

Basic principles of ultrafast Raman loss spectroscopy[#]

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Abstract. When a light beam passes through any medium, the effects of interaction of light with the material depend on the field intensity. At low light intensities the response of materials remain linear to the amplitude of the applied electromagnetic field. But for sufficiently high intensities, the optical properties of materials are no longer linear to the amplitude of applied electromagnetic field. In such cases, the interaction of light waves with matter can result in the generation of new frequencies due to nonlinear processes such as higher harmonic generation and mixing of incident fields. One such nonlinear process, namely, the third order nonlinear spectroscopy has become a popular tool to study molecular structure. Thus, the spectroscopy based on the third order optical nonlinearity called stimulated Raman spectroscopy (SRS) is a tool to extract the structural and dynamical information about a molecular system. Ultrafast Raman loss spectroscopy (URLS) is analogous to SRS but is more sensitive than SRS. In this paper, we present the theoretical basis of SRS (URLS) techniques which have been developed in our laboratory.

Keywords. Nonlinear spectroscopy; phase matching condition; third order nonlinear process; SRS; URLS.

1. Introduction

When light beam passes through a medium, the response of the material depends on the field intensity. For low field intensity, materials behave as linear medium i.e., induced polarization, P , is directly proportional to the electric field vector E ($P \propto E$)

$$P = \varepsilon_0 \chi^{(1)} E, \quad (1)$$

where, ε_0 and $\chi^{(1)}$ are the permittivity and the linear susceptibility of the medium, respectively. The applied electromagnetic field (EM field) $E(z, t)$ of frequency ω is given by

$$E(z, t) = E_0 e^{i(kz - \omega t)} + c.c., \quad (2)$$

c.c. denotes the complex conjugate. Commonly used optical spectroscopic techniques such as absorption, normal Raman scattering, fluorescence, reflection, refraction etc. can be described by the linear optical polarization. In the linear regime, when more than one field interact with matter, the total polarization is a sum of the polarizations due to each of the input fields, i.e., the total polarization obeys the superposition principle. For example, if there are two input fields E_1 and E_2 , the

total polarization induced can be written as

$$P = \varepsilon_0 \chi^{(1)} (E_1 + E_2) = \varepsilon_0 \chi^{(1)} E_1 + \varepsilon_0 \chi^{(1)} E_2 = P_1 + P_2. \quad (3)$$

In the case of normal reflection, two separate light fields (say, blue and red light fields) will be reflected independent of each other. The presence of the red light never influences the reflection of blue and vice versa. For high field intensities, the material response becomes nonlinear to the applied EM field. i.e., polarization induced in the medium remains no longer proportional to the applied electric field E but depends on the higher powers of E

$$P = \varepsilon_0 [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots] = P_L + P_{NL}. \quad (4)$$

First term in equation 4 is the linear polarization and second, third and higher order terms give the nonlinear polarization. $\chi^{(i)}$, ($i > 1$) are the nonlinear susceptibilities. At low intensities, the higher order terms are negligible and only the linear term is retained. But for sufficiently strong fields, the nonlinear terms begin to play a role. If two fields (E_1 and E_2) of sufficiently high intensity are interacting with the medium, the second order term in equation 4 can be written as

$$\begin{aligned} P^{(2)} &= \varepsilon_0 \chi^{(2)} E^2 = \varepsilon_0 \chi^{(2)} (E_1 + E_2)^2 \\ &= \varepsilon_0 \chi^{(2)} (E_1^2 + E_2^2 + 2E_1 E_2). \end{aligned} \quad (5)$$

[#] Dedicated to Prof. N Sathyamurthy on his 60th birthday

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It can be seen that, unlike the linear case in equation 3, the polarization in this case does not obey the superposition principle. The three terms in equation 5 are responsible for the generation of frequencies [second harmonic and sum (or difference)] other than the incident frequencies. A detailed account of the second and third order nonlinear optical processes are given in the subsequent sections.

1.1 Nonlinear susceptibility

From equation 4, it can be seen that the material property that is responsible for linear and nonlinear optical properties is the susceptibility $\chi^{(i)}$ of the material. Linear susceptibility $\chi^{(i)}$ is responsible for the linear optical properties and nonlinear susceptibilities $\chi^{(2)}$, $\chi^{(3)}$, ... are responsible for the second order, third order and higher order nonlinear optical properties.¹⁻⁵ A method to determine the susceptibility using principles of classical physics is outlined in this section.

Classically, the linear response of materials to applied EM field can be described by the motion of electrons in a harmonic potential ($U = kx^2/2$). A simple picture of the motion of electrons can be drawn by assuming an atom whose electron is attached to the nucleus by means of a spring of force constant k (a spring mass system).⁶ The spring mass system has a natural frequency of oscillation given by $\omega_0 = \sqrt{k/m}$. The forces acting on the electron are as follows.

Restoring force: As the electron moves away from the nucleus, the restoring force (attractive force due to the nucleus) tries to pull it back to its equilibrium position. Hence, the force is always directed in a direction opposite to the displacement of the electron. If x is the displacement, the restoring force in the case of a harmonic oscillator can be written as

$$F_{restoring} = -kx = -m\omega_0^2 x. \quad (6)$$

Driving force: The electric field of the applied EM field tries to drive the electron with its frequency. If the applied field is of the form $E = E_0 e^{i\omega t}$, the driving force is given by

$$F_{driving} = qE = qE_0 e^{i\omega t}. \quad (7)$$

Damping force: The free oscillation of the electron is hindered due to many factors (like frictional forces).

