Stimulated Raman Spectroscopy overview

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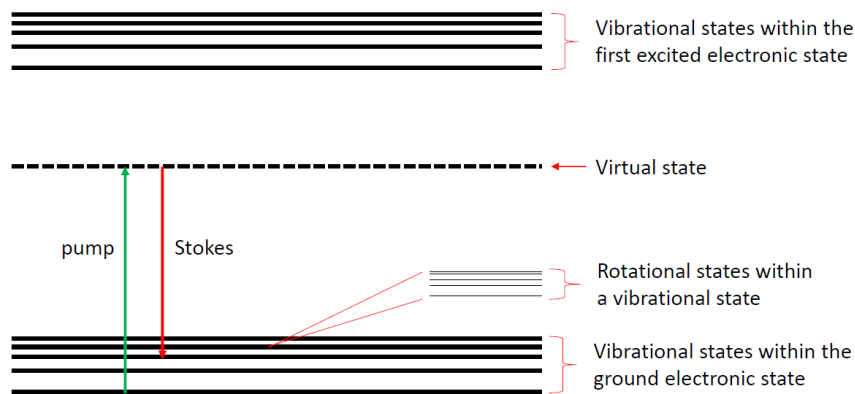
Stimulated Raman spectroscopy, also referred to as Stimulated Raman scattering (**SRS**) is a form of spectroscopy employed in physics, chemistry, biology, and other fields. The basic mechanism that lies in the basis of SRS resembles that of spontaneous Raman scattering: a pump photon, of the angular frequency ω_p, which is scattered by a molecule has some small probability of inducing some rovibrational transition, as opposed to inducing a simple Rayleigh transition. This will then result with the molecule emission of a photon in a shifted color. However, SRS, as opposed to spontaneous Raman spectroscopy, is a third-order non-linear phenomenon involving a second photon – the Stokes photon of angular frequency ω_S which stimulates a specific transition. When the difference in frequency between both photons (ω_p-ω_S) resembles that of a specific rovibrational transition (Ω) the occurrence of this transition is resonantly enhanced. In SRS, the signal is equivalent to changes in the intensity of the pump and Stokes beams. Employing a pump laser beam of a constant frequency and a Stokes laser beam of a scanned frequency (or vice versa) allows for the unravelling of the spectral fingerprint of the molecule. This spectral fingerprint differs from those obtained by other spectroscopy methods such as Rayleigh scattering as the Raman transitions obey to different exclusion rules than those apply for Rayleigh transitions.

History .

The phenomenon of SRS was discovered by an accident by Woodbury and Ng in 1962. In their experiment, they've introduced a cell with nitrobenzene into a ruby laser cavity. This resulted with a strong emission at a wavelength that could not be associated with the characteristic wavelengths of the ruby gain medium. At first, this was explained as some fluorescence/luminescence emission. Only at a later stage, that this was interpreted correctly as the first experimental observation of SRS. A year later, Garmier et al introduced a two-wave mixing framework for the description of SRS. These pioneering works has opened a new avenue of research and were followed by many theoretical and experimental works in the field of SRS.

Qualitative description of SRS .

The principle of SRS can be quiet intuitively understood by adopting the quantum mechanical description of the molecule's energy levels. Initially, the molecule lies in the ground state, that is, the lowest energy level. Then, it simultaneously scatters both pump and Stokes photons which then results with the occurrence of a rovibrational transition with some probability. The transition can be thought of as a two-step transition where in the first step the molecule is excited by the pump photon to a virtual state and in the second it is relaxed into a rovibrational state other than the ground state (but allowed by the Raman transitions rules). The virtual state, which is actually a superposition of probability tails of real states, cannot be occupied by the molecule. However, for a simultaneous scattering of two photons, it might provide a coupling route between the initial and final states. When the energy difference between both pump and Stokes photons matches the energy difference between some rovibrational state and the ground state, the probability for a transition due to this stimulated process is enhanced greatly by order of magnitudes.

Vibrational states within the first excited electronic state

Virtual state

pump   Stokes

Rotational states within a vibrational state

Vibrational states within the ground electronic state

Quantitative description of SRS

Each photon that undergoes SRS is shifted in color from pump to Stokes color. Thus, the SRS signal is proportional to the decrease or increase in the pump or Stokes beams intensities, respectively. These changes in the beams intensities are described by the following rate equations

$$\begin{cases} \dfrac{dI_S}{dz} = g_R I_p I_S - \alpha I_S, & (1a) \\ \dfrac{dI_p}{dz} = -\dfrac{\omega_p}{\omega_S} g_R I_p I_S - \alpha I_p, & (1b) \end{cases}$$

where, I_p and I_S are the pump and Stokes beams intensities, respectively, ω_p and ω_S are the pump and Stokes angular frequencies, respectively, z is the coordinate along which the beams propagate, g_R is the Raman gain coefficient, its typical values are in the order of 10^-30[cm^2/molecule*sr], and α is the lose coefficient. The lose coefficient is an effective coefficient that might account for loses due to a variety of processes such as Rayleigh scattering, Absorption, etc. Eq. 1a describes the change in Stokes beam intensity along the SRS interaction length. The first term on the right hand side is equivalent to the amount of intensity gained by the Stokes beam due to SRS. As SRS involves both beams, this term is dependent both on I_p and I_S. The second term is equivalent to the amount of intensity lost and is thus dependent only on I_S . Eq. 2a describes the change in pump beam intensity, its form is quite similar to that of Eq. 1a. The first term on its right hand side equals its counterpart from Eq. 1a up to a multiplicative factor of $-\omega_p/\omega_S$. This factor reflects the fact that each photon (as opposed to intensity units) lost from the pump beam due to SRS is gained by the Stokes beam.

