Tutorial: Coherent Raman light matter interaction processes

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Coherent Raman scattering processes such as coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering (SRS) are described in a tutorial way keeping simple physical pictures and simple derivations. The simplicity of the presentation keeps however most of the key features of these coherent and resonant processes and their intimate relation with spontaneous Raman scattering. This tutorial provides a digest introduction to the fundamental physics at work, it doesn’t focus on the numerous technological implementations, rather it provides the concepts and the physical tools to understand the extensive literature in this field. The presentation is made simple enough for under-graduated, graduated students, and newcomers with various scientific backgrounds.

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The stimulated Raman effect\textsuperscript{1} was discovered accidentally by Eckhardt in 1962 shortly after the first ruby-laser action was demonstrated\textsuperscript{2}. This is because the weak molecular stimulated Raman cross section requires laser flux density of the order of 10\textsuperscript{8} W/cm\textsuperscript{2} that can only be achieved through stimulated emission of radiation. In 1965 Maker and Terhune who were studying nonlinear wave mixing, reported a four wave mixing process that can be made resonant with a molecular vibration\textsuperscript{3}, the coherent anti-Stokes Raman scattering (CARS) effect was just discovered. Since this early time and until the early 80’s both stimulated Raman scattering (SRS) and CARS light matter interaction processes were extensively discussed and used in the context of nonlinear optical spectroscopy\textsuperscript{4–9}. The first implementation of CARS in the context of imaging was reported in 1982 by Duncan\textsuperscript{10} using two synchronized dye lasers pumped by an Ar-Ion laser whereas the real revival using solid state lasers was reported in 1999 by Zumbusch\textsuperscript{11}, a seminal work that launched a very active field known nowadays as coherent Raman scattering (CRS) imaging among which the first implementation of SRS microscopy imaging has been reported in 2007\textsuperscript{12–14}. This active field has been recently reviewed\textsuperscript{15,16} and takes advantage of the last technological developments in the fields of lasers, detectors and fast imaging modalities to improve the ability of CRS microscopes to image a variety of compounds in the fields of biology, chemistry and material sciences. The key asset of the CRS technology is being label-free contrary to \"\\textsuperscript{\textregistered} fluorescence. Coherent Raman processes are addressing chemical bonds that are inherently present in matter.

The basics of coherent Raman light matter interaction processes can be found in reference text books such as\textsuperscript{15,17–21}. However the information is sometime scattered or embedded in more general considerations that require significant efforts from the reader to be brought together. The scope of this tutorial is to present the fundamental basics of CRS in a concise yet rigorous manner. The content is certainly not new but is aimed to provide to newcomers in the CRS field the necessary background to grasp the physics at work that is common to the numerous technical implementations that have been reported so far.
I. MOLECULAR RESONANCES

The light matter interaction in the near infra-red (NIR) is dominated by the absorption of molecular vibrational levels, the latter giving birth to narrow or broad absorption bands for electromagnetic radiation with wavelengths ranging from 3 µm to 1000 µm\(^2\). Absorption is a resonant process that can be viewed in the simplest case as the interaction of a monochromatic electromagnetic wave with a molecule being modelled as a mass-spring system. We will go through this simple picture to present the NIR molecular absorption, the spontaneous Raman process, and later on, the coherent Raman processes such as CARS and SRS.

A. Harmonic oscillator

The harmonic oscillator is an ideal physical object whose temporal oscillations is a sine wave with constant amplitude and with a frequency that is solely dependent on the system parameters. It is found in many fields of physics and it is a good approximation of physical systems that are close to a stable position. In the mechanical framework the simplest harmonic oscillator is a mass \(m\) attached to a spring with a stiffness \(k\) (Fig. 1). Being set vertical the mass feels the gravity attraction \(g\) and its center of mass is described by:

\[
mg - kx_0 = 0. \tag{1}
\]

It is possible to study the mass displacement \(x\) from its equilibrium position \(x_0\). Using the fundamental principals of dynamics (energy conservation), it can be shown\(^{23}\) that the mass displacement \(x\) follows

\[
\frac{d^2x}{dt^2} + \omega_0^2 x = 0, \tag{2}
\]

where \(\omega_0 = \sqrt{k/m}\) is the system resonant frequency.
FIG. 1. A mass-spring system. $x_0$ is the equilibrium position and $x$ the relative displacement.

**Damped harmonic oscillator**

Consider now that the mass experiences a friction force: $F = -2\gamma m (dx/dt)$, where $\gamma$ is the damping. This force is zero when the mass is at rest, but increases with the mass speed. The equation describing the mass movement is now

$$\frac{d^2x}{dt^2} + 2\gamma \frac{dx}{dt} + \omega_0^2 x = 0.$$  \hspace{1cm} (3)

**B. Driven harmonic oscillator**

We are now interested in the mass movement when it is driven by a periodic excitation force $F(t) = F_0 \cos(\omega t)$, where $F_0$ is the force amplitude and $\omega$ its angular frequency. The mass movement equation becomes

$$\frac{d^2x}{dt^2} + 2\gamma \frac{dx}{dt} + \omega_0^2 x = \frac{F(t)}{m}. \hspace{1cm} (4)$$

It is convenient to use the complex notation $F(t) = F_0 e^{-i\omega t}$, with this notation a phase lag is noted positive.

We are now looking for a displacement solution of the form $x(t) = x(\omega)e^{-i\omega t}$. Inserting this generic solution in Eq.4, it comes

$$( -\omega^2 - i2\gamma \omega + \omega_0^2 ) x(\omega)e^{-i\omega t} = \frac{F_0 e^{-i\omega t}}{m}, \hspace{1cm} (5)$$

where $x(\omega)$ can be expressed as
\[ x(\omega) = \frac{F_0/m}{\omega_0^2 - \omega^2 - i2\gamma \omega}. \] (6)

Close to the resonance (\(\omega \approx \omega_0\)), and for small damping coefficient (\(\gamma \ll \omega_0\)), the harmonic oscillator solution 6 can be approximated by a complex Lorentzian function

\[ x(\omega) = \frac{-F_0/(2m\omega_0)}{(\omega - \omega_0) + i\gamma}. \] (7)

C. Study at resonance

The complex plane \([\text{Re}(x), \text{Im}(x)]\) is a nice way to display this Lorentzian function (Fig. 2(a)) as the displacement \(x(\omega)\) describes a circle when the angular frequency \(\omega\) varies.\(^{24}\)

**FIG. 2.** System at resonance. (a) \(x(\omega)\) describes a circle in the complexe plane. (b) Amplitude spectrum. (c) Phase spectrum. At resonance, \(x(\omega)\) experiences a \(\pi/2\) phase shift as compared to the phase of the field (red). (d) Time domain description of the 3 regimes: below, at, and above resonance.
Denoting $\rho$ and $\varphi$ the amplitude and phase of the displacement $x(\omega) = \rho(\omega)e^{i\varphi(\omega)}$. Figure 2(b) displays the displacement amplitude squared with the excitation frequency $\omega$. Figure 2(c) shows the phase response. We note that the system response can be split into three regimes depending the value of $\omega$ (Fig. 2(d)):

1. $\omega \ll \omega_0$. The displacement amplitude is weak and its phase is close to zero. The oscillation is in phase with the excitation drive.

2. $\omega = \omega_0$. The displacement amplitude is strong at its phase is $\pi/2$. The oscillation is lagging by 90° with respect to the excitation drive (phase quadrature).

3. $\omega \gg \omega_0$. The displacement amplitude is weak and its phase is close to $\pi$. The oscillation is lagging by 180° with respect to the excitation drive (phase opposition).

Using a simple oscillator model we have described the phenomenon of resonance. We will now move to vibrational molecular resonances that can be probed by an electromagnetic wave.