The damping is proportional to the velocity of the electron. Hence, the damping force can be written as

$$F_{damping} = -m\gamma \frac{dx}{dt}. \quad (8)$$

The total force acting on the electron is then $F_{total} = F_{restoring} + F_{driving} + F_{damping}$. Using Newton's second law,

$$m \frac{d^2 x}{dt^2} = -m\omega_0^2 x + qE_0 e^{i\omega t} - m\gamma \frac{dx}{dt} \quad (9)$$

or, $\frac{d^2 x}{dt^2} + \gamma \frac{dx}{dt} + \omega_0^2 x = \frac{qE_0}{m} e^{i\omega t}$.

Thus, in the harmonic oscillator approximation, the displacement of the electron $x(E)$, and hence the induced dipole moment ($qx(E)$), as a function of the applied electric field E , can be obtained by solving equation 9. If N is the number of atoms per unit volume, the total induced polarization can be calculated as $P = Nqx(E)$. This equation can be inverted to determine the linear susceptibility $\chi^{(1)} = P/E = Nqx(E)$.

For sufficiently strong applied fields, the harmonic oscillator approximation is no longer valid. The nonlinear optical effects are described by assuming an anharmonic oscillator model for the atom. In the anharmonic oscillator model, the restoring force is not linearly proportional to the displacement (x) of the electron, but depends on higher powers of x . The same treatment can be repeated with the nonlinear restoring force to determine the nonlinear optical susceptibilities.

2. Basic nonlinear optics

2.1 Second order nonlinear optical effects

Second order nonlinear optical processes³ are described by the second term in equation 4

$$P^{(2)} = \varepsilon_0 \chi^{(2)} E^2, \quad (10)$$

where, $\chi^{(2)}$ is the second order nonlinear susceptibility and E is the total applied EM field. If there are two fields $E_1(k_1, \omega_1)$ and $E_2(k_2, \omega_2)$ interacting with the medium, the second order polarization can be written as,

$$P^{(2)} = \varepsilon_0 \chi^{(2)} [E_1(k_1, \omega_1) + E_2(k_2, \omega_2)]^2$$

assuming $E_1(k_1, \omega_1)$ and $E_2(k_2, \omega_2)$ to be plane monochromatic waves of the form

$$\begin{aligned} E_1(k_1, \omega_1) &= E_{10} e^{i(k_1 z - \omega_1 t)} + c.c = \Re E_1(k_1, \omega_1) \\ &= 2E_{10} \cos(k_1 z - \omega_1 t) \\ E_2(k_2, \omega_2) &= E_{20} e^{i(k_2 z - \omega_2 t)} + c.c = \Re E_2(k_2, \omega_2) \\ &= 2E_{20} \cos(k_2 z - \omega_2 t). \end{aligned}$$

Using the above expression for the fields, the second order polarization can be expanded as

$$\begin{aligned}
 P^{(2)} &= \varepsilon_0 \chi^{(2)} \left[2E_{10} \cos(k_1 z - \omega_1 t) \right. \\
 &\quad \left. + 2E_{20} \cos(k_2 z - \omega_2 t) \right]^2 \\
 &= \varepsilon_0 \chi^{(2)} \left[4E_{10}^2 \cos^2(k_1 z - \omega_1 t) \right. \\
 &\quad + 4E_{20}^2 \cos^2(k_2 z - \omega_2 t) \\
 &\quad \left. + 4E_{10}E_{20} \cos(k_1 z - \omega_1 t) \cos(k_2 z - \omega_2 t) \right] \\
 &= \varepsilon_0 \chi^{(2)} \left\{ 2E_{10}^2 + 2E_{20}^2 + 2E_{10}^2 \cos(2k_1 z - 2\omega_1 t) \right. \\
 &\quad + 2E_{20}^2 \cos(2k_2 z - 2\omega_2 t) \\
 &\quad + 2E_{10}E_{20} \cos[(k_1 + k_2)z - (\omega_1 + \omega_2)t] \\
 &\quad \left. + 2E_{10}E_{20} \cos[(k_1 - k_2)z - (\omega_1 - \omega_2)t] \right\} \\
 &\quad \dots \quad (11)
 \end{aligned}$$

The terms within $\{\dots\}$ correspond to different signals generated due to the second order nonlinearity. The first two terms in equation 11 correspond to DC field generation, also known as optical rectification. The third and fourth terms correspond to second harmonic generation, as it involves frequency components at $2\omega_1$ and $2\omega_2$ (double of the input frequencies), respectively. The fifth and sixth terms correspond to sum and difference frequency generation, as it involve frequencies at $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$. A schematic representation of the sum frequency mixing is shown in figure 1.

