

Module 4 : Third order nonlinear optical processes

Lecture 29 : Stimulated Raman scattering(SRS)

Objectives

In this lecture we will present the

- Quantum mechanical picture of the stimulated Stokes Raman scattering.
- Stimulated Stokes Raman scattering as a third order nonlinear optical process-A classical model for the corresponding nonlinear polarization and Raman susceptibility.
- Spatial evolution of the Stokes wave propagating through the Raman active medium.
- Some applications of SRS.

Stimulated Raman scattering(SRS)

Spontaneous Raman scattering of the incident photon of energy $\hbar\omega_i$ by a molecule was described in the lecture 28 as a two-photon process. It was shown there that the transition probability of the scattering (see equation 28.16 and 28.17) increases with the intensity of incident light. For very intense light fields available from lasers- now onwards we will call it the pump field- apart from the increased spontaneous Raman scattering, another process called the stimulated Raman scattering occurs. This effect was discovered by Woodbury and Ng⁽¹⁾ in 1962 when experimenting with Q-switched lasers in an experimental setup similar to the one shown in figure 29.1. They observed that the laser radiation from a Q-switched laser cavity containing

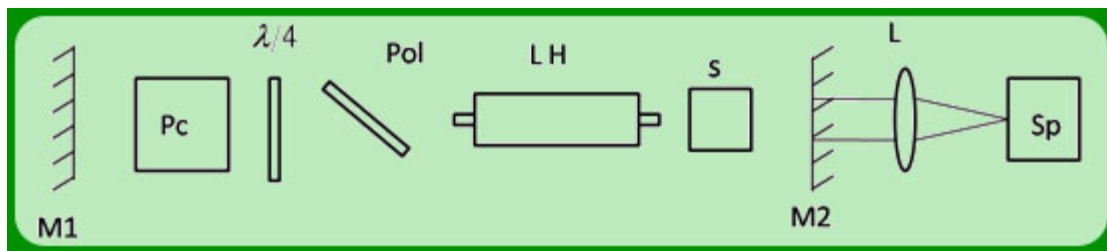


Figure 29.1: Schematic representation of the experimental setup used by Woodbury and Ng for the observation of SRS. Here $M_{1,2}$ —laser cavity mirrors, $\lambda/4$ - quarter wave plate, Pc- Pockels cell, Pol- polarizer, LH —laser head, S—sample, L—lens, Sp—spectrometer.

materials was accompanied by coherent radiation at frequencies shifted from that of the laser. Frequency shifts were found to match with the molecular vibrational frequencies or their integral multiples.

This phenomenon was attributed to the induced scattering process and was, therefore, termed stimulated Raman scattering. The nature of this radiation was found to be different from that generated by spontaneous Raman effect. Some subtle differences between the two processes are

- Due to the coherent nature of the Stokes photons in the stimulated Raman scattering, interference of the radiation occurs. For the spontaneous process, there is no such interference.
- Width of Stokes and anti-Stokes Raman lines represent the energy width of the vibrational state in the spontaneous scattering. In the stimulated process, it is considerably less as the output occurs where the gain is maximum.
- Stimulated Stokes Raman scattering is highly directional unlike its spontaneous counterpart

A complete theoretical account of the stimulated Raman scattering was given by Eckhardt⁽²⁾ in 1962. A simple classical treatment⁽³⁾ of the same was given by Garmire in 1963. An excellent tutorial by Bloembergen⁽⁴⁾ is recommended for the beginners. In this lecture, we will pay attention to the induced Stokes Raman Scattering only. Other, stimulated scattering processes will be covered in the subsequent lectures.

In this process a pump photon induces an upward transition $|i\rangle \rightarrow |j\rangle$ from the ground to the virtual state. If a Stokes photon created elsewhere is available simultaneously, it can stimulate a down ward

transition $|j\rangle \rightarrow |f\rangle$ from the virtual state to the final state of the system with the creation of a Stokes photon which is the replica of the stimulating photon in terms of the direction, frequency, phase and polarization.