II. MOLECULAR VIBRATIONAL RESONANCES

A. Vibrational modes

A molecular structure sustains many vibrational and rotational intra-molecular vibrations that can be described in terms of normal modes. Each of these "roto-vibrational" normal mode is independent from the other normal modes, it has a center of mass that is preserved and a specific energy that is quantized as described by the quantum mechanical theory. The atomic mass, the number of involved chemical bonds, the atomic species, the molecule geometry and symmetry and the possible hydrogen bonds interactions affect the stiffness of the vibrational forces at work, that at end, dictate the possible vibrational energies. All these vibrational energies belong to the infrared domain and can be probed by absorption spectroscopy. Rotational modes are only observable when molecules are in the gas phase and correspond to energies ranging from 10 to $400 \text{ cm}^{-1}$, which correspond to the far infrared electromagnetic domain (wavelengths between 25 and 10000 $\mu\text{m}$). Roto-vibrational modes
correspond to energies ranging from 1 to 4000 \( cm^{-1} \) corresponding to the mid-infrared domain (wavelengths between 2.5 and 25 \( \mu m \)). Near infrared radiations ranging from 4000 to 14000 \( cm^{-1} \) (wavelengths from 0.7 to 2.5 \( \mu m \)) can also excite overtones of these vibrations.

A molecule having a geometry which is not linear and constituted of \( n \) atoms will have \( 3n-6 \) normal vibration modes. For instance, water molecules (H\(_2\)O) have 3 modes of vibrations that are shown in figure 3, other molecules may exhibit other modes of vibration such as scissoring modes, twisting modes, rocking modes, torsion modes and wagging modes\(^{25}\). A molecule having a linear geometry will have only \( 3n-5 \) normal vibration modes because any rotation along its molecular axis keep the molecule unchanged. Therefore diatomic molecules \((n = 2)\) will have only one normal vibration mode.

**B. Modelling a diatomic molecule**

For the sake of clarity we will consider now a single and isolated diatomic molecule. We suppose that this molecule is made with two nuclei, separated by \( x_0 \), that are considered as two points with masses \( m_1 \) et \( m_2 \). We consider now that the elongation vibrational mode can be described by a simple harmonic oscillator with a resonant frequency \( \Omega_R \). Within this simple picture the two nuclei are connected with a spring as displayed in figure 4(a).

**C. Infrared (IR) absorption**

We consider now a polar diatomic molecule where an asymmetric distribution of positive and negative charges induces a dipole moment \( \vec{p} \). We suppose that the first atom holds the charge \( q \) whereas the second atom has the charge \(-q\). The dipole moment of this
FIG. 4. Infrared (IR) absorption. (a) Classical view of a diatomic molecule absorbing an IR radiation. (b) Energy diagram showing the absorption of a photon exciting a molecule from the ground state $|f\rangle$ to the first excited vibrational state $|v\rangle$.

two punctual charge system can then be expressed in vector form: $\vec{p} = q \vec{d}$ where $\vec{d}$ is the displacement vector oriented from the negative to the positive charge.

We consider now the molecule embedded in an electromagnetic field $\vec{E}(t)$ with angular frequency $\omega$ that is linearly polarized along the molecule axis. This electric field generates a force on the molecule $F_{\text{lorentz}}(t) = qE_0 e^{-i\omega t}$ and the elongation response of the molecule $x$ follows a driven harmonic oscillation (Eq. 4)

$$\frac{d^2 x}{dt^2} + 2\gamma \frac{dx}{dt} + \Omega_R^2 x = \frac{F_{\text{lorentz}}(t)}{\mu}$$

(8)

with $\mu$ the reduced mass: $\mu = m_1 m_2/(m_1 + m_2)$. The damping term $\gamma$ expresses the radiation loss of this oscillating dipole.

Let’s consider now a macroscopic medium constituted with $N$ of these molecules. Under the electric field influence, the electronic cloud displacement of each molecule induces a polarization

$$P(\omega) = Nq x(\omega) .$$

(9)

The linear electronic susceptibility $\chi^{(1)}$ is defined as

$$P(\omega) = \varepsilon_0 \chi^{(1)}(\omega) E(\omega) .$$

(10)

Comparing equation 10 with 9, and introducing the solution $x(\omega)$ of equation 8, we get
\[ \chi^{(1)}(\omega) = -\frac{Nq^2/(2\varepsilon_0 m\Omega_R)}{(\omega - \Omega_R) + i\gamma}, \]  

(11)

which gives the vibrational contribution to susceptibility \( \chi^{(1)} \) of the molecular assembly\(^2\). For diluted media, the real part of \( \chi^{(1)} \) is related to the refractive index dispersion (figure 5(b))

\[ n(\omega) = n_0 - \frac{\text{Re} \left[ \chi^{(1)}(\omega) \right]}{2n_0}, \]  

(12)

where \( n_0 \) is the mean refractive index of the medium.

whereas the imaginary part of \( \chi^{(1)} \) is related to the absorption coefficient of the medium (Fig. 5(c)).

\[ \alpha(\omega) = \frac{2\pi}{\lambda_0 n_0} \text{Im} \left[ \chi^{(1)}(\omega) \right] \]  

(13)

where \( \alpha \) is often expressed in cm\(^{-1}\), and is the key parameter involved in the Beer-Lambert law that describes the intensity loss of a light beam that propagates in a medium over the distance \( L \)

\[ I(L) = I(0) \exp(-\alpha L). \]  

(14)

IR absorption is a powerful spectroscopic method to identify and quantify the absorption bands corresponding to molecular species in a sample\(^2\).

D. Spontaneous Raman scattering

At thermodynamic equilibrium the interaction of light with matter is governed by absorption (the molecule retains the light energy for a certain time) and scattering (the molecule instantaneously scatters the incoming light in a different direction). When a molecule scatters light, most of the scattered photons keep their original frequencies, a phenomenon known as elastic scattering or 'Rayleigh scattering' (Fig. 6). However a small fraction of the incident light is scattered in an inelastic way, i.e. scattered with a frequency that is different from the original incoming light, a phenomenon known as the 'Raman effect'. Inelastic Raman
FIG. 5. Spectral evolution of the linear susceptibility $\chi^{(1)}$ across a molecular resonance. (a) Complex plane representation. (b) The real part of $\chi^{(1)}$ is related to the medium dispersion. (c) The imaginary part of $\chi^{(1)}$ is related to the medium absorption. A: Real part maximum - B: Resonance - C: Real part minimum.

scattering was first observed in 1928 by Raman and Krishnan\textsuperscript{27} in India and independently by Landsberg and Mandelstam\textsuperscript{28} in USSR. By focusing the spectrally filtered sun light they could observe new frequencies into the scattered light.

FIG. 6. Spontaneous Raman scattering mechanisms.

To understand the Raman effect let's consider again the diatomic molecule described earlier. The molecule is not necessary polar but its polarizability (mostly from electronic origin) depends on the intra-molecular distance $x$. This distance fluctuates at the resonant molecular bond frequency $x(t) = x_f \cos(\Omega_R t)$, where $x_f$ is the amplitude fluctuation. For tiny displacements, it is possible to perform a Taylor expansion of the polarizability $\alpha(t)$ near its initial value $\alpha_0$. 


\[ \alpha(t) = \alpha_0 + \left( \frac{\partial \alpha}{\partial x} \right)_0 x(t) . \]  

(15)

The exciting field \( E(t) = E_0 \cos(\omega_p t) \) induces a dipole moment into the molecule

\[ \vec{p}(t) = \varepsilon_0 \alpha(t) \vec{E}(t) . \]  

(16)

Introducing the polarizability expression 15 into 16, we get

\[ p(t) = \varepsilon_0 \left[ \alpha_0 + \left( \frac{\partial \alpha}{\partial x} \right)_0 x f \cos(\Omega_R t) \right] E_0 \cos(\omega_P t) \]  

(17)

\[ = \varepsilon_0 \alpha_0 E_0 \cos(\omega_P t) \]  

(18)

\[ + \frac{\varepsilon_0 (\partial \alpha/\partial x)_0 E_0 x f}{2} \cos \left[ (\omega_P - \Omega_R) t \right] \]  