As described earlier, the second order nonlinear optical effects are determined by the existence of $\chi^{(2)}$ in a medium. The existence of $\chi^{(2)}$ is determined by the symmetry property of the medium.^{3,4} If the medium has a centre of inversion (or centrosymmetric), the anharmonic potential can have only terms in even powers of the displacement x .

$$U(x) = \frac{1}{2}m\omega_0^2 x^2 + \frac{1}{4}mbx^4.$$

This results in a symmetric potential (as shown in figure 2a), where $U(x) = U(-x)$ which causes $\chi^{(2)}$ to vanish in such media. Thus, centrosymmetric media such as

glass, liquids and gases cannot display any second order nonlinear optical effects. In media without an inversion centre (non-centrosymmetric), the anharmonic potential function can have terms containing even and odd powers of the displacement x .

$$U(x) = \frac{1}{2}m\omega_0^2 x^2 + \frac{1}{4}mbx^3.$$

Since there are even and odd powers involved, the potential function will be asymmetric (as shown in figure 2b) resulting in a nonzero $\chi^{(2)}$. Thus, only non-centrosymmetric materials, such as beta barium borate (BBO), potassium dihydrogen phosphate (KDP), etc., can be used for the generation of second harmonic or sum (or difference) frequency mixing signals. Hence, the lowest order optical nonlinearity that can be observed in all media, irrespective of the symmetry, is the third order nonlinearity given by $\chi^{(3)}$.

2.2 Third order nonlinear optical effects

The third order nonlinear optical effects are described by the third term in equation 4 given by

$$P^{(3)} = \chi^{(3)} E^3. \quad (12)$$

Similar to the expansion of second order polarization in the previous section, the third order polarization can also be expanded which will result in many terms corresponding to different third order processes. Typical third order nonlinear spectroscopic techniques commonly used are, third harmonic generation (THG, tripling of the incident frequency), optical Kerr effect (inducing birefringence), four wave mixing (FWM, mixing of three input frequencies).⁷ Some of these processes are schematically represented in figure 3. *Four wave mixing* is a more general term which encompasses all the third order nonlinear optical processes where, the involvement of three input fields result in the generation of the fourth signal field. Since third order nonlinearity

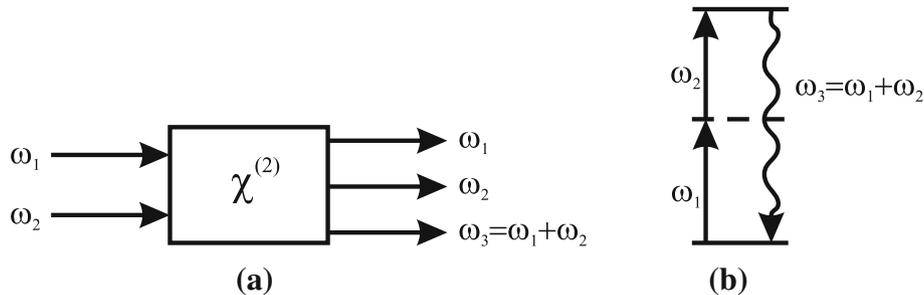


Figure 1. Schematic representation of sum frequency mixing (a) a second order nonlinear optical process, in which two incident frequencies resulting in the generation of sum frequency. The corresponding energy level diagram is shown in (b).

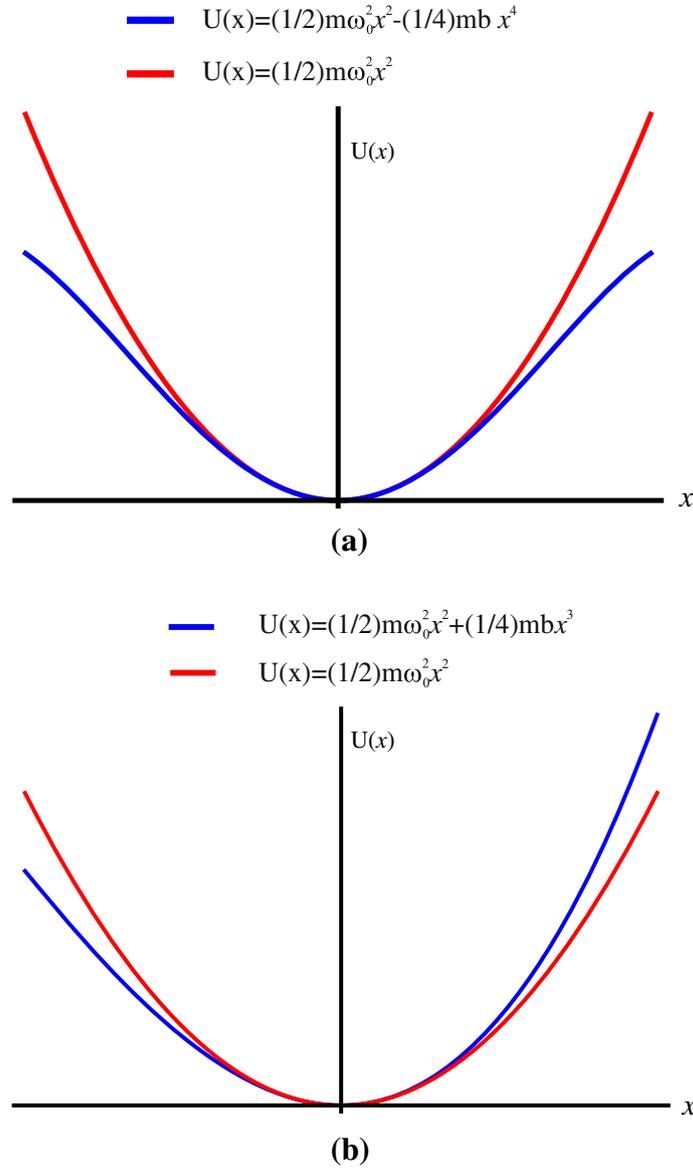


Figure 2. The anharmonic potential functions for a centrosymmetric and non-centrosymmetric material. (a) Shows the potential function for a centrosymmetric material ($U(x) = U(-x)$). (b) Shows the potential function for a non-centrosymmetric material ($U(x) \neq U(-x)$). The harmonic potential function (red line) is also shown for comparison.

