

Stimulated Raman Spectroscopy

1. Introduction

The Raman effect, discovered in 1928 by Sir Chandrasekhara Venkata Raman is an inelastic scattering of light by elementary excitations of matter¹⁻². As illustrated in Fig. 1a, an incident photon is annihilated and a new photon of a different frequency is created. This implies that scattering is inelastic and the medium is left in a different energy state.



Fig. 1. Schematic diagram of (a) Spontaneous Raman scattering and (b) stimulated Raman scattering.

When the scattered photon is lower in energy, or frequency, it is said to be Stokes shifted. The shift in frequency of the Stokes is related to the characteristic of the medium. This is illustrated in Fig. 2. Calling this material characteristic frequency ω_v , the Stokes frequency is then $\omega_S = \omega_p - \omega_v$. The Raman Stokes scattering results in an excitation from the ground state of the medium to an excited state mediated by a two photon inelastic scattering. If the material is already in the excited state (e.g. by thermal excitation), then the scattered photon can be higher in energy and is called anti-Stokes photon (Fig. 2). The probability of the anti-Stokes scattering is smaller than that of Stokes by a Boltzmann factor $\exp(-\hbar\omega_v/k_B T)$.

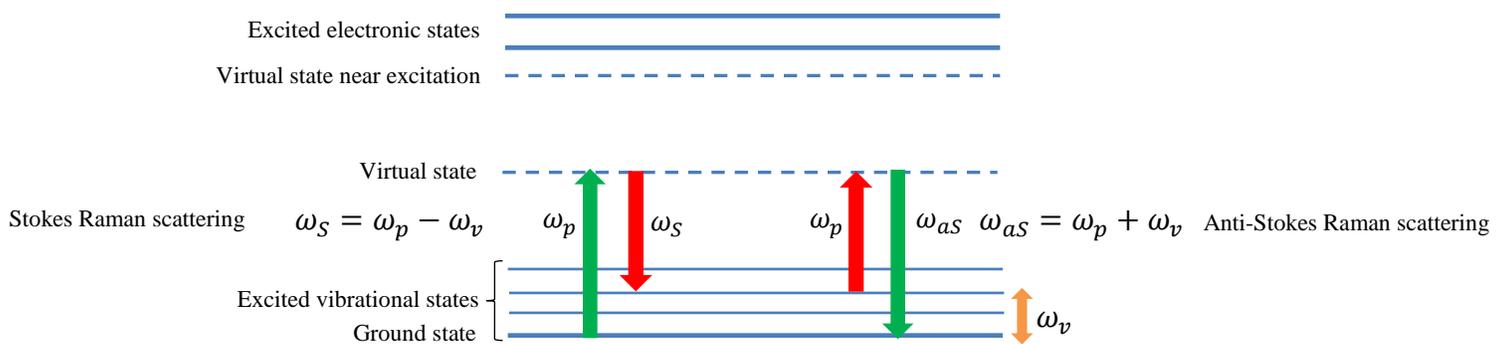


Fig. 2. Mechanism of Raman Scattering.

Stimulated Raman scattering (SRS) involves the incident of both Stokes and laser photons as depicted in Fig. 1b. The result is the stimulation of an additional Stokes photon coherent with the incident Stokes photons. Thus the Stokes photon field experiences gain. As in spontaneous Raman scattering, SRS leaves the medium in excited state.

2. Stimulated Raman Scattering Described by Nonlinear Polarization¹⁻²

SRS can be characterized by the imaginary part of a complex third-order nonlinear susceptibility of the form $\chi_S(\omega_S = \omega_S + \omega_p - \omega_p)$ for the Stokes interaction and one of the form $\chi_{aS}(\omega_{aS} = \omega_p + \omega_p - \omega_{aS})$ for the anti-Stokes interaction. The scattering of light may be thought of as the redirection of light that takes place when an electromagnetic (EM) wave (i.e. an incident light ray) encounters an obstacle or inhomogeneity, in our case the scattering material (solid, liquid or gas). As the EM wave interacts with the matter, the electron orbits within the constituent molecules are perturbed periodically with the same frequency (ω_p) as the electric field of the incident wave. The oscillation or perturbation of the electron cloud results in a periodic separation of charge within the molecules, which is called an induced dipole moment. The oscillating induced dipole moment is manifest as a source of EM radiation, thereby resulting in scattered light. The majority of light scattered is emitted at the identical frequency (ω_p) of the incident light, a process referred to as elastic scattering (Brillouin scattering). However, as explained above, additional light is scattered at different frequencies, a process referred to as inelastic scattering (Raman scattering).