(19)

\[ + \frac{\varepsilon_0 (\partial \alpha/\partial x)_0 E_0 x f}{2} \cos \left[ (\omega_P + \Omega_R) t \right] . \]  

(20)

The first term with frequency \( \omega_P \) describes the Rayleigh scattering (Fig. 6). The second term with frequency \( \omega_S = \omega_P - \Omega_R \) describes a red shifted scattering known as the Raman Stokes scattering. In this case the molecule moves from its ground state \( |f\rangle \) to an excited vibrational state \( |v\rangle \) (phonon creation) whereas the incoming field loses energy. The third term with frequency \( \omega_{AS} = \omega_P + \Omega_R \) describes a blue shifted scattering known as the anti-Stoke Raman scattering where the molecule goes from the excited vibrationnel level \( |v\rangle \) toward its ground state \( |f\rangle \) giving energy to the incoming photon (and absorbing a phonon). Experimentally, the anti-Stokes scattered intensity is less than the Stokes scattered intensity (Fig. 7). This is because at thermal equilibrium atomic level populations are described by the Boltzman statistic telling that the excited level \( |v\rangle \) is less populated than the ground state. Stokes and anti-Stokes scattered intensity become equally intense only for infinite temperature.

The selection rules for a vibration to be Raman active tells that the vibration must affect the polarizability: \( (\partial \alpha/\partial x)_0 \neq 0 \). Similar to IR absorption spectroscopy, Raman spectroscopy enables to identify and quantify the chemical composition of a medium looking at the inelastic scattered Raman spectrum. However a normal mode of a molecule with inversion symmetry is Raman active and not IR active or vice versa. Vibrations symmetric with
FIG. 7. Scattered Raman light for a molecule having a single vibrational frequency mode $\Omega_R$. The anti-Stokes scattered line is less intense than the Stokes one.

respect of the inversion symmetry are Raman active, anti-symmetric are IR active.

The Raman scattered field can be depolarized as compared to the incident electromagnetic field. This is described by the Raman depolarization ratio $\rho_R$ (Fig. 8)

$$\rho_R = \frac{I_R(\perp)}{I_R(\parallel)}.$$  \hspace{1cm} (21)

This coefficient $\rho_R$ differs for various roto-vibrational modes and varies between 0 and $\frac{3}{4}$.

FIG. 8. The Raman scattered light can be depolarized as compared to the incident pump light $I_p$.

Contrary to IR absorption, confocal Raman microscopy can perform imaging with a sub-micron resolution, however the Raman scattering efficiency process is extremely weak. Raman scattering cross sections are of the order of $10^{-30}$ cm$^2$ (as compared to a 1 photon absorption fluorescence cross section that reaches $10^{-16}$ cm$^2$.)
E. Coherent Raman scattering

Nonlinear optics

Nonlinear optics encompasses optical processes that result from the nonlinear response of a medium to the incoming electric field\(^{30}\). These processes appear when the amplitude of the electric field becomes large as compared to the intra-atomic field (typically, \(E_{\text{Coulomb}} = \frac{1}{4\pi\varepsilon_0 a_0^2} \approx 3\times10^{11} \text{ V/m}\), where \(a_0 \approx 5\cdot10^{-11} \text{ m}\) is the Bohr radius). Nonlinear optical phenomena were observed when the laser was invented in 1960. One year after this discovery, the group from P.A. Frenkel could observe the first second harmonic generation (SHG)\(^{31}\). The same year W. Kaiser and C.G.B. Garret could generate two photons excited fluorescence (TPEF)\(^{32}\). In 1965, most of the nonlinear processes were already discovered, among them are the coherent Raman processes.

Coherent Raman scattering processes

![Coherent Raman scattering processes](image)

FIG. 9. (a) Classical description of coherent Raman scattering. (b) Two incoming fields, pump and Stokes, are beating at frequency \(\Omega = \omega_P - \omega_S\) that can be equal to the molecular vibrational resonance \(\Omega_R\). Spectral domain representation. (c) Time domain representation.

Coherent Raman scattering (CRS) is a resonant and coherent process that allows to gain a factor of \(10^7\) in efficiency as compared to spontaneous Raman scattering\(^{30}\). Let’s consider two incoming plane waves, that we denote pump and Stokes, with frequencies \(\omega_P\) and \(\omega_S\), respectively. These waves interact with a medium having a roto-vibrational vibrations \(\Omega_R\). The total field can be written
\[ E(z, t) = A_P e^{i(k_P z - \omega_P t)} + A_S e^{i(k_S z - \omega_S t)} + c.c. \]

(22)

where “c.c.” is the complex conjugate.

The interference between these two fields generates a beating (Fig. 9) with the frequency \( \Omega = \omega_P - \omega_S \)

\[ \langle E^2(z, t) \rangle = A_P A_S^* e^{i(K z - \Omega t)} + c.c. \]

(23)

where \( \langle \cdot \rangle \) is the time average over one optical period, and \( K = k_P - k_S \). If the frequency difference \( \Omega = \omega_P - \omega_S \) is set to \( \Omega = \Omega_R \), the roto-vibrational mode enters in resonance with the wave beating.

**Excitation force calculation**

Let’s consider again our driven harmonic oscillator describing a diatomic molecule

\[
\frac{d^2 x}{dt^2} + 2 \gamma \frac{dx}{dt} + \Omega_R^2 x = \frac{F(t)}{\mu} .
\]

(24)

The energy necessary to create a dipolar moment \( \vec{p}(t) = \varepsilon_0 \alpha(t) \vec{E}(t) \) is given by\(^{30}\)

\[ W = \frac{1}{2} \langle \vec{p}(z, t) \cdot \vec{E}(z, t) \rangle = \frac{1}{2} \varepsilon_0 \alpha(t) \langle E^2(z, t) \rangle . \]

(25)

Similar to spontaneous Raman scattering, we assume that the polarizability is related to the intra-molecular distance following equation 15. Inserting 23 in 25, gives the excitation force produced by the two incoming fields on the molecule.

\[ F(t) = \frac{dW}{dx} = \varepsilon_0 \left( \frac{\partial \alpha}{\partial x} \right)_0 [A_P A_S^* e^{i(K z - \Omega t)} + c.c.] \]

(26)

**Harmonic oscillator solution**

To solve Eq.24 considering the force 26, we look for a solution as
\[ x(z, t) = x(\Omega)e^{i(Kz-\Omega t)} + c.c. \]  

(27)

Near the resonance (Eq. 7), the molecular vibration amplitude is given by

\[ x(\Omega) = \frac{-\left(\varepsilon_0/2m\Omega_R\right) (\partial\alpha/\partial x)_0 A_P A_S^*}{(\Omega - \Omega_R) + i\gamma}. \]  

(28)

If the beating frequency is such that \( \Omega = \Omega_R \), the molecular vibration amplitude becomes large and the excitation fields will now also induce nonlinear polarizations that will be specific to the molecular resonance.