is the lowest order optical nonlinearity observable in all media, it has become a valuable nonlinear spectroscopic tool for the investigation of structure and dynamics of matter.

In the case of FWM, three input fields at frequencies ω_1 , ω_2 and ω_3 and wave vectors \vec{k}_1 , \vec{k}_2 and \vec{k}_3 creates a polarization at frequency $\omega_1 + \omega_2 + \omega_3$. This polarization results in the generation of the FWM signal at $\omega_{sig} = \omega_1 + \omega_2 + \omega_3$. The input and output frequencies will have different refractive indices (due to material dispersion) which leads to difference in their phase velocities ($v_\phi = \omega/k$). For the efficient generation of

the FWM signal, the phase of the induced polarization, $\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ should match with the phase of the FWM signal with wave vector \vec{k}_{sig} . This is known as *phase matching condition* which has to be fulfilled in any nonlinear optical signal generation and it is given by.³⁻⁵

$$\vec{k}_{sig} = \vec{k}_1 + \vec{k}_2 + \vec{k}_3. \quad (13)$$

The difference between the phases of the induced polarization and the output signal is referred to as the *phase mismatch*, which is given by

$$\Delta k = \vec{k}_{sig} - \vec{k}_1 + \vec{k}_2 + \vec{k}_3. \quad (14)$$

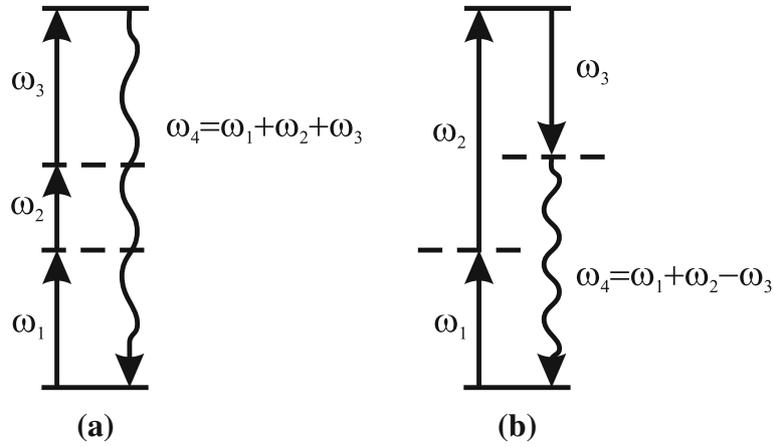


Figure 3. Energy level diagrams corresponding to two third order nonlinear optical processes. **(a)** Energy level diagram corresponding to sum frequency mixing of three input fields. THG is a special case of this process when $\omega_1 = \omega_2 = \omega_3$. **(b)** A possible FWM process in which output frequency $\omega_3 = \omega_1 + \omega_2 - \omega_3$.

The variation of the intensity of the FWM signal with Δk is given by

$$I_{sig} = K |\chi^{(3)}|^2 I_1 I_2 I_3 L^2 \left[\frac{\sin \frac{\Delta k L}{2}}{\frac{\Delta k L}{2}} \right]^2, \quad (15)$$

where, K is proportionality constant, I_1 , I_2 and I_3 are the intensities of the input fields and L is the interaction length in the medium. As can be seen from figure 4 the effect of wave vector mismatch is integrated entirely in the sinc function appearing in equation 15. Thus, the efficiency of the FWM process decreases as $\Delta k L$ increases. A detailed derivation of equation 15 is provided in Appendix A.

3. Nonlinear Raman spectroscopy

Four wave mixing, based on third order nonlinearity, is a highly versatile spectroscopic tool to investigate different material properties by the choice of different input frequencies and phase matching conditions. In general, the input and output frequencies should match the following relation:

$$\omega_{sig} = \pm \omega_1 \pm \omega_2 \pm \omega_3 \quad (16)$$

$$\vec{k}_{sig} = \pm \vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3. \quad (17)$$

Equation 16 implies that any linear combination of the input frequencies has to match with the output frequency. Physically, this equation represents the

