and Raman spectra (8). Besides Raman spectroscopy is used to offer unparalleled advantages for chemical analysis. Being a non-destructive scattering technique, it typically does not require sample sectioning and fixing. Raman spectra can be collected from an extremely small volume (< 1 μm in diameter). These spectra allow the identification of species present in that volume.

Water does not generally interfere with Raman spectral analysis – unlike Fournier Transform Infrared Spectroscopy. It is insensitive to aqueous absorption bands. Thus, Raman spectroscopy is suitable for the microscopic examination of minerals, materials such as polymers and ceramics, cells, proteins, and forensic trace evidence. Apart from the advantage of speed – a typical analysis requires only a few seconds - Raman also has advantage of fast analysis time. Raman technique is highly selective being able to differentiate between molecules in chemical species that are very similar. In addition, polarization analysis of Raman-scattered light contains useful information. The spectral information arising from this analysis gives insight into molecular orientation and vibrational symmetry. In essence, it allows the user to obtain valuable information relating to the molecular shape, for example in synthetic chemistry or polymorph analysis. It is often used to understand macromolecular orientation in crystal lattices, liquid crystals, or polymer samples (9). In comparison with the complementary spectroscopy technique, Raman spectra are ``"cleaner`` " than mid – infra red spectra. Raman bands are narrower, and overtone and combination bands are generally weak. Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infra-red spectrum (10).

Energy-level diagram Figure 3 showing the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

5. Chemometric Analysis

Data derived from Raman spectra are interpreted by chemo metric analysis. Chemo metrics software uses mathematical and statistical models to obtain chemical or spectral data.

Thereby provides information for qualitative and quantitative analysis. For qualitative information, correlation analysis is applied for material identification and/or verification. It involves the use of built-in databases of known standards for

identification of unknowns. Quantitative information can also be obtained by multivariate analysis of complex systems with large data sets. This allows hidden trends and outliers of the classifications to be uncovered. Moreover, it is possible to develop prediction response in unknown sets. Thus, constructing a calibration curve for identification of unknown concentration provides information for optimal experimental design. A typical example is BWID qualitative software, which is used for development of spectral libraries or databases. It also provides subsequent identification of unknowns.

BWID enables preprocessing of some data with use of baseline corrections, sample smoothing, derivatives, and others. After this, methods or models using partial least square algorithms are developed to predict unknowns.

6. Conclusion:

Label free vibrational spectroscopy is invaluable to chemical analysis. Raman spectroscopy offers preferable option without staining for scattering and identification of fingerprint of chemical sample. Finally its non-destructive chemical analysis characteristics will enable wide applications in the industry for provision of detailed information on chemical structure, crystallinity and molecular interactions in the foreseeable future.

Compliance with ethical standards

Acknowledgments

Disclosure of conflict of interest

The authors declare no conflicts of interest regarding publication for this paper.

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