**Induced nonlinear polarization**

If \( N \) denotes the molecular density. The induced polarization in the medium is given by

\[ P(z, t) = N\varepsilon_0 \left[ x(\Omega)e^{i(Kz-\Omega t)} + c.c. \right] E(z, t). \]  

(29)

which is the sum of a linear polarization \( P_L(z, t) = N\varepsilon_0 \alpha_0 E(z, t) \) and a nonlinear polarization

\[ P^{NL}(z, t) = x(\Omega)e^{i(Kz-\Omega t)} + c.c. \times \left[ A_P e^{i(k_p z - \omega_P t)} + A_S e^{i(k_S z - \omega_S t)} + c.c. \right]. \]  

(30)

Expanding this expression, it appears that the nonlinear polarization radiates at 4 different frequencies: \( \omega_{AS} = 2\omega_P - \omega_S \), \( \omega_{CS} = 2\omega_S - \omega_P \), \( \omega_P \) and \( \omega_S \).

\[ P^{NL}(z, t) = P(\omega_{AS})e^{-i\omega_{AS}t} + P(\omega_{CS})e^{-i\omega_{CS}t} + P(\omega_P)e^{-i\omega_P t} + P(\omega_S)e^{-i\omega_S t} + c.c., \]  

(31)

where the complex amplitudes \( P(\omega_{AS}), P(\omega_{CS}), P(\omega_P), P(\omega_S) \) are

\[ P(\omega_{AS}) = N\varepsilon_0(\partial\alpha/\partial x)_0 x(\Omega)A_P e^{i(2k_p - k_S)z}, \]  

(32)

\[ P(\omega_{CS}) = N\varepsilon_0(\partial\alpha/\partial x)_0 x^*(\Omega)A_S e^{i(2k_S - k_P)z}, \]  

(33)

\[ P(\omega_P) = N\varepsilon_0(\partial\alpha/\partial x)_0 x(\Omega)A_S e^{ik_P z}, \]  

(34)

\[ P(\omega_S) = N\varepsilon_0(\partial\alpha/\partial x)_0 x^*(\Omega)A_P e^{ik_S z}. \]  

(35)
Figure 10 shows the energy diagrams associated to these 4 different processes (following the polarization order above):

- Coherent anti-Stokes Raman Scattering (CARS),
- Coherent Stokes Raman Scattering (CSRS),
- Stimulated Raman Loss (SRL),
- Stimulated Raman Gain (SRG).

\[ \chi_R(\omega_{AS}) = \chi^{(3)}(\omega_{AS};\omega_p,\omega_p,\omega_S) \]

\[ \chi_R(\omega_{CS}) = \chi^{(3)}(\omega_{CS};-\omega_p,\omega_S,\omega_S) \]

\[ \chi_R(\omega_P) = \chi^{(3)}(\omega_P;\omega_P,-\omega_S,\omega_P) \]

\[ \chi_R(\omega_S) = \chi^{(3)}(\omega_S;\omega_S,-\omega_P,\omega_P,\omega_P) \]

FIG. 10. Coherent Raman processes. (a) Coherent Anti-Stokes Raman Scattering. (b) Coherent Stokes Raman Scattering. (c) Stimulated Raman Loss. (d) Stimulated Raman Gain.

In the following we will not consider the CSRS process whose frequency \( \omega_{CS} \) is in the IR domain where measurements are noisy and hampered by non ideal detectors. We will concentrate first on the CARS process and latter on the SRL and SRG processes.
III. THE CARS PROCESS

A. Resonant and non-resonant CARS processes

The CARS process was first observed by Maker and Terhune en 1965 while Levenson and Bloembergen presented a detailed investigation 1972. One of the discovery was to find that the CARS signal at frequency $\omega_{AS}$ was always present, even if the frequency difference between the pump and the Stokes beams didn’t match a molecular vibrational resonance ($\Omega \neq \Omega_R$).

To understand this, let’s consider the Jablonski diagram in Fig. 11(a). As described earlier, the resonant CARS process involves the beating between the pump and the Stokes beam frequency $\Omega$ that is resonant with the molecular vibration at frequency $\Omega_R$. This molecular vibration is further probed by the pump pulse to generate the anti-Stokes signal. However there is another route, using the frequencies $\omega_P$ and $\omega_S$, to generate a scattered light with frequency $\omega_{AS}$ (Fig. 11(b)). This other four wave mixing (FWM) process is known as the non-resonant CARS as the exciting beams do not interact with the molecular vibrational state, rather it originates from the instantaneous electronic response of the medium.

\[ \begin{align*}
|v\rangle & \rightarrow |f\rangle \\
\omega_P & \rightarrow \omega_S \\
|v\rangle & \rightarrow |f\rangle
\end{align*} \]

Resonant CARS

\[ \begin{align*}
|v\rangle & \rightarrow |f\rangle \\
\omega_p & \rightarrow \omega_S \\
|v\rangle & \rightarrow |f\rangle
\end{align*} \]

Non-resonant CARS (Four-Wave mixing)

FIG. 11. CARS processes. (a) Resonant CARS. (b) Non-resonant CARS. Dashed lines are virtual states, continuous lines are real molecular states.

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B. Nonlinear polarization and susceptibility

Formally, the nonlinear CARS polarization at location $\vec{r}$ reads

$$\vec{P}(\vec{r}, \omega_s) = \varepsilon_0 \chi^{(3)} (\vec{r}, -\omega_s; \omega_p, -\omega_s, \omega_p) \vec{E}_p (\vec{r}, \omega_p) : \vec{E}_s^* (\vec{r}, \omega_s) : \vec{E}_p (\vec{r}, \omega_p) ,$$  \hspace{1cm} (36)

where $\chi^{(3)}$ is the third order nonlinear susceptibility, a third rank tensor that describes the possible interaction between the pump and Stokes exciting fields with the medium.

Avoiding for a short time the pump and Stokes field spectral dependance, the $i$-th Cartesian component ($i=x,y,z$) of the nonlinear polarization $\vec{P}^{(3)}$ generated in point $\vec{r}$, reads

$$P_i(\vec{r}) = 3 \varepsilon_0 \sum_{j,k,l} \chi^{(3)}_{ijkl} E_{pj}(\vec{r}) E_{pk}(\vec{r}) E_{s l}^*(\vec{r}) ,$$  \hspace{1cm} (37)

where indices $j$, $k$ and $l$ permute over spatial coordinates $x$, $y$ and $z$.

It can be shown that in the case of isotropic media, where one photon transition at $\omega_P$ and $\omega_S$ are not occurring, the nonlinear polarization can be simply expressed in terms of the tensor element $\chi^{(3)}_{xxyy}$ and the Raman depolarization ratio $\rho_R^{35,36}$.

$$\vec{P}(\vec{r}, \rho_R) = 6 \varepsilon_0 \chi^{(3)}_{xxyy} \left\{ \left[ \vec{E}_p (\vec{r}) \cdot \vec{E}_s^* (\vec{r}) \right] \vec{E}_p (\vec{r}) \right. + \left. \frac{\rho_R}{1 - \rho_R} \left[ E_{px}^2 (\vec{r}) + E_{py}^2 (\vec{r}) + E_{pz}^2 (\vec{r}) \right] \vec{E}_s^* (\vec{r}) \right\}$$  \hspace{1cm} (38)

from which we note that

1. When the pump and Stokes beam are linearly polarized and with the same polarization state, the induced nonlinear polarization is collinear with the excitation fields.

2. When the pump and Stokes beams are linearly polarized with orthogonal polarizations ($\vec{E}_p \cdot \vec{E}_s = 0$), the induced nonlinear polarization is always collinear with the Stokes beam. Totally polarized Raman bands cannot be observed.

This relation gives also an insight into the Raman depolarization ratio for the generation of the anti-Stokes field.
3. When the Raman line is totally polarized ($\rho_R = 0$), the induced nonlinear polarization is collinear with the pump field and largest for parallel polarization of pump and Stokes.

4. The more the Raman line is depolarized ($\rho_R$), the larger is the second contribution of equation 38, i.e., the anti-Stokes field along the $\vec{E}_S$ direction. For the maximum depolarization of 0.75, the second contribution is at least 3 times larger than the first term.

Some more information on polarization resolved CARS can be found in 37.

For the sake of simplicity, we will consider from now that the Raman line is totally polarized ($\rho_R = 0$). Furthermore, we suppose that the pump and Stokes beams propagate along the $z$ direction, with the same and linear polarization state. In these conditions equation 38 reads

$$P(\omega_{AS}) = 3\varepsilon_0\chi^{(3)}(\omega_{AS})A_P^2A_S^*e^{i(2k_P-k_S)z},$$

(39)

where $\chi^{(3)}(\omega_{AS}) = 2\chi^{(3)}_{xxyy}$.