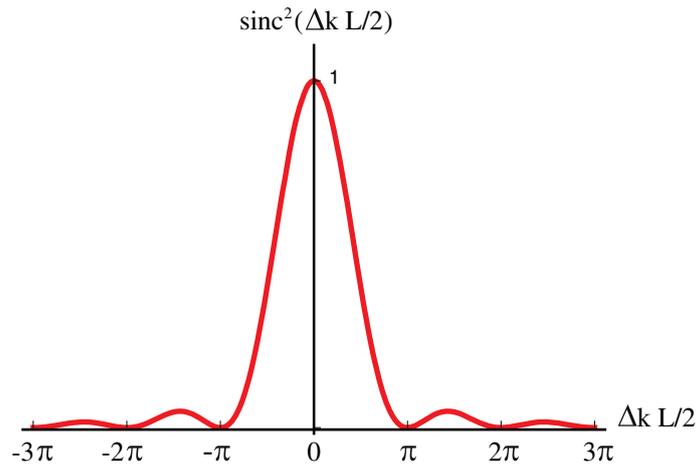


Figure 4. Variation of FWM signal intensity as a function of the phase mismatch Δk . The FWM signal is maximum when $\Delta k = 0$, or when the phase matching condition is fulfilled.

energy conservation principle (photon energy = $\hbar\omega$). Similarly equation 17 implies that any linear combination of the input wave vectors has to match with the output wave vector and it represents the momentum conservation principle (photon momentum = $\hbar k$). A typical example of one of the possible combinations is the sum frequency generation, where $\omega_{sig} = \omega_1 + \omega_2 + \omega_3$ and $\vec{k}_{sig} = \vec{k}_1 + \vec{k}_2 + \vec{k}_3$. Third harmonic generation is a special case of sum frequency generation when all the input frequencies and wave vectors are degenerate.

The FWM signal can be resonantly enhanced if a combination of any of the input frequencies matches with a transition (vibrational, electronic, etc.) frequency of the material. If one uses light pulses, instead of continuous waves, temporal delay between the input pulses can be manipulated to study time dependent variation of the material properties. Modern femtosecond lasers can provide pulses as short as ≈ 5 fs. The shortness in pulse duration results in high peak power which makes them ideal for inducing optical nonlinearities easily. Thus, most of the time resolved nonlinear spectroscopic techniques use femtosecond lasers and third order nonlinearity of the material to extract important material properties and their temporal behaviour.

Nonlinear Raman spectroscopy is based on the third order optical nonlinearity in which a combination of the two input fields is used to generate a vibrational coherence in the material. The interaction of the third field with the induced vibrational coherence results in a Raman signal. Commonly used nonlinear Raman techniques are coherent anti-Stokes Raman scattering

(CARS),⁸ coherent Stokes Raman scattering (CSRS), stimulated Raman gain spectroscopy (SRGS) and ultra-fast Raman loss spectroscopy (URLS).^{3-5,9-12} A detailed description of URLS is given in the following section.

4. Stimulated Raman spectroscopy

In general, all the nonlinear Raman spectroscopic techniques are based on the stimulated Raman process. In the stimulated Raman process, the interaction of a pump beam with frequency ω_p and a Stokes beam with frequency ω_s with the system excites a vibrational mode at frequency $\omega_v = \omega_p - \omega_s$. The vibrational coherence prepared by the pump and Stokes pulses can be probed by a third pulse, which results in signal generation. The energy and phase matching condition for the process can be written as

$$\omega_{SR} = (\omega_p - \omega_s) \pm \omega_p = \omega_v \pm \omega_p \quad (18)$$

$$\vec{k}_{SR} = (\vec{k}_p - \vec{k}_s) \pm \vec{k}_p = \vec{k}_v \pm \vec{k}_p, \quad (19)$$

where, ω_{SR} and \vec{k}_{SR} are the frequency and wave vector of the stimulated Raman signal. Equation 18 determines the energy of the stimulated Raman signal and equation 19 determines the signal direction. The terms within brackets in equations 18 and 19 is common for all nonlinear Raman processes.^{3,4} This term is responsible for the generation of the vibrational coherence. The choice of the probe field ($\pm\omega_3$ and $\pm\vec{k}_3$) distinguishes

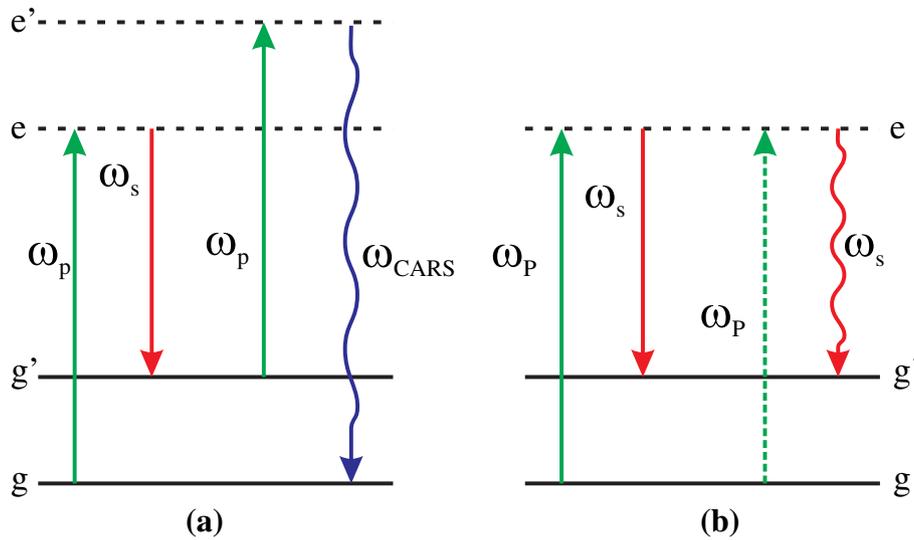


Figure 5. Two possible processes when using the same pump and probe frequencies. (a) Shows the CARS process which requires three separate input beams in a phase matching direction for the generation of the signal. (b) Shows the stimulated Raman gain or loss process in which only two beams are required and it is a self phase matched process.

between the different nonlinear Raman techniques mentioned in the previous section. When the probe field is chosen to be the same as the pump field, the choice of sign of the probe field in equations 18 and 19 results in two possible processes as shown in figure 5.