It thus generates a coherent Stokes wave in phase with the incident fields.

Energy balance is simply given by

$$\hbar\omega_p + \hbar\omega_s = 2\hbar\omega_s + \hbar\omega_m \quad (29.1)$$

Quantum mechanical representation of the process is given schematically in figure 29.2.

Total transition probability or the growth rate of the Stokes photons is given by the equation

$$P(\hbar\omega_s) = Dn_p(n_s + 1)N_0 = \frac{dn_s}{dt} \quad (29.2)$$

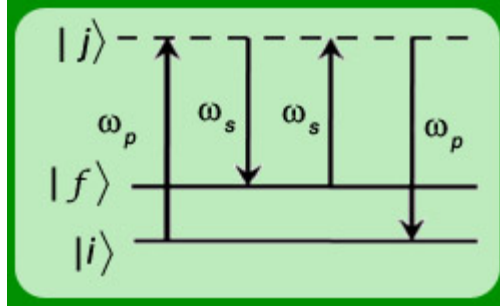


Figure 29.2 Quantum mechanical representation SRS

Spatial rate of change on the propagation distance $z = \frac{c}{\mu}t$, where μ is the refractive index of the medium, can thus be written as

$$\frac{dn_s}{dz} = \frac{\mu}{c} \frac{dn_s}{dt} = \frac{\mu}{c} Dn_p(n_s + 1)N_0 \quad (29.3)$$

Integration of this equation then describes the growth of the Stokes mode with the distance of propagation through the scattering medium. Let us consider the following two cases.

1. $n_s \ll 1$ - case of spontaneous Raman scattering

$$n_s(z) = \frac{\mu}{c} Dn_p N_0 z$$

\Rightarrow linear growth of the Stokes mode intensity with the length of the scattering medium.

2. $n_s \gg 1$ - case of stimulated Raman scattering.

$$n_s(z) = n_s(0) \exp(Gz) \quad (29.4)$$

where

$$G = \frac{\mu}{c} Dn_p N_0 \quad (29.5)$$

is the Raman gain coefficient. Due to exponential growth in stimulated Raman scattering process more than 10% of the incident pump field can be scattered in to the Stokes mode as against the 10^{-6} fraction of it in the spontaneous scattering. If no initial seed photons at Stokes

frequency are present, then the generation of Stokes photons first occurs by spontaneous Raman scattering. Among these, the Stokes photons that run parallel to the pump beam serve as the seed and get amplified by SRS process at the expense of the pump beam photons whose number decreases. Under this condition, unlike spontaneous Raman scattering, stimulated Raman scattering does not take place at all the Stokes frequencies for a molecule. It is rather limited only to those vibrational modes where the gain is maximum. These Stokes lines sap the pump field so rapidly that the gain for the weaker Stokes lines gets suppressed (see equation 29.5). Thus those Stokes modes which have better access to the gain win out the competition to survive and others just perish analogous to the Darwin's principle of the 'survival of the fittest'. Some of these become amplified to an extent so as to generate their own Stokes frequencies so that in the output we get cascade of lines shifted from the pump line by $m\omega_m$ where $m=1,2,3---$. Of course, due to anharmonicity of the vibrational potential subsequent observed shifts are not exact overtones.

Thus, SRS can be an effective frequency conversion process. Being a two-photon process, in classical electromagnetic theory, it can be described as a third order nonlinear phenomenon.

Classical model of Stimulated Raman Scattering- a Nonlinear Optical Process:

We can understand the process of scattering in terms of the following physical picture. Pump laser field of frequency ω_p interacting with a molecule vibrating with frequency ω_m , generates a Stokes field at frequency $\omega_s = \omega_p - \omega_m$ by spontaneous Raman scattering. This Stokes field beats with the pump field to produce the intensity modulation of the form

$$I(t) = I_0 + I_1 \cos(\omega_p - \omega_s)t$$

This modulated light field coherently drives the molecular vibration at the frequency $\omega_m = \omega_p - \omega_s$ and leads to stronger molecular vibration which in turn reinforces the Stokes field and vice versa. For detailed description of the response of the vibrating molecule to the total radiation (pump + Stokes) field at the location z of the molecule

$$E(z, t) = (E_p e^{i(k_p z - \omega_p t)} + E_s e^{i(k_s z - \omega_s t)} + c.c.) \quad (29.6)$$

we will develop the classical model based on the driven damped oscillator similar to the anharmonic oscillator model.