We point out that tackling the problem using 1-D plane wave propagation is useful to capture basic properties of nonlinear optical microscopy. However, a full consideration of focused fields in 3D is necessary to provide a more accurate picture.

C. Anti-Stokes field generation and propagation

We concentrate in this section on the generation and propagation of the anti-Stokes field. Under the slowly varying envelope approximation, the anti-Stokes $E_{AS}(z,t) = A_{ASE}e^{i(k_{AS}z-\omega_{AS}t)} + c.c.$ field propagation writes

$$\frac{\partial A_{AS}}{\partial z} = \frac{i\omega_{AS}}{2n_{AS}\varepsilon_0 c} P(\omega_{AS})e^{-ik_{AS}z}. \quad (40)$$

With the expression of the polarization $P(\omega_{AS})$ defined in (39), it comes

$$\frac{\partial A_{AS}}{\partial z} = \frac{3i\omega_{AS}}{2n_{AS}c} \chi^{(3)}(\omega_{AS})A_P^2A_S^*e^{i\Delta k z}, \quad (41)$$

where $\Delta k = \Delta \vec{k} \cdot \vec{e}_z = (2\vec{k}_P - \vec{k}_S - \vec{k}_{AS}) \cdot \vec{e}_z$. 

19
Suppose that the anti-Stokes signal is generated in a medium with length $L$. The anti-Stokes field in $z = L$ reads

$$A_{AS}(L) = \int_0^L \frac{\partial A_{AS}}{\partial z} dz = \frac{3 i \omega_{AS}}{2 n_{AS} c} \chi^{(3)}(\omega_{AS}) L \sin\left(\frac{\Delta k L}{2}\right) e^{i\Delta k L} A_P^2 A_S^* ,$$

with $\sin(x) = \frac{\sin(x)}{x}$.

From which we get the expression of the anti-Stokes intensity

$$I_{AS}(L) \propto |\chi^{(3)}(\omega_{AS})|^2 L^2 \sin^2\left(\frac{\Delta k L}{2}\right) I_P^2 I_S .$$

It is interesting to note that the anti-Stokes intensity in $z = L$ is proportional to $\sin^2(\Delta k L/2)$ (Fig. 12(a)). The anti-Stokes signal is efficiently generated only if $\Delta k L/2 \ll 1$ because the total anti-Stokes field is the result of the coherent summation of the anti-Stokes fields emitted from each points along $z$, and this interference is constructive only if all fields are in phase. For this, the anti-Stokes field must be in phase with the induced nonlinear polarization for every points along the $z$ axis. This is what is known as the 'phase matching condition' that requires

$$\Delta \vec{k} = 2\vec{k}_P - \vec{k}_S - \vec{k}_{AS} = \vec{0} ,$$

the wave vectors being

$$\vec{k}_P = \frac{n_P \omega_P}{c} \vec{e}_P, \quad \vec{k}_S = \frac{n_S \omega_S}{c} \vec{e}_S, \quad \vec{k}_{AS} = \frac{n_{AS} \omega_{AS}}{c} \vec{e}_{AS} .$$

In the considered collinear situation ($\vec{e}_P = \vec{e}_S = \vec{e}_{AS} = \vec{e}_z$), the phase matching condition is rarely fulfilled ($\Delta k \neq 0$) because of the medium dispersion ($n_P \neq n_S \neq n_{AS}$). It is useful to define the ”nonlinear coherence length" $L_c$ as the length over which the maximum of the anti-Stokes signal develops

$$L_c = \frac{\pi}{\Delta k} .$$

When the interaction length of the exciting fields $L$ is larger than the nonlinear coherence length, the anti-Stokes signal generation becomes less efficient (Fig. 12(c)) because of destructive interferences. It is therefore important to minimize $\Delta k$ to get the longest possible coherence length.
I_{AS} \propto \sin^2(x) = \frac{\Delta k L}{2\pi}

FIG. 12. (a) CARS signal generation efficiency depending on the phase mismatch and the interaction length $L$. (b) Phase matching condition for collinear pump and Stokes beams. (c) Anti-Stokes generation efficiency with the interaction length $L$ (the phase mismatch being fixed).

In the context of microscopy, CARS signal is efficiently generated for two reasons. First, the phase matching condition is relaxed when the pump and Stokes beams are strongly focused into the nonlinear medium. The broad angular spectrum of the wave vectors $\vec{k}$ allows many combinations for the pump, Stokes and anti-Stokes wave vectors to satisfy the relation $44$. Second, a tight focusing of the exciting fields leads to a small nonlinear excitation volume, of the order of $10\mu m$, such that the interaction length $L$ is too short for destructive interference.

D. $\chi^{(3)}$ in the spectral domain

We focus in this section on the anti-Stokes intensity spectrum. We have seen previously that the CARS signal has two contributions.

- A resonant contribution described by the susceptibility $\chi_{R}^{(3)}$. Comparing $32$ with $39$, and inserting $x(\Omega)$ previously derived (Eq. 28), we get the CARS resonant nonlinear susceptibility

$$\chi_{R} = \frac{a}{(\Omega - \Omega_{R}) + i\gamma}, \quad (47)$$
with \( a = - (2N\varepsilon_0/6\mu\Omega_R)(\partial\alpha/\partial x)_0^2 \), a negative number that represents the oscillator strength of the molecular vibration.

- A non-resonant contribution described by the susceptibility \( \chi_{NR}^{(3)} \). Far from electronic resonances this non-resonant contribution is real and constant\(^3,{}^3\).

The total CARS susceptibility writes

\[
\chi^{(3)} = \chi_R^{(3)} + \chi_{NR}^{(3)} .
\]  

(48)

Introducing this expression in 43, we get

\[
I_{AS} \propto \left| \chi_R^{(3)} + \chi_{NR}^{(3)} \right|^2
\]

(49)

\[
\propto \left| \chi_R^{(3)} \right|^2 + \left| \chi_{NR}^{(3)} \right|^2 + 2\text{Re} \left[ \chi_R^{(3)} \cdot \chi_{NR}^{(3)} \right] 
\]

(50)

\[
\propto \left| \chi_R^{(3)} \right|^2 + \left| \chi_{NR}^{(3)} \right|^2 + 2\chi_{NR}^{(3)} \cdot \text{Re} \left[ \chi_R^{(3)} \right] .
\]

(51)

Where it appears that the anti-Stokes intensity is the sum of three contributions that we describe now following their order.

- A resonant contribution that contains all the vibrational mode spectral information.
  
  This is the one that is most wanted in spectroscopy applications.

- A non-resonant contribution that is constant in the spectral domain.

- A resonant and non-resonant mixing contribution know as the heterodyne contribution, proportional to the real part of \( \chi_R^{(3)} \).

Therefore, one can see the anti-Stokes spectral signal as the output of a two-waves interferometer, the interference being the heterodyne term. Figure 13 shows the spectral behavior of the three contributions, together with the total resulting anti-Stokes signal. Because of the heterodyne term the CARS spectrum is distorted as compared to the Raman spectrum. The anti-Stokes maximum signal is blue shifted from \( \Omega_R \) and an intensity minimum appears on the red side of the intensity maximum. Furthermore the CARS spectrum is not symmetric on both sides of \( \Omega_R \).
FIG. 13. The anti-Stokes signal in the spectral domain. Contributions of the resonant, heterodyne and non-resonant intensities. We consider here a Raman line with a half width at half maximum \( \gamma = 5 \text{ cm}^{-1} \).

We will now focus on the spectral evolution of the nonlinear susceptibility \( \chi^{(3)} \) in the complex plane. As every resonance, it can be described as a circle, as already presented in the case of the spring resonance. Figure 14(a) shows the resonant contribution \( \chi^{(3)}_R \) as a dashed black circle. As \( \chi^{(3)}_{NR} \) is real the total CARS susceptibility \( \chi^{(3)} = \chi^{(3)}_R + \chi^{(3)}_{NR} \) also describes a circle (in blue), but shifted on the real axis by \( \chi^{(3)}_{NR} \) (in red). This shift has strong consequences on the \( \chi^{(3)} \) phase and on the CARS intensity\(^{40} \) (Fig. 14(b)).