In most cases, the parameters\experiment conditions support two simplifying assumptions:

I.   Photon lose along the Raman interaction length is negligible. Mathematically this corresponds to $\dfrac{\alpha}{g_R} \ll I_p, I_S$.

II.   The change in beams intensity is linear. Mathematically this corresponds to $g_R * z * Max(I_p, I_S) \ll 1$.

Upon these assumptions, the SRS signal, that is, the intensity changes in pump and Stokes beams is approximated by

$$\begin{cases} \Delta I_S \simeq g_R I_{p,0} I_{S,0} \Delta z, & \text{(2a)} \\ \Delta I_p \simeq -\dfrac{\omega_p}{\omega_S} g_R I_{p,0} I_{S,0} \Delta z, & \text{(2b)} \end{cases}$$

where $I_{p,0}$ and $I_{S,0}$ are the initial pump and Stokes beams intensities, respectively, and Δz is the total length over which SRS interaction occurs. In many cases, this length can be evaluated in a similar fashion to the evaluation of the Rayleigh length as $\Delta z = 4\pi n \omega_0^2/(\lambda_p + \lambda_S)$. Here, n and ω_0 are the averaged refractive index and waist, respectively, and λ_p and λ_S are the pump and Stokes wavelengths, respectively.

Each molecule has some characteristic Raman shifts, each associated with a specific rovibrational transition of the molecule. The relation between a Raman shift, $\Delta\omega$, and the pump and Stokes photon wavelengths is given by

$$\Delta\omega[\text{cm}^{-1}] = \left(\frac{1}{\lambda_p[\text{nm}]} - \frac{1}{\lambda_S[\text{nm}]} \right) \times \frac{[10^7 \text{nm}]}{[\text{cm}]} \qquad \text{(3)}$$

When the difference in wavelengths between both lasers is close to some Raman transition, the Raman gain coefficient receives values of the order of 10^-30[cm^2/molecule*sr] resulting with an efficient SRS. As this difference starts to differ from a specific Raman transition the value of the Raman gain coefficient drops down and the process becomes increasingly less efficient and less detectable.

An SRS experimental setup includes two laser beams (usually co-linear) of the same polarization, one is employed as pump and the other as Stokes. Usually, at least one of the lasers is pulsed. This modulation in the laser intensity helps to detect the signal, furthermore, it helps to increase the signal's amplitude which also helps with detection. Designing the experimental setup, one has a great liberty when choosing the pump and Stokes lasers as the Raman condition (Eq.3) applies only on the difference in wavelengths. Typical choice of SRS lasers will include a set of two near IR lasers.

Comparison to other Raman spectroscopy variants

Since SRS is a resonantly enhanced process, its signal is several orders of magnitude higher than that of a spontaneous Raman scattering making it a much more efficient spectroscopic tool. Furthermore, the signal intensity of SRS is also several orders of magnitude higher than another highly common sort of spectroscopy – coherent anti-Stokes Raman spectroscopy. SRS involves only two photons as opposed to the latter which involves three photons. Thus, the occurrence of SRS is more probable and results with a higher signal. There are two additional prominent variants of spontaneous Raman spectroscopy – surface-enhanced Raman spectroscopy and resonance Raman spectroscopy. The former is designated for Raman spectroscopy of molecules adsorbed on rough surfaces such as metal surfaces or nanostructures where it magnifies the Raman signal by many orders of magnitude[1a]. The later corresponds to a spontaneous Raman scattering process which is performed by a laser with a frequency close to the electronic transition of the subject in study. This may result with a great amplification of the signal. However, it requires the use of highly powerful UV or X-ray lasers that might cause photodegradation and might also induce fluorescence.

Applications

SRS is employed in various applications from a wide verity of fields. All applications utilize the ability of SRS to detect the rovibrational spectral signature (or some of it) of the subject in study. Here are some examples:

- **Study of molecular conformational structures**. Works in this field were done both in the Cina and Bar groups. Each conformer is associated with a slightly different SRS spectral signature. Detection of these different landscapes is an indication of the different conformational structures of the same molecule.
- **Material composition analysis**. This is done in optiQGain LTD. Here, the SRS signal dependency on the concentration of the material is utilized. Measuring different SRS signals, associated with the different materials in the composition, allow for the determination of the stochiometric relations of the composition.
- **SRS imaging**. This technique is mostly employed for living tissue as it allows a non-invasive label-free imaging. In this method, pioneered by the Xie group, a construction of an image is obtained by preforming SRS measurements over some grid, where each measurement adds a pixel to the image.
- **Ultrafast microscopy.** Employing femtosecond laser pulses, as was done in the Katz, Silberberg, and Xie groups, allows for an instant generation of a very large portion of the spectral signature by a single laser pulse. The broad signal is a result of the width of the laser band as dictated by the uncertainty principle which determines an inverse proportion between the uncertainty in time and uncertainty in frequency. This method is far faster than traditional microscopy methods as it circumvents the need in preforming long time-consuming frequencies scanning.