The theoretical background of SRS is well understood¹⁻² and will not be discussed here. In a classical model, assuming that the optical polarizability of the molecule is not constant and depends on the inter-nuclear separation, the third order Raman susceptibility of the Stokes frequency is given by¹,

$$\chi_S(\omega_S = \omega_S + \omega_p - \omega_p) = \frac{\epsilon_0(N/6m_e)(\partial\alpha/\partial q)_0^2}{\omega_v^2 - (\omega_p - \omega_S)^2 + 2i(\omega_p - \omega_S)\gamma} \quad (1)$$

Where, N is the number density of molecules, m_e is the mass of electron, $(\partial\alpha/\partial q)_0$ is the first term in a Taylor series expansion of optical polarizability about the equilibrium point and γ is the phenomenological damping coefficient. Near the Raman resonance ($\omega_S \approx \omega_p - \omega_v$), the Raman Susceptibility can be approximated as,

$$\chi_S(\omega_S = \omega_S + \omega_p - \omega_p) = \frac{\epsilon_0(N/12m_e \omega_v)(\partial\alpha/\partial q)_0^2}{[\omega_S - (\omega_p - \omega_v)] + i\gamma} \quad (2)$$

The real and imaginary parts of $\chi_S(\omega_S) = \chi_R(\omega_S) + i\chi_I(\omega_S)$ are depicted in Fig. 3.

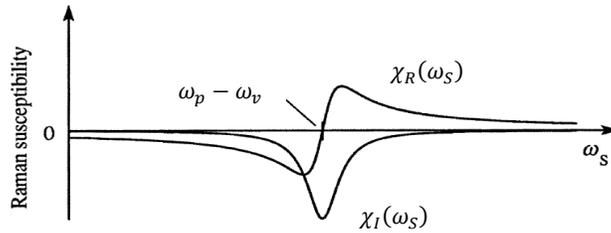


Fig. 3. Resonance structure of the Raman susceptibility.

Note that at the exact Raman resonance ($\omega_S = \omega_p - \omega_v$), Raman susceptibility is negative imaginary ($1/i = -i$) which accounts for the gain of the Raman field. The spatial evolution of the amplitude of the Stokes wave, A_S , can be evaluated using nonlinear susceptibility as follows,

$$\frac{dA_S}{dz} = -\alpha_S A_S \quad \text{where} \quad \alpha_S = -3i \frac{\omega_S}{n_S C} \chi_S(\omega_S) |A_p|^2 \quad (3)$$

Since the imaginary part of $\chi_S(\omega_S)$ is negative, the Stokes wave experiences exponential growth.

SRS is strictly a Stokes generation process. However, in practice, coherent anti-Stokes photons are also produced, sometimes in nearly equal amounts as Stokes photons. The anti-Stokes generation can be understood in terms of third order nonlinear optics and a four-wave mixing process. As the Stokes wave is amplified along its path, it can be recombined with the pump laser to produce the anti-Stokes component using $\chi_{aS}(\omega_{aS} = \omega_p + \omega_p - \omega_{aS})$.

3. Photoacoustic Raman Spectroscopy (PARS)³⁻⁴

The photoacoustic (PA) effect⁵⁻⁸ is the process of acoustic wave generation in a sample resulting from the absorption of photons. This process was first invented by A. G. Bell, in 1880⁶. Sunlight was focused onto a sample contained in a cell that was connected to a listening tube. When the sunlight was repeatedly blocked and unblocked, sound could be heard through the listening tube at the sunlight chopping frequency. The technique saw few applications until about 1968 when a rise in its use began due to the availability of laser sources. It has since been used to study a variety of chemical and physical phenomena in a number of fields. Some of the applications are trace analysis, spectroscopy of weak optical transitions, and probing of optically thick samples.

The basic theory behind photoacoustic detection is quite simple. Light absorbed by a sample will excite a fraction of the ground-state molecular population into higher energy levels. These excited states will subsequently relax through a combination of radiative and nonradiative pathways. The nonradiative component will ultimately generate heat in the localized region of the excitation light beam and generate a pressure wave that propagates away from the source. The pressure wave is then detected with a suitable sensor such as a microphone used for a gaseous sample. Photoacoustic detection is unique in that it is a direct monitor of the nonradiative relaxation channel and, hence, complements absorption and fluorescence spectroscopic techniques. It is also an extremely sensitive technique, with the ability to detect highly forbidden optical transitions and trace components in a mixture. The basic experimental arrangement is illustrated in Fig. 4.

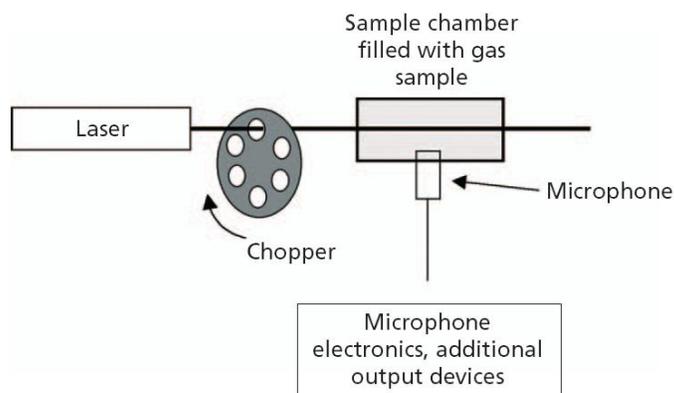


Fig. 4. General experimental setup for performing photoacoustic spectroscopy on a gas.