Equation of motion which governs the time dependent internuclear displacement Q (defined in lecture 26) of the oscillator with respect to the equilibrium can be written as

$$\frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_m^2 Q = \frac{F(z, t)}{m} \quad (29.7)$$

Here ω_m is the natural frequency of the molecular oscillator, γ is the damping constant, m is the reduced mass and F is the driving force due to the applied optical field and is responsible for the induced dipole moment

$$\mu(z, t) = \epsilon_0 \alpha \cdot E(z, t) \quad (29.8)$$

where $\alpha = \alpha_e + \left(\frac{\partial \alpha}{\partial Q} \right)_e Q(t)$ is the polarizability of the vibrating molecule

Energy required to create the induced dipole moment is given by

$$W = \frac{1}{2} \left\langle \vec{\mu}(z, t) \cdot \vec{E}(z, t) \right\rangle \quad (29.9)$$

Here the angular bracket represents the time average over one optical cycles as the molecular vibration is much slower than the optical field.

Using equations (29.8) and (29.9), we can calculate the driving force

$$F = \frac{dW}{dQ} = \frac{\varepsilon_0}{2} \left(\frac{\partial \alpha}{\partial Q} \right)_e \langle E^2(z, t) \rangle \quad (29.10)$$

From equations (29.6) and (29.10), driving field then can be written as

$$F = \frac{\varepsilon_0}{2} \left(\frac{\partial \alpha}{\partial Q} \right)_e \left[E_p E_s^* e^{i(k_p - k_s)z - (\omega_p - \omega_s)t} + c.c. \right] \quad (29.11)$$

or

$$F = \varepsilon_0 \left(\frac{\partial \alpha}{\partial Q} \right)_e \left[E_p E_s^* e^{i(Kz - \Omega t)} + c.c. \right] \quad (29.12)$$

Where we have used $K = k_p - k_s$ and $\Omega = \omega_p - \omega_s$. Higher frequency terms oscillating at frequencies $2\omega_p$, $2\omega_s$ and $\omega_p + \omega_s$ average to zero as the molecular response is much slower than the optical oscillations.

Using the ansatz

$$Q(t) = \left[Q_0 e^{i(Kz - \Omega t)} + c.c. \right] \quad (29.13)$$

in the oscillator equation (29.7), one gets

$$\left(-\Omega^2 - 2i\gamma\Omega + \omega_m^2 \right) Q_0 = \frac{\varepsilon_0}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e E_p E_s^* \quad (29.14)$$

Therefore,

$$Q_0 = \frac{\varepsilon_0}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e \frac{E_p E_s^*}{\left(\omega_m^2 - \Omega^2 + 2i\gamma\Omega \right)} \quad (29.15)$$

If there are N oscillators/ volume, the induced polarization can be written as

$$\begin{aligned} P(t) &= N\mu(z, t) \\ &= N\varepsilon_0 \alpha(z, t) E(z, t) \\ &= N\varepsilon_0 \left(\alpha_e + \left(\frac{\partial \alpha}{\partial Q} \right)_e Q(z, t) \right) E(z, t) \\ &= P_L + P_{NL} \end{aligned} \quad (29.16)$$

The nonlinear part of the induced polarization can thus be written as

$$P_{NL} = N \frac{\varepsilon_0^2}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e^2 \left[\frac{E_p E_s^*}{(\omega_m^2 - \Omega^2 - 2i\gamma\Omega)} e^{i(Kz - \Omega t)} + c.c. \right] \left(E_p e^{i(k_p z - \omega_p t)} + E_s e^{i(k_s z - \omega_s t)} + c.c. \right) \quad (29.17)$$