- As we have seen previously, the CARS maximum intensity, or equivalently \( \chi^{(3)} \), (point 2) is shifted with respect to the Raman resonance (point 3).

- The \( \chi^{(3)} \) phase is lower than \( \pi/2 \) at the Raman resonance (point 3). Its spectrum shows a maximum (point 4) that is red shifted with respect to the Raman resonance.

- The CARS minimum intensity is in point 5, red shifted with respect to the Raman peak.

In practise the coherent nature of the CARS process makes the resonant and non-resonant contributions difficult to separate. These two contributions manifest themselves as:

- At resonance, the resonant anti-Stokes field is dephased with respect to the anti-Stokes non-resonant field\(^{41,42} \).
FIG. 14. CARS spectrum. (a) CARS susceptibility in the complex plane. The resonant contribution $\chi^{(3)}_R$, associated to the Raman resonance describes a circle (dashed black line). The total CARS susceptibility $\chi^{(3)}$ (solid blue circle) is the sum of the resonant $\chi^{(3)}_R$ and the non-resonant $\chi^{(3)}_{NR}$, a real quantity (red line). (b) Spectral CARS intensity (green) and CARS phase (orange).

- If the pump and Stokes field polarization states are different, the resulting resonant and non-resonant anti-Stokes fields will not have the same polarization state. This effect is related to the Raman depolarization ratio and the tensor properties of $\chi^{(3)}$.

- In the case of the resonant CARS process, the vibrational level is populated in a coherent way. This coherence is conserved during a time $T_2$ (known as the “coherence time”), of the order of the picosecond. The CARS signal generation is efficient only if the second photon with frequency $\omega_P$ probes the vibration within a time shorter than
$T_2$ as demonstrated in$^{43}$. In the case of the non-resonant CARS, $T_2$ is much shorter (few hundreds of femtoseconds).

Even with this non-resonant background the CARS process is a powerful spectroscopic tool. CARS can bring similar information than spontaneous Raman but its resonant and coherent character makes it much more efficient and therefore, compatible with imaging. Contrary to spontaneous Raman scattering, the CARS signal is blue shifted as compared to the pump and Stokes beams and not polluted by possible molecular unwanted single photon fluorescence. P. Regnier et J.-P. Taran were the first to use CARS spectroscopy to measure specific molecular concentration in gas in 1973$^{44}$. R. Begley et al could measure one year later specific molecular concentrations in toluene-benzene mixtures/solutions$^8$ using CARS.

IV. THE SRS PROCESS

In this section we will describe in detail the SRL and SRG processes. Those two processes and intimately linked and are usually described under the same stimulated Raman scattering (SRS) process. They were discovered in 1962 by Woodbury and Ng$^{45}$ as they were studying Q-switching processes in a Ruby laser containing a nitrobenzene Kerr cell. They could detect a strong IR radiation coming from the Kerr cell which remained mysterious for some times. Some months later, Woodbury and Eckhardt hypothesized that this was coming from a stimulated Raman process that could be confirmed experimentally$^4$. A detailed SRS process description can be found in review articles from Hellwarth$^4$, Bloembergen$^6$, and Shen and Bloembergen$^5$.

A. Coherence and interferometry

As in the CARS process, we define the third order nonlinear susceptibilities $\chi_R^{(3)}(\omega_P)$ and $\chi_R^{(3)}(\omega_S)$ associated to the SRL and SRG processes, respectively, through their respective induced polarizations

$$P(\omega_P) = 6\varepsilon_0\chi_R^{(3)}(\omega_P)|A_S|^2A_Pe^{ik_Pz}$$

$$P(\omega_S) = 6\varepsilon_0\chi_R^{(3)}(\omega_S)|A_P|^2A_Se^{ik_Sz}.$$
FIG. 15. Spectral domain view of coherent Raman scattering. Different to CARS and CSRS processes that generate new frequencies, SRL and SRG processes appear as intensity loss $\Delta I_P$ on the pump beam and intensity gain $\Delta I_S$ on the Stokes beam. These intensity variations $\Delta I_P$ et $\Delta I_S$ are amplified by the excitation fields in a heterodyne way.

Contrary to the CARS process, the SRS polarizations are induced at the same frequencies than the incoming pump and Stokes beams. The pump and Stokes field generate $P(\omega_P)$ that, itself, generates a weak “nonlinear” field $E_P^{(3)} = A_P^{(3)} e^{i(k_P z - \omega_P t)} + c.c.$ Having the same frequency as the incoming pump beam, and being coherent, this weak “nonlinear” field interferes with the incoming excitation pump field $E_P$. As a result the SRS signal can be viewed as the result of an interference between a weak “nonlinear” field, with the strong incoming field. To understand better this phenomenon let’s consider the nonlinear medium as a single dipole located in $z = 0$. The resulting intensity of this interference can be written as

$$I_P^{SRL} \propto \left| A_P + A_P^{(3)} \right|^2$$

$$\propto |A_P|^2 + \left| A_P^{(3)} \right|^2 + 2 |A_P A_P^{(3)}| \cos \left[ \varphi \left( A_P^{(3)} \right) - \varphi (A_P) \right].$$

(54)

(55)

In a similar way the weak “nonlinear” field $E_S^{(3)} = A_S^{(3)} e^{i(k_S z - \omega_S t)} + c.c.$ interferes with the strong incoming Stokes field $E_S$.  

26
\[ I_{SRG}^{S} \propto \left| A_{S} + A_{S}^{(3)} \right|^2 \]  
\[ \propto |A_S|^2 + |A_S^{(3)}|^2 + 2 A_S A_S^{(3)} \cos \left[ \varphi \left( A_S^{(3)} \right) - \varphi \left( A_S \right) \right]. \]

The second term \( |A^{(3)}|^2 \) is negligible in comparison to \( |A|^2 \). However, the quantity \( |A A^{(3)}| \) can be significant and depends on the phase difference between the generated weak field and the incoming strong field. Let’s have a closer look at this phase difference term.

The generated fields are related to the nonlinear polarizations by the expressions:

\[
\begin{align*}
A_p^{(3)} &\propto i P(\omega_P) \\
A_s^{(3)} &\propto i P(\omega_S).
\end{align*}
\]

Note that the above mentioned expressions between the generated fields and the induced polarizations are strictly true in the molecule far field but a more complex approach leads to the same final result. From the induced polarizations 52 and 53, we get

\[
\begin{align*}
\varphi \left( A_p^{(3)} \right) - \varphi \left( A_p \right) &= \frac{\pi}{2} + \varphi \left( \chi_R^{(3)}(\omega_P) \right) \\
\varphi \left( A_s^{(3)} \right) - \varphi \left( A_S \right) &= \frac{\pi}{2} + \varphi \left( \chi_R^{(3)}(\omega_S) \right).
\end{align*}
\]

Comparing 34 and 35 with 52, 53, and inserting the expression of \( x(\Omega) \) previously computed (Eq. 28), we get the nonlinear susceptibility involved into the SRL and SRG processes

\[
\begin{align*}
\chi_R(\omega_P) &= \frac{a/2}{(\Omega - \Omega_R) + i\gamma} \\
\chi_R(\omega_S) &= \frac{a/2}{(\Omega - \Omega_R) - i\gamma}.
\end{align*}
\]

Where \( a \) is a negative constant that describes the oscillator strength of the molecular vibration \( a = - (2N\varepsilon_0/6\mu\Omega_R) (\partial\alpha/\partial x)^2_0 \). It appears the SRL susceptibility is intimately linked to the resonant CARS susceptibility (Eq. 47) as \( \chi_R(\omega_P) = \frac{1}{2} \chi_R(\omega_{AS}) \). Furthermore, the SRL and SRG processes are symmetrical \( \chi_R(\omega_S) = \chi_R(\omega_P)^* \).