SRGS and URLS are described by

$$\begin{aligned}\omega_{signal} &= (\omega_p - \omega_s) - \omega_p = \omega_s \\ \vec{k}_{signal} &= (\vec{k}_p - \vec{k}_s) - \vec{k}_p = \vec{k}_s\end{aligned}\quad (20)$$

and coherent anti-Stokes Raman scattering is described by

$$\begin{aligned}\omega_{CARS} &= (\omega_p - \omega_s) + \omega_p \\ \vec{k}_{CARS} &= (\vec{k}_p - \vec{k}_s) + \vec{k}_p.\end{aligned}\quad (21)$$

In SRGS and URLS, the interaction of the pump and Stokes beams (usually known as Raman pump and probe beams) results in the creation of a vibrational coherence. The interaction of the probe beam, which in this case is the same as the pump beam, causes signal to be generated in the direction of the Stokes beam. Thus, the signal appears as a gain in the intensity of the Stokes beam and hence the name SRGS.^{11,13,14} Since, according to equation 20, the total energy is conserved, the gain in the Stokes signal should be compensated by a loss in one of the input beams. The pump beam loses the energy which appears as a gain in the Stokes energy. Thus, one can probe either the gain in the Stokes beam or loss in the pump beam to gain information about the vibrational mode being investigated.

The use of ultra short laser pulses for doing stimulated Raman spectroscopy enables one to investigate the temporal dynamics of vibrational modes (changes occurring with respect to time) by varying the time delay between the pulses.¹⁵⁻¹⁷ Thus stimulated Raman spectroscopy using short pulses enables one to investigate both the structural and temporal dynamics of a system. One particularly useful technique is the URLS, which is described in detail in the next section.

4.1 URLS

In URLS, one uses the combination of a picosecond Raman pump (RP) pulse and a femtosecond broadband white light continuum (WL continuum) to obtain structural and dynamical information about a system. As described in the previous section, the interaction of the pump and Stokes pulses creates a vibrational coherence in the system. In this case, the Stokes pulse is replaced

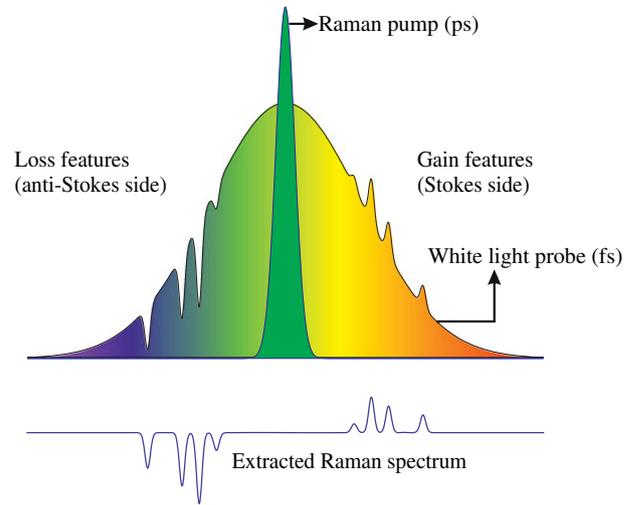


Figure 6. Schematic diagram of SRGS and URLS.

by broadband WL continuum which contains several frequency components. This results in the simultaneous excitation of a large number of vibrational modes in the system. If the WL continuum contains frequencies less than that of RP, the signal appears as gain features in the WL continuum at frequencies corresponding to the vibrational modes excited in the system. If the WL contains frequencies higher than that of RP, the signal appears as loss features in the WL continuum. A schematic of the process is represented in figure 6. By detecting either the gain features or loss features, and subtracting the bare WL spectrum from it, one can obtain a Raman spectrum of the sample under investigation. The detection of loss features in the WL continuum is referred to as URLS.^{12,18-20}

The WL spectrum is shown as a broad gaussian. The signal can be seen as the loss (or gain) features on the anti-Stokes (or Stokes) side of the WL spectrum with respect to the Raman pump. The Raman spectrum that can be extracted from the signal, after subtraction of the gaussian WL background is also shown.