Evidently induced polarization consists of a linear part and a nonlinear part which oscillates at many different frequencies. Here we are only interested in the one which oscillates with the Stokes frequency

$$\omega_s = \omega_p - \Omega \quad (29.18)$$

$$P_{NL}(z, t, \omega_s) = N \frac{\epsilon_0^2}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e^2 \left[\frac{E_p E_p^* E_s}{(\omega_m^2 - \Omega^2 + 2i\gamma\Omega)} e^{i[(k_p - k)s - (\omega_p - \Omega)t]} + c.c. \right] \quad (29.19)$$

$$\equiv (P_{NL}(\omega_s) e^{i(k_p s - \omega_p t)} + c.c.)$$

The amplitude of the induced nonlinear polarization oscillating at the Stokes frequency can thus be identified as

$$P_{NL}(\omega_s) = N \frac{\epsilon_0^2}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e^2 \frac{|E_p|^2 E_s}{(\omega_m^2 - \Omega^2 + 2i\gamma\Omega)} \quad (29.20)$$

$$= N \frac{\epsilon_0^2}{m} \left(\frac{\partial \alpha}{\partial Q} \right)_e^2 \frac{|E_p|^2 E_s}{(\omega_m^2 - (\omega_p - \omega_s)^2 + 2i\gamma(\omega_p - \omega_s))}$$

It is clear from the expressions above that in the Raman scattering three fields, namely, the pump field at frequency ω_p , an input Stokes wave with frequency ω_s and one material excitation of frequency ω_m mix together to produce the fourth field again at the Stokes frequency.

As one input and one output field are in the same mode, this four-wave-mixing process belongs to the case#2 discussed in lecture 19 on general theory of four-wave-mixing and the output field will grow exponentially as will be shown here explicitly. Alternatively, Stimulated Raman Scattering can be interpreted as a parametric process in which a pump wave generates a Stokes wave and a materials excitation wave. Material excitation is a localized Raman excitation between two energy levels whether a molecular vibration described classically by equation (29.7), an optical phonon, electronic excitation or a plasmon.

Corresponding third order susceptibility $\chi^{(3)}(-\omega_s; \omega_p, -\omega_p, \omega_s) \equiv \chi_R(\omega_s)$ for this four-wave-mixing process is defined through the expression

$$P_{NL}(\omega_s) = 6\epsilon_0 \chi_R(\omega_s) |E_p|^2 E_s \quad (29.21)$$

Comparing equations (29.21 and 29.22), Raman Susceptibility for the stimulated scattering is

$$\chi_R(\omega_s) = \frac{B}{(\omega_m^2 - (\omega_p - \omega_s)^2 + 2i\gamma(\omega_p - \omega_s))} \quad (29.22)$$

where

$$B = N \frac{\epsilon_0}{6m} \left(\frac{\partial \alpha}{\partial Q} \right)_e^2 \quad (29.23)$$

Near Raman Resonance, Raman susceptibility can be written as

$$\chi_R(\omega_s) = \frac{B}{2\omega_m (\omega_s^2 - (\omega_p - \omega_m)^2 + i\gamma)} \quad (29.24)$$