At resonance, we note that \( \varphi \left( \chi_R^{(3)}(\omega_P) \right) = \pi/2 \) and \( \varphi \left( \chi_R^{(3)}(\omega_S) \right) = -\pi/2 \). Inserting expression 59 into equations 55 and 57, we get the SRL and SRG intensities at the Raman resonance
\[
\begin{align*}
I_{P}^{SRL} & \propto |A_{P}|^2 + 2 |A_{P}A_{P}^{(3)}| \cos(\pi) \propto I_{P} - 2\sqrt{I_{P}I_{P}^{(3)}} \\
I_{S}^{SRG} & \propto |A_{S}|^2 + 2 |A_{S}A_{S}^{(3)}| \cos(0) \propto I_{S} + 2\sqrt{I_{S}I_{S}^{(3)}}.
\end{align*}
\]

(61)

Where it clearly appears that, at resonance ($\Omega = \Omega_{R}$), the pump intensity experiences a depletion whereas the Stokes field experiences a gain, this is the origin of the terminologies “Stimulated Raman Loss” and “Stimulated Raman Gain”.

B. Field propagation

![Figure 16: SRS process description when the pump and Stokes beams propagate into a medium with length L.](image)

We focus now on the interaction of the pump and Stokes fields with a nonlinear medium of length $L$ (Fig. 16). Within the slowly varying envelope approximation, the propagation equations for the pump and Stokes fields write

\[
\begin{align*}
\frac{\partial A_{P}}{\partial z} & = \frac{i\omega_{P}}{2n_{P}\varepsilon_{0}c}P(\omega_{P})e^{-ik_{P}z} \\
\frac{\partial A_{S}}{\partial z} & = \frac{i\omega_{S}}{2n_{S}\varepsilon_{0}c}P(\omega_{S})e^{-ik_{S}z}.
\end{align*}
\]

(62)

Inserting the nonlinear polarization expressions 52 and 53, it comes

\[
\begin{align*}
\frac{\partial A_{P}}{\partial z} & = \frac{3i\omega_{P}}{n_{P}c}\chi^{(3)}_{R}(\omega_{P})|A_{S}(z)|^2 A_{P}(z)e^{i\Delta k z} \\
\frac{\partial A_{S}}{\partial z} & = \frac{3i\omega_{S}}{n_{S}c}\chi^{(3)}_{R}(\omega_{S})|A_{P}(z)|^2 A_{S}(z)e^{i\Delta k z}.
\end{align*}
\]

(63)

(64)

One of the feature of the SRS process is that phase matching is always fulfilled as $\Delta \vec{k} = (\vec{k}_{P} - \vec{k}_{P} + \vec{k}_{S} - \vec{k}_{S}) = \vec{0}$. Therefore the nonlinear field generated at distance $z$ is always in phase with the nonlinear fields generated in any other distances $z'$ in the medium. Let’s
compute now the total field resulting from the interference between the nonlinear fields and the incoming excitation field. For the sake of simplicity we consider that the incoming Stokes beam (respectively the incoming pump beam) doesn’t feel the result of its possible weak intensity variation when it generates the weak nonlinear pump field (respectively the weak nonlinear Stokes field) in equation 63 (respectively 64). This often valid hypothesis is usually refereed as “non depleted pump” approximation, where the “pump” terminology refers to the excitation field that induces the nonlinear parametric process\(^{20}\). Within this hypothesis it comes

\[
\begin{align*}
A_P(L) &= A_P(0) \exp \left[ \frac{3\omega_P}{n_P c} \chi_R^{(3)}(\omega_P) |A_S(0)|^2 L \right] \\
A_S(L) &= A_S(0) \exp \left[ i \frac{3\omega_S}{n_S c} \chi_R^{(3)}(\omega_S) |A_P(0)|^2 L \right].
\end{align*}
\]

(65)  (66)

Where it is useful to separate \(\chi_R^{(3)}\) into its real and imaginary parts. Furthermore, we have seen previously that, following equation 60, \(\chi_R^{(3)}(\omega_S) = \chi_R^{(3)}(\omega_P)^*\). In the following we set \(\chi_R^{(3)} = \chi_R^{(3)}(\omega_P) = \chi_R^{(3)}(\omega_S)^*\). With this we can write

\[
\begin{align*}
A_P(L) &= A_P(0) \exp \left[ \frac{3\omega_P}{n_P c} {\text{Im}}(\chi_R^{(3)}) |A_S(0)|^2 L \right] \exp \left[ i \frac{3\omega_P}{n_P c} {\text{Re}}(\chi_R^{(3)}) |A_S(0)|^2 L \right] \\
A_S(L) &= A_S(0) \exp \left[ + \frac{3\omega_S}{n_S c} {\text{Im}}(\chi_R^{(3)}) |A_P(0)|^2 L \right] \exp \left[ i \frac{3\omega_S}{n_S c} {\text{Re}}(\chi_R^{(3)}) |A_P(0)|^2 L \right].
\end{align*}
\]

(67)  (68)

Where it appears clearly that the pump amplitude loss and the Stokes amplitude gain along propagation depend on the imaginary part of the susceptibility \(\text{Im}(\chi_R^{(3)})\). The real part of the susceptibility induces a variation of the refractive index for the pump (respectively Stokes), depending on the Stokes (respectively pump) intensity. Using the pump intensity \(I_P(z) = 2n_P c_0 |A_P(z)|^2\) and the Stokes intensity \(I_S(z) = 2n_S c_0 |A_S(z)|^2\), this refractive index variation writes

\[
\begin{align*}
\delta n_P &= \frac{3 \text{Re}(\chi_R^{(3)}) I_S(0)}{2n_P n_S c_0} \\
\delta n_S &= \frac{3 \text{Re}(\chi_R^{(3)}) I_P(0)}{2n_P n_S c_0}.
\end{align*}
\]

(69)  (70)

This is known as “crossed phase modulation” (XPM) and can be viewed as a crossed Kerr effect, the refractive index at one frequency is changed by a wave at another frequency.
Therefore XPM can induce some spurious effects of focusing or defocusing, by one beam on the other. This is the origin of small non-resonant background signals in SRS described in 47.

Let’s focus now on the pump and Stokes intensity after the interaction with a nonlinear medium of length $L$.

\[
I_p(L) = I_p(0) \exp \left[ -\frac{3\omega_p}{2n_p n_s \varepsilon_0 c^2} \text{Im}(\chi^{(3)}_R) I_s(0) L \right] 
\]

(71)

\[
I_s(L) = I_s(0) \exp \left[ +\frac{3\omega_s}{2n_p n_s \varepsilon_0 c^2} \text{Im}(\chi^{(3)}_R) I_p(0) L \right] .
\]

(72)

It appears that the pump gain and the Stokes loss have an exponential dependance with the length $L$ of the medium. A property interesting for applications that use long propagation distances such as in fiber optics. In the microscopy context the length $L$ where the SRS process is efficient, and that corresponds to the volume where pump and Stokes beam are in focus, is sufficiently small for the quantity within the exponential to be much smaller than 1. Therefore it is possible to perform a first order development

\[
I_p(L) \approx I_p(0) - \frac{3\omega_p L}{2n_p n_s \varepsilon_0 c^2} \text{Im}(\chi^{(3)}_R) I_s(0) I_p(0) 
\]

(73)

\[
I_s(L) \approx I_s(0) + \frac{3\omega_s L}{2n_p n_s \varepsilon_0 c^2} \text{Im}(\chi^{(3)}_R) I_p(0) I_p(0) .
\]

(74)

Where the second terms of expressions 73 and 74 are the pump intensity loss $\Delta I_p$ and the Stokes intensity gain $\Delta I_s$, respectively. We note that these quantities are linked by $\Delta I_p = (\omega_s/\omega_p) \Delta I_s$. And the SRS process can be viewed as an energy transfer from the pump beam towards the Stokes beam. Another feature of expressions 73 and 74 is that both loss and gain are proportional to $\text{Im}(\chi^{(3)}_R)$ which is the key property that links directly SRS to spontaneous Raman as we shall see now.