The experimental set up and the importance of URLS were well-discussed by using a variety of systems ranging from pure solvents, biological systems to highly fluorescent systems by Umapathy *et al.*^{19,20} Here, we give the flavour of the URLS by using some pure solvents and highly fluorescent system. Figure 7 gives the URLS spectrum of some pure solvents and a highly fluorescent system. Figure 7a-d shows the URLS spectrum of pure solvents like dioxane, benzonitrile, toluene and nitrobenzene. Figure 7a-d were recorded by setting the Raman pump at 562 nm with bandwidth of 16 cm⁻¹ and WL broad band probe which was ranging from 430 nm to 700 nm. These spectra were recorded just by exposing the detector for 10 ms time and averaging for ten

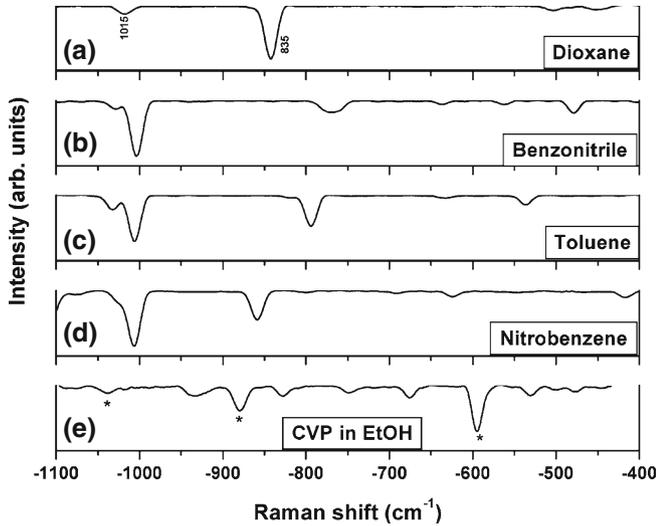


Figure 7. URLs spectrum of pure solvents recorded by using Raman pump at 562 nm (16 cm^{-1}) with Raman probe as WL broadband (a–d). URLs spectrum of Cresyl violet perchlorate in ethanol by using Raman pump at 670 nm and Raman probe as WL broadband (e).

times and thus it is clear from the loss signal in the figure that URLs is very sensitive. Figure 7e represents the URLs spectrum of cresyl violet perchlorate (a highly fluorescent system also used as laser dye) in ethanol. The bands marked with asterisks represent solvent (ethanol) Raman bands. Figure 7e is obtained by using the Raman pump at 670 nm which is off-resonant with the absorption band of cresyl violet perchlorate, and the Raman probe is a WL. Here, we can see the intense Raman loss spectrum at positions 590, 673, 750, 835 cm^{-1} etc. Cresyl violet perchlorate is a highly fluorescent system, and an excitation in the absorption band there is an interference of the fluorescence with the Raman transitions (if the observation is in the Stokes side). But, the nature of the URLs set up does not have any interference of the fluorescence with the Raman signals due to observation in the blue region. Thus, URLs provides a high signal to noise ratio Raman loss spectrum even at resonant excitation.

5. Conclusion

In this paper, we have presented the basic principles behind stimulated Raman spectroscopy and in particular, URLs both the non-linear spectroscopic methods developed in our laboratory. URLs has been observed to be more advantageous when dealing with fluorescent systems. Since, in URLs, the detection is on the higher frequency side with respect to the Raman pump, the fluorescence, which appears on the lower frequency side,

is automatically rejected. Also, the signal intensity in the case of URLs is about 2 times greater than that in SRGS.^{19,20}

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Appendix A

Derivation of the phase matching condition

Propagation of EM waves in any medium is described by the Maxwell's wave equation given by

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P_{NL}}{\partial t^2}. \quad (22)$$

The source of the signal in any optical process is the polarization induced by the applied EM field. Mathematically, the induced polarization (P) appears as the source term in the Maxwell's wave equation which results in the generation of new waves. In general, the polarization P in equation 22 can be expanded as the sum of a linear and nonlinear terms $P = P^{(1)} + P^{(NL)}$. Then the displacement $D = \epsilon_0 E + P = \epsilon_0 E (P^{(1)} + P^{(NL)}) = D^{(1)} + P^{(NL)}$. Then the wave equation can be written as

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 (P^{(1)} + P_{NL})}{\partial t^2}$$

$$\nabla^2 E - \frac{1}{\epsilon_0 c^2} \frac{\partial^2 D^{(1)}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P_{NL}}{\partial t^2}, \quad (23)$$

where, $D^{(1)}$ is the linear displacement. For a lossless, dispersive medium, $D^{(1)}$ can be expressed in terms of the frequency dependent susceptibility tensor $\chi^{(1)}(\omega)$ as

$$D^{(1)} = \epsilon_0 (1 + \chi^{(1)}(\omega)) E = \epsilon_0 (1 + \chi^{(1)}(\omega)) E, \quad (24)$$

$1 + \chi^{(1)}(\omega) = n(\omega)^2$, the frequency dependent refractive index of the material. Thus, in the case of a dispersive medium, if there are multiple fields of different frequencies interacting with the medium, each frequency component has to be considered separately. Representing

the fields, polarizations and linear displacements as a sum of individual frequency components (ω_n),

$$\begin{aligned} E(r, t) &= \sum_n (E_n(r) e^{-i\omega_n t} + c.c) \\ D^{(1)}(r, t) &= \sum_n (D_n^{(1)}(r) e^{-i\omega_n t} + c.c) \\ P^{(NL)}(r, t) &= \sum_n (P_n^{(NL)}(r) e^{-i\omega_n t} + c.c). \end{aligned} \quad (25)$$

