Princeton Instruments

Raman Spectroscopy Basics

Introduction

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

1. Origins of Raman

The Raman effect is based on molecular deformations in electric field E determined by molecular polarizability α. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency υ_m.
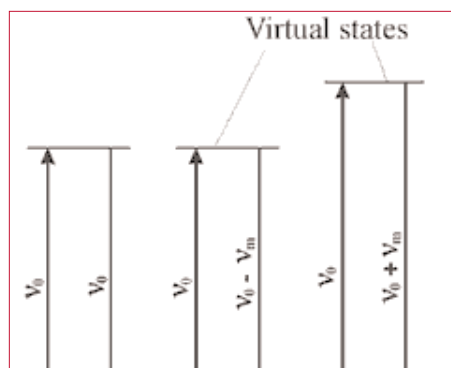

Figure 1: Raman transitional schemes

Amplitude of vibration is called a **nuclear displacement**. In other words, monochromatic laser light with frequency υ_0 excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (Fig.1) when:

1. A molecule with no Raman-active modes absorbs a photon with the frequency υ_0. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency υ_0 as an excitation source. This type if interaction is called an elastic **Rayleigh scattering**.

2. A photon with frequency υ_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency υ_m and the resulting frequency of scattered light is reduced to $\upsilon_0 - \upsilon_m$. This Raman frequency is called Stokes frequency, or just "**Stokes**".

3. A photon with frequency υ_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Ramanactive mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\upsilon_0 + \upsilon_m$. This Raman frequency is called Anti-Stokes frequency, or just "**Anti-Stokes**".

...SEE the Future

About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $\upsilon_0 \pm \upsilon_m$. Spontaneous Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering. Instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are used to reduce Rayleigh scattering and obtain high-quality Raman spectra.

2. Instrumentation

A Raman system typically consists of four major components:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample.

Since spontaneous Raman scattering is very weak the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. 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 close 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. People use commercially available interference (notch) filters which cut-off spectral range of $\pm$ 80-120 cm^{-1} from the laser line. 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 normally have much less manufacturing defects in their structure then the ruled once. Stray light produced by holographic gratings is about an order of magnitude less intense then from ruled gratings of the same groove density.

Using multiple dispersion stages is another way of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In such systems Raman-active modes with frequencies as low as 3-5 cm^{-1} can be efficiently detected.

In earlier times people primarily used single-point detectors such as photon-counting Photomultiplier Tubes (PMT).   However, a single Raman spectrum obtained with a PMT detector in wavenumber scanning mode was taking substantial period of time, slowing down any research or industrial activity based on Raman analytical technique. Nowadays, more and more often researchers use multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD) to detect the Raman scattered light. Sensitivity and performance of modern CCD detectors are rapidly improving. In many cases CCD is becoming the detector of choice for Raman spectroscopy.

3. Ways to improve Raman signal intensity

Raman signal is normally quite weak and people are constantly improving Raman spectroscopy techniques.   Many different ways of sample preparation, sample illumination or scattered light detection were invented to enhance intensity of Raman signal. Here we will examine some of them.

3.1. Stimulated Raman

It was found that if the sample was irradiated with a very strong laser pulse, new "non-linear" phenomena were observed in Raman signal. In comparison with continuous wave (CW) lasers with electric field of about only 10^4 V·cm^{-1} pulsed lasers with electric field of about 10^9 V·cm^{-1} transform a much larger portion of incident light into useful Raman scattering and substantially improve signal-to-noise ratio.
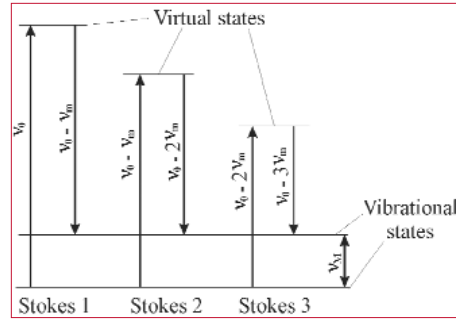
Figure 2: Stimulated Raman transitional schemes

Stimulated Raman scattering is an example of "non-linear" Raman spectroscopy. Very strong laser pulse with electric field strength > 10^9 V·cm^{-1} transforms up to 50% of all laser pulse energy into coherent beam at Stokes frequency $\upsilon_0 - \upsilon_m$ (Fig. 2). The Stokes beam is unidirectional with the incident laser beam. Only the mode um which is the strongest in the regular Raman spectrum is greatly amplified. All other, weaker Ramanactive modes are not present. The Stokes frequency is so strong it acts as a secondary excitation source and generates the second Stokes line with frequency $\upsilon_0 - 2\upsilon_m$. The second Stokes line generates the third one with the frequency $\upsilon_0 - 3\upsilon_m$ etc. Stimulated Raman technique enjoys 4-5 orders of magnitude enhancement of Raman signal as compared to the spontaneous Raman scattering.

3.2. CARS
Coherent Anti-Stokes Raman, CARS, is another type of "non-linear" Raman spectroscopy. It stands for Coherent Anti-Stokes Raman Spectroscopy. Instead of the traditional one laser, two very strong collinear lasers irradiate a sample. Frequency of the first laser is usually constant, while the frequency of the second one can be tuned in a way that the frequency difference between the two lasers equals exactly the frequency of some Raman-active mode of interest. This particular mode will be the only extremely strong mode in the Raman signal.

With CARS we can obtain only one strong Raman peak of interest. In this case a monochromator is not really required. A wideband interference filter and a detector behind the filter would do the job. Below is more specific description with a little bit of math to understand CARS more in depth.

Figure 3: Transitional scheme for CARS

Two laser beams with frequencies υ_1 and υ_2 ($\upsilon_1 > \upsilon_2$) interact coherently, and because of the wave mixing, produce strong scattered light of frequency $2\upsilon_1 - \upsilon_2$ (Fig. 3). If the frequency difference between two lasers $\upsilon_1 - \upsilon_2$ is equal to the frequency um of a Raman-active rotational, vibrational or any other mode then a strong light of frequency $\upsilon_1 + \upsilon_m$ is emitted.

In other words, to obtain strong Raman signal the second laser frequency should be tuned in a way that $\upsilon_2 = \upsilon_1 - \upsilon_m$. Then the frequency of strong scattered light will be $2\upsilon_1 - \upsilon_2 = 2\upsilon_1 - (\upsilon_1 - \upsilon_m) = \upsilon_1 + \upsilon_m$, which is higher then the excitation frequency u1 and therefore considered to be Anti-Stokes frequency.
Coherent Anti-Stokes Raman Spectroscopy derives its name from the fact that it uses two **Coherent** laser beams and the resulting signal has **Anti-Stokes** frequency.

The SERRS technique, Surface-Enhanced Resonance Spectroscopy, was developed because of such complications. It utilizes both Surface-Enhancement effect and Raman Resonance effect so the resulting enhancement in Raman signal intensity can be as high as 10^{14}. The main advantage of SERRS is its spectra resemble very much regular Resonance Raman spectra, which makes it much easier to interpret.

About Princeton Instruments

Over the past two decades, Princeton Instruments (PI) has been the leading pioneer of high-performance detection systems for spectroscopy. PI's innovations include the world's first spectroscopy camera to use a photodiode array (and later, the first to use a CCD), as well as the introduction of the first high-performance, gated, intensified CCD camera. In addition to breaking new ground in the field of spectroscopy, PI has also designed the highest-sensitivity CCD cameras available for scientific imaging applications (read noise of approximately 2 e- rms with quantum efficiency eclipsing 90%). Today, Princeton Instruments continues to expand the boundaries of technology:

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