**Spontaneous Raman viewed as a stimulated Raman process**

In quantum optics, spontaneous emission is described as a stimulated emission from the vacuum field fluctuations. The vacuum fluctuations are present in any allowed electromagnetic modes, in homogeneous media all the $k$ vectors are allowed but in an electromagnetic cavity the local density of state can be different and the vacuum spectrum follows the
FIG. 17. Spontaneous Raman scattering viewed as stimulated Raman processes. The Stokes fields $I_S(0, \varphi_i)$ are present as fluctuations (thermal, vacuum field, etc.) and have random phases and random incoming directions. Each of these Stokes fields are amplified as experiencing SRG due to the presence of the pump beam. The final process is a spontaneous Raman scattering where the scattered Stokes photons have random phases and random directions.

electromagnetic modes that can exist within the cavity. As a consequence the spontaneous emission of a resonant atom located into such a cavity concentrates in the cavity mode only. Conversely if the cavity has no available mode, the spontaneous emission is hampered. The possible enhancement or inhibition of the spontaneous emission rate is known as the Purcell effect, it is a direct consequence of the Fermi golden rule that links the spontaneous emission rate and the local density of electromagnetic states.

In the spontaneous Raman scattering process a beam with frequency $\omega_P$ interact with a medium having molecular species. Because the vacuum fluctuations are present in the Stokes modes with frequency $\omega_S$ such that $\omega_P - \omega_S = \Omega_R$, the vacuum fluctuation will be amplified through SRG as described in equation 74

$$\delta I_S(L) \approx \delta I_S(0) + \frac{3\omega_S L}{2n_p n_s \varepsilon_0 c^2} \text{Im}(\chi_R^{(3)}) \delta I_S(0) I_P(0).$$

(75)

Where the first term can be neglected as compared to the second one that takes advantage of the heterodyne amplification through $I_P(0)$. Because they are coming from fluctuations, the amplified Stokes fields with intensities $\delta I_S$ have a random phases and propagate in every directions. The SRG process can operate between the pump field and any Stokes field directions because in SRS the phase matching is always fulfilled. As a result SRG processes
between the incoming pump beam and the random vacuum fluctuations generate incoherent
Stokes fields, in every directions, satisfying \( \omega_P - \omega_S = \Omega_R \), it is nothing but the spontaneous
Raman scattering process\(^{50}\)

\[
I_{\text{Raman}} \propto \text{Im}(\chi_R^{(3)}) .
\] (76)

In 1993 Cairo et al put a Raman medium (C\(_6\)H\(_6\)) in a cavity to study the spontaneous
Raman process\(^{51}\). They observed that the fluctuation spectrum of \( \delta I_S(0) \) was related to the
cavity modes. They demonstrated that, as spontaneous emission, it is possible to enhance
or inhibit spontaneous Raman scattering for a specific Raman line, just by spectral tuning
of the cavity.

C. CARS, SRS and Raman spectral responses

We have seen that the non-resonant background distorts the CARS intensity spectrum.
This is why the CARS spectrum (Eq. 76) is fundamentally different from the Raman spec-
trum.

\[
I_{\text{CARS}} \propto |\chi_R^{(3)} + \chi_{NR}^{(3)}|^2 \neq \text{Im}(\chi_R^{(3)}) .
\] (77)

Conversely in the SRG and SRL processes the intensity pump depletion \( \Delta I_P \) and inten-
sity Stokes gain \( \Delta I_S \) are proportional to \( \text{Im}(\chi_R^{(3)}) \) as shown by equations 73 et 74. Therefore
measuring \( \Delta I_P \) and \( \Delta I_S \) gives a direct and rigourous access to the Raman spectrum.

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Antisymmetric Stretching mode

Symmetric Stretching mode

Shear mode

$\Omega_R = 3750 \text{ cm}^{-1} - \lambda = 2,66 \mu m$

$\Omega_R = 3650 \text{ cm}^{-1} - \lambda = 2,74 \mu m$

$\Omega_R = 1600 \text{ cm}^{-1} - \lambda = 6,27 \mu m$
\[ q \xrightarrow{\Omega_R} x_0 + x \]

\[ |e\rangle \quad \text{Infrared Absorption} \]

\[ |v\rangle \quad \Omega_R \]

\[ |f\rangle \]
(a) Complex plane

(b) Dispersion

(c) Absorption

\[ \text{Re}(\chi^{(1)}) \]

\[ \text{Im}(\chi^{(1)}) \]

\[ \Omega_R \]

\[ \gamma \]
Rayleigh Scattering

Stokes Raman Scattering

anti-Stokes Raman Scattering

\(|e\rangle\)  \(\omega_P\)  \(\omega_P\)  

\(|v\rangle\)  \(\omega_P\)  \(\omega_S\)  

\(|f\rangle\)  \(\omega_P\)  \(\omega_{AS}\)  

\(\Omega_R\)

\(|v\rangle\)  \(\omega_P\)  \(\omega_S\)  

\(|f\rangle\)  \(\omega_P\)  \(\omega_{AS}\)  

\(|f\rangle\)  \(\omega_P\)  \(\omega_{AS}\)
The text appears to be discussing the relationship between the energy levels of two systems, $E_s(t)$ and $E_p(t)$, and the resonance frequency, $\Omega_R$. The figure shows a schematic of a system with a spring, indicating the displacement $x_0 + x$ and the resonant frequency $\Omega_R$. The diagrams in the figure illustrate the frequency response and the current $I$ over time $t$, with peaks at certain frequencies $\omega_p$ and $\omega_S$. The mathematical equations and expressions seem to be related to the resonance phenomenon, with $\Omega = \omega_p - \omega_S$.
(a) CARS

\[ \chi_R(\omega_{AS}) = \chi^{(3)}(\omega_{AS};\omega_p,-\omega_s,\omega_p) \]

(b) CSRS

\[ \chi_R(\omega_{CS}) = \chi^{(3)}(\omega_{CS};-\omega_p,\omega_s,\omega_s) \]

(c) SRL

\[ \chi_R(\omega_p) = \chi^{(3)}(\omega_p;\omega_p,-\omega_s,\omega_s) \]

(d) SRG

\[ \chi_R(\omega_s) = \chi^{(3)}(\omega_s;-\omega_p,\omega_s,\omega_p) \]
Resonant CARS

Non-resonant CARS (Four-Wave mixing)
\( I_{AS} \propto \sin^2(x) \)

\[
x = \frac{\Delta k L}{2\pi}
\]

\[
I_{AS} \propto \sin^2(x)
\]

\[
x = \frac{L}{L_C}
\]
Anti-Stokes Intensity (u.a.)

Raman Shift : $\Omega - \Omega_R$ (cm$^{-1}$)

- Total AS Intensity
- Resonant term
- Heterodyne term
- Non-Resonant term
(a) CARS intensity (a.u.)

1. Off res.
2. CARS peak.
3. Raman peak.
4. max Phase
5. CARS dip.
6. Off res.

(b) Raman Shift : $\Omega - \Omega_R$ (cm$^{-1}$)

NR Background
\[ \delta I_p(0) \rightarrow \delta I_S(L, \phi_1) \rightarrow \delta I_S(0, \phi_1) \rightarrow \delta I_S(L, \phi_3) \rightarrow \delta I_S(0, \phi_3) \rightarrow \delta I_S(L, \phi_5) \rightarrow \delta I_S(0, \phi_5) \rightarrow \delta I_S(L, \phi_4) \rightarrow \delta I_S(0, \phi_4) \rightarrow \delta I_S(L, \phi_2) \rightarrow \delta I_S(0, \phi_2) \rightarrow \chi_R^{(3)} \]