Photoacoustic Raman spectroscopy (PARS) is a nonlinear spectroscopic technique. The first experimental demonstration of the PARS technique was accomplished using low-power cw laser excitation of a gaseous sample³. As mentioned above, photoacoustic techniques are based on the direct absorption of light in the sample; however, the PARS technique is different because the light is not absorbed by the sample. Population of the upper energy level of a transition is accomplished by a stimulated Raman process rather than by direct absorption. This stimulated Raman excitation requires the simultaneous illumination of the sample by two laser beams whose frequencies differ by a Raman transition frequency. The conditions required for this process are that (1) the transition involving the initial and final energy levels must be Raman active, i.e., the transitions must involve a change in the molecular polarizability, and (2) the frequency difference of the two incident laser beams must be adjusted to equal the

frequency of this Raman-active transition. This makes PARS a particularly attractive analytical technique for studying molecules that have no infrared spectrum. The PARS process is shown schematically in Fig. 5.

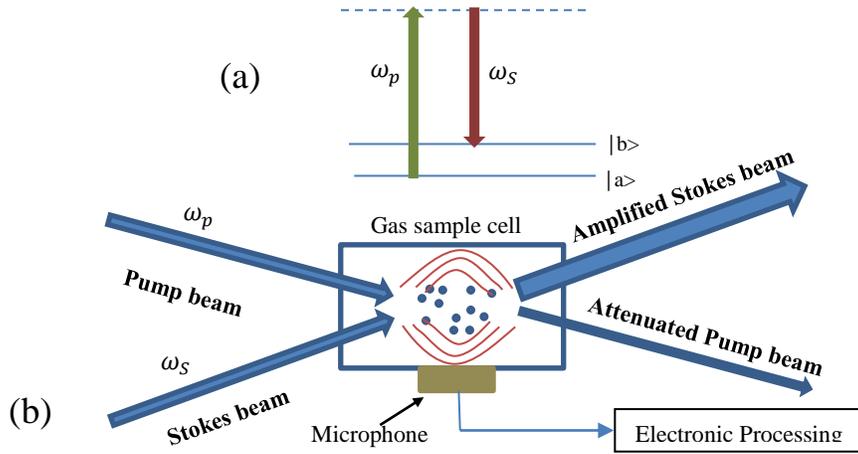


Fig. 5. Schematic representation of the PARS process. (a) An energy level diagram for a Raman-type process involving the interaction of pump and Stokes (b) Schematic representation of the arrangement for generating a PARS signal in a gas. The pump and Stokes beams are overlapped spatially and temporally in the gas sample. When the frequency difference $\omega_p - \omega_s$ equals a Raman frequency of the gas, amplification of the Stokes beam and attenuation of the pump beam occurs, and the molecular population of the upper energy level |b> is increased. Relaxation of these excited molecules by vibration-translation (V-T) processes results in the generation of an acoustic wave that is detected by a microphone.

It has been shown⁴ that the acoustic power due to the pressure change in the gas sample as a result of vibrational transitions of Raman active medium is proportional to the imaginary part of the $\chi_S(\omega_S)$ and is given by,

$$P_a = (\gamma - 1) \left(\frac{\omega_p}{\omega_s} \right) z P_S(0) G_S \quad (4)$$

Where G_S is the Stokes gain coefficient and is given by,

$$G_S = -6 \left(\frac{\omega_s}{n_S c} \right) \text{Im}[\chi_S(\omega_S = \omega_s + \omega_p - \omega_p)] \quad (5)$$

PARS has successfully been demonstrated on a wide range of gases and trace detections in the order of parts per million (ppm) is obtained.

4. References

- [1] R. W. Boyd, *Nonlinear Optics 3rd ed.* Academic Press 2008
- [2] R. L. Sutherland, *Handbook of Nonlinear Optics (Chapter 12)*, Marcel Dekker Inc. 1995
- [3] J. J. Barrett and M. J. Berry, *Appl. Phys. Lett.* 34, 144-146 (1979)
- [4] J. J. Barrett and D. F. Heller, *J. Opt. Soc. Am.* 71, 1299-1308 (1981)
- [5] G. A. West, J. J. Barrett, D. R. Siebert and K. V. Reddy, *Rev. Sci. Instrum.* 54, 797-817 (1983)
- [6] A. G. Bell, *Philos. Mag.* 11,510 (1881).
- [7] A. Rosencwaig, *Photoacoustic and Photoacoustic Spectroscopy*, John Wiley & Sons 1980
- [8] Yoh-Han Pao (Editor), *Optoacoustic Spectroscopy and Detection*, Academic Press 1977