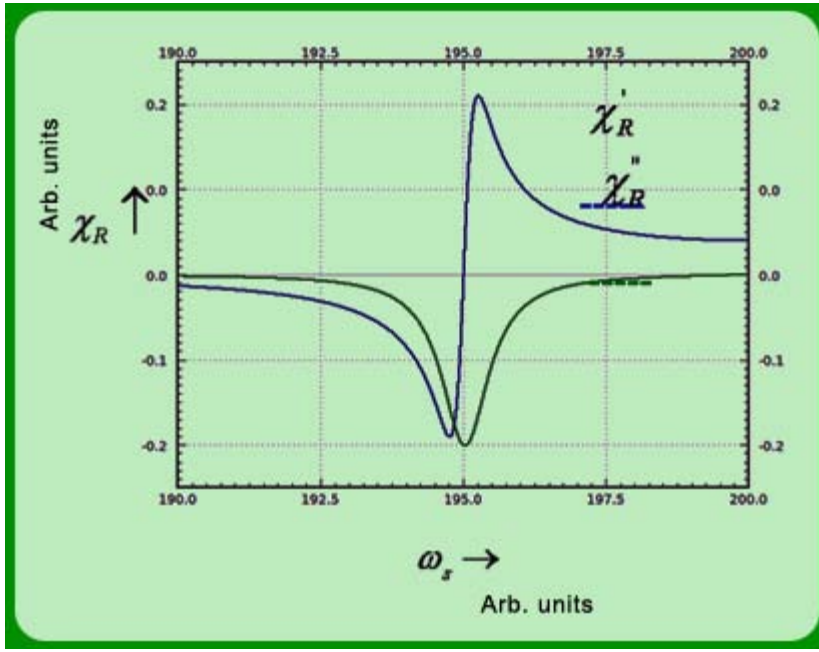


Figure 29.3 Frequency dispersion of the Real and imaginary parts of Raman susceptibility

Figure 29.3 shows the frequency dispersion of the real and imaginary parts of $\chi_R(\omega_s) = \chi_R'(\omega_s) + i\chi_R''(\omega_s)$. It can be seen from the figure that at the resonance, $\omega_s = \omega_p - \omega_m$ the Raman susceptibility is purely imaginary and negative. This would imply a negative nonlinear absorption or in other words gain for the Stokes wave.

In the following we will explore the spatial evolution of the coupled pump and Stokes waves upon propagation in the Raman active medium. Nonlinear polarizations which drive the two fields at frequencies ω_s and ω_p can occur via the processes $\omega_s = \omega_s - \omega_p + \omega_p$ and $\omega_p = \omega_s - \omega_s + \omega_p$ only.

We have already derived the expressions (equations 29.21 and 29.23) for the nonlinear polarization and the corresponding susceptibility for the former one. Using the symmetry relations, it can be shown that nonlinear susceptibility for the later one is

$$\begin{aligned}\chi^{(3)}(-\omega_p; \omega_s, -\omega_p, \omega_p) &= \chi^{(3)}(-\omega_s; \omega_s, -\omega_s, \omega_p)^* \\ &\equiv \chi_R^*(\omega_s) =: \chi_R\end{aligned}\quad (29.25)$$

And the corresponding nonlinear polarization is

$$P_{NL}(\omega_p) = 6\epsilon_0 \chi_R^* |E_s|^2 E_p \quad (29.26)$$

Using slowly varying envelope approximation (SVEA) the propagation of the two fields is described by

$$\frac{\partial}{\partial z} E_p = 3i \frac{\omega_p}{\mu_p c} \chi_R^* |E_s|^2 E_p \quad (29.27)$$

and

$$\frac{\partial}{\partial z} E_s = 3i \frac{\omega_s}{\mu_s c} \chi_R |E_p|^2 E_s \quad (29.28)$$

$$\because \exp[i(k_p - k_s + k_s - k_p)] = 1$$

The oscillating phase factor in the R.H.S. is cancelled \Rightarrow phase matching is not necessary.

Introducing the abbreviation

$$g_s = \frac{3i\omega_s}{\mu_s c} \chi_R \quad (29.29)$$

and

$$g_s' = \frac{g_s}{2\mu_p \epsilon_0 c} \quad (29.30)$$

Then from equations (29.28 and 29.29) one gets

$$\frac{\partial I_p}{\partial z} = -\frac{\omega_p}{\omega_s} g_s' I_p(z) I_s(z) \quad (29.31)$$

and

$$\frac{\partial I_s}{\partial z} = g_s' I_p(z) I_s(z) \quad (29.32)$$

It can be easily shown that

$$\frac{I_p(z)}{\omega_p} + \frac{I_s(z)}{\omega_s} = \frac{I_p(0)}{\omega_p} + \frac{I_s(0)}{\omega_s} = C = \text{constant} \quad (29.33)$$

\Rightarrow Total photon number in pump and Stokes wave is constant. For each Stokes photon creation, a pump photon is annihilated.