Using equation 25 the general wave equation for the individual frequency components can be written as

$$\nabla^2 E_n - \frac{n(\omega)^2}{c^2} \frac{\partial^2 E_n}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P_n^{NL}}{\partial t^2}. \quad (26)$$

Evaluating the time derivatives using the expressions in equation 24 we get the simplified wave equation

$$\nabla^2 E_n(r) - \frac{n(\omega)^2 \omega_n^2}{c^2} E_n(r) = -\frac{\omega_n^2}{\epsilon_0 c^2} P_n^{NL}(r). \quad (27)$$

As an example, consider the case of sum frequency mixing due to third order optical nonlinearity ($\chi^{(3)}$). Three input fields at frequencies ω_1 , ω_2 and ω_3 generate the sum frequency $\omega_s = \omega_1 + \omega_2 + \omega_3$. The wave equation 27 must hold for all frequency components. The equation for the newly generated sum frequency component can be written as (assuming the wave to be propagating in the z-direction, the spatial coordinate r can be replaced by z)

$$\nabla^2 E_s(z) - \frac{n(\omega)^2 \omega_s^2}{c^2} E_s(z) = -\frac{\omega_s^2}{\epsilon_0 c^2} P_s^{NL}(z), \quad (28)$$

where, $P_s^{NL}(z)$ is the source for the generation of the sum frequency field $E_s(z)$. Representing fields as plane waves with amplitude A_i , ($i = 1, 2, 3, s$)

$$E_i(z, t) = A_i e^{i(k_i z - \omega_i t)} \quad (i = 1, 2, 3, s).$$

The nonlinear polarization responsible for the generation of sum frequency can be written as

$$P_s^{NL}(z) = \epsilon_0 \chi^{(3)} A_1 A_2 A_3 e^{i(k_1 + k_2 + k_3)z}. \quad (29)$$

Substituting expressions ($E_i(z, t)$) and equation 29 into the wave equation 28, one obtains

$$\begin{aligned} \left[\frac{d^2 A_s}{dz^2} + 2ik_s \frac{dA_s}{dz} - k_s^2 A_s + \frac{n(\omega_s)^2 \omega_s^2 A_s}{c^2} \right] e^{i(k_s z - \omega_s t)} \\ + c.c = -\frac{\chi^{(3)} \omega_s^2}{c^2} A_1 A_2 A_3 e^{i(k_1 + k_2 + k_3)z - \omega_s t} + c.c. \end{aligned} \quad (30)$$

Since, $k_s^2 = n(\omega_s)^2 \omega_s^2 / c^2$, the third and fourth terms on the left hand side of the equation cancel. Taking the exponential part from the LHS to RHS we can write

$$\left[\frac{d^2 A_s}{dz^2} + 2ik_s \frac{dA_s}{dz} \right] = -\frac{\chi^{(3)} \omega_s^2}{c^2} A_1 A_2 A_3 e^{i(k_1 + k_2 + k_3)z}. \quad (31)$$

Invoking slowly varying amplitude approximation,

$$\left| \frac{d^2 A_s}{dz^2} \right| = \left| k_s \frac{dA_s}{dz} \right| \quad (32)$$

the first term in equation 31 can be neglected to obtain the simplified equation

$$\frac{dA_s}{dz} = \frac{i\chi^{(3)} \omega_s^2}{2k_s c^2} A_1 A_2 A_3 e^{i\Delta k z}, \quad (33)$$

where we have introduced the identity $\Delta k = k_1 + k_2 + k_3 - k_s$. For a medium of length L , we can integrate equation 33 to obtain the amplitude of the sum frequency signal (A_s) at the exit surface of the sample.

$$\begin{aligned} A_s(L) &= \frac{i\chi^{(3)} \omega_s^2}{2k_s c^2} A_1 A_2 A_3 \int_0^L e^{i\Delta k z} dz \\ &= \frac{i\chi^{(3)} \omega_s^2}{2k_s c^2} A_1 A_2 A_3 \left[\frac{e^{i\Delta k L} - 1}{i\Delta k} \right]. \end{aligned} \quad (34)$$

The intensity of the sum frequency signal at the exit surface of the sample is then given by the squared modulus of the amplitude equation 33.

$$I_s = \left(\frac{i\chi^{(3)} \omega_s^2}{2k_s c^2} \right)^2 |A_1|^2 |A_2|^2 |A_3|^2 \left| \frac{e^{i\Delta k L} - 1}{i\Delta k} \right|^2. \quad (35)$$

The absolute square of the exponential term can be expanded in terms of the trigonometric functions to get the final result as

$$I_s = \left(\frac{i\chi^{(3)} \omega_s^2}{2k_s c^2} \right)^2 I_1 I_2 I_3 \left(\frac{\sin \frac{\Delta k L}{2}}{\frac{\Delta k L}{2}} \right)^2, \quad (36)$$

where, $I_1 (= |A_1|^2)$, $I_2 (= |A_2|^2)$, $I_3 (= |A_3|^2)$ are the intensities of the input beams and the last term is the *sinc* function which is mentioned in section 2.2. The intensity of the sum frequency signal drops as Δk deviates from zero. Thus, the condition when $\Delta k = 0$, where we have the maximum signal for any length L of the medium is known as the *phase matching condition*.

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