One can readily write near Raman resonance i.e. $\omega_m \approx \omega_p - \omega_s$

$$g_s = \frac{3\omega_s}{2\epsilon_0 \mu_s c \omega_m} \frac{B\gamma}{\left[\left(\omega_m - (\omega_p - \omega_s) \right)^2 + \gamma^2 \right]} \quad (29.34)$$

g_s and g_s' are the Raman gain coefficients which can be written near Raman resonance using equation (29.31) as

$$g_s' = \frac{3\omega_s B}{4\epsilon_0 \mu_s^2 c^2 \gamma \omega_s} \frac{1}{1 + \left[\frac{\omega_m - (\omega_p - \omega_s)}{\gamma} \right]^2} \quad (29.35)$$

This gives the spectrum of the Raman gain which is clearly Lorentzian distribution with FWHM $= \gamma$ = Raman line width. Typically $\gamma = 10^{-2} \omega_m$

For weak conversion limit, we can assume the pump field to remain constant - undepleted pump case i.e.

$$I_p(z) = I_p(0) \quad I_s(z) = I_s(0) \exp(g_s' I_p(0) z) \quad (29.36)$$

\Rightarrow exponential growth of the stokes wave

Exercise: Show that in the strong conversion regime pump intensity depletes as

$$I_p(z) = \frac{C\omega_p}{1 + \frac{\omega_p}{\omega_s} \frac{I_s(0)}{I_p(0)} \exp(Cg_s' \omega_p z)} \quad (29.37)$$

and the Stokes wave gets amplified according to

$$I_s(z) = \frac{C\omega_s}{1 + \frac{\omega_s}{\omega_p} \frac{I_p(0)}{I_s(0)} \exp(Cg_s' \omega_p z)} \quad (29.38)$$

Unlike the spontaneous Raman scattering,

In the spontaneous Raman effect anti-Stokes wave is also generated. Do we expect the amplification of an anti-Stokes wave when it propagates through Raman active medium? We will address this question in the next lecture.

Some Applications of SRS:

1. **Raman Frequency shifter:** This is a simple device meant for the frequency conversion of a strong pump laser pulse to the cascade of the Stokes frequencies through SRS process. It usually consists of half meter long high pressure cell filled with hydrogen or methane gas at ~50 atm. pressure. The end faces are fitted with the transparent windows to admit the pump and transmit the Stokes field. These gases give large Stokes shift and can shift the original frequency substantially away.

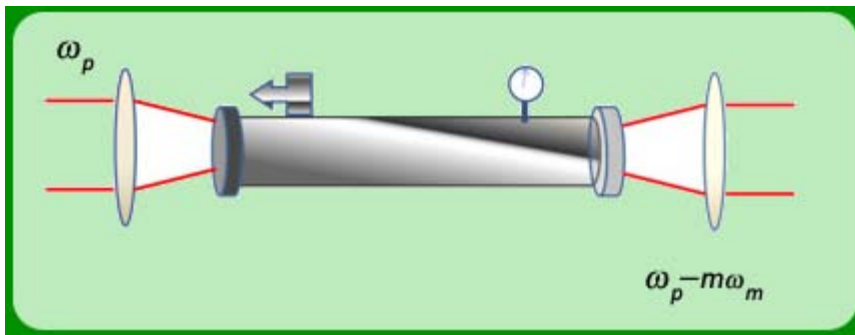


Figure 29.4

2. **Raman Oscillator:**
Stimulated Raman process can be used to convert the original frequency of a pulsed laser to coherent light at the Raman shifted frequency. If the Raman active medium is placed in a resonator cavity resonant at the frequency ω_s and pumped strongly, oscillation can build up once gain overcomes the losses in the optical cavity.
3. **Stimulated Raman gain spectroscopy:**
In Spontaneous Raman scattering the signals are very weak and the resolution is limited by that of the spectrometer which often may not be adequate as the molecular vibrational modes are very narrow. These limitations can be overcome by Stimulated Raman Gain Spectroscopy (SRGS) as the signals are well directed and resolution is only limited by laser line width. In this technique, the sample is pumped by a strong fixed wavelength laser and one measures the amplification of another co-propagating weak probe beam as it is tuned across the Raman Stokes frequencies.
4. **Inverse Raman Scattering:**
According to equation (29.33) for each photon created in the Stokes field a photon from the higher frequency field, the pump field, is annihilated irrespective of the intensities of the two fields.

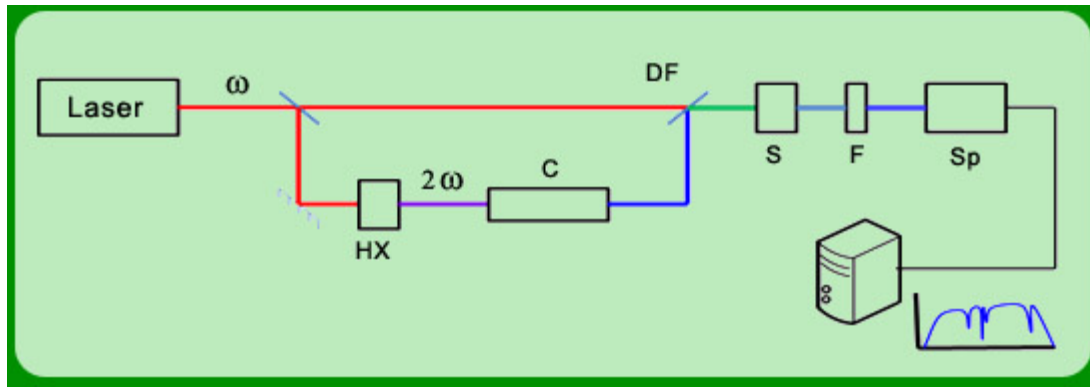


Figure 29.5: Inverse Raman Scattering: HX- SHG Crystal; C-Eye Cuvette; S-Sample; F-Filter; Sp- Spectrometer; DF-Beam Combiner

⇒ If a strong laser light at frequency $\omega_L = \omega_s$ co-propagates with a weak probe beam at frequency $\omega_p = \omega_L + \omega_m$ in a Raman active medium, the probe beam will deplete due to stimulated Raman scattering of photons of energy $\hbar\omega_p$ from probe field to the laser beam. This is the inverse Raman effect. Thus if the weak probe beam is the continuum of higher frequencies, it will bear the signatures of the stimulated Raman scattering by various vibrational modes of the medium as absorption dips provided that Stokes scattering exceeds the anti-Stokes scattering which, usually, is the case. The typical experimental setup for the inverse Raman spectroscopy is shown in the figure 29.5. The weak probe continuum is generated by the excitation of dye solution with the second harmonic of the laser.

References:

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4. N. Bloembergen, Am. J. of Physics, **35**,989(1967)

Recap

To sum up this lecture

- After a brief introduction and history of stimulated Stokes Raman scattering. We have given a quantum mechanical picture and described it as a two-photon process. Some subtle differences between this and spontaneous Raman scattering have been outlined.
- Next we have described it as a four-wave-mixing process. Corresponding nonlinear polarization and nonlinear susceptibility have been derived using simple classical oscillator model.
- Spatial evolution of the Stokes wave propagating through a Raman active medium in the presence of a pump wave has been described using SVEA and we have demonstrated that near Raman resonance the Stokes wave experiences gain and can be amplified.
- Applications of SRS such as Raman shifter, Raman oscillator, Stimulated Raman gain spectroscopy(SRGS) and inverse Raman spectroscopy have been discussed.