

Module 4 : Third order nonlinear optical processes

Lecture 28 : Inelastic Scattering Processes

Objectives

In this lecture you will learn the following

- Light scattering- elastic and inelastic-processes, their causes and examples.
- Spontaneous Raman scattering and its origin in terms of classical and quantum pictures.
- Application of the spontaneous Raman scattering to the spectroscopy.

Light Scattering:

Light scattering refers to the process of spontaneous dispersal of light beam into random directions upon interaction with an object.

It originates from the spatial or temporal fluctuations of the optical properties of the medium.

The process can be visualized as collisions- elastic or inelastic- between the photons and the inhomogeneities of the medium i. e. the scattering centers.

Antiresonant Ring Interferometric Nonlinear Spectroscopy (ARINS) Technique:

The ARINS technique utilizes the dressing of two unequal-intensity counter-propagating pulsed beams with differential nonlinear phases, which occurs upon traversing the sample. This difference in phase manifests itself in the intensity dependent transmission. Photodetection of the transmission of the ARINS yields spatially and temporally integrated response. Consequently, it is the pulse energy and not the instantaneous power that is detected. Figure 27.1 shows the schematic diagram of ARINS setup.

- In case of elastic collisions the energy of the incident and scattered photons and so is the initial and final state of scattering center. Rayleigh scattering is an example of the elastic scattering.
- In inelastic scattering processes such as Raman or Brillouin scattering, the frequency of the incident and scattered photons differ. The energy difference appears as change in internal energy of the scattering center, that is to say, the energy difference of the initial and final states of the scattering center.

Under specific conditions one can induce or stimulate the scattering to be enhanced preferentially in a specific direction. Here, we will focus, qualitatively, on the origin and applications of the spontaneous Raman scattering

Spontaneous Raman Scattering:

This inelastic scattering by molecules was first discovered by Sir C. V. Raman in 1928. He was awarded Nobel Prize for this fundamental work in 1930.

He observed that when a monochromatic beam of light passed through a nonabsorbing medium, the scattered light spectrum contained, in addition to the strong line corresponding to Rayleigh scattering at the frequency of the incident radiation, some weak spectral lines on either side of it which were later shown to be related to molecular vibrational frequencies.

Example:

When strong light of 19436 cm^{-1} (514.5nm) is scattered by a material consisting of molecules containing carbonyl group, its spectrum exhibits two rather weak lines at 17786 cm^{-1} (562.24nm) and 21086 cm^{-1} (474.25nm) apart from the line at 19436 cm^{-1} .

A Classical Picture:

Since its discovery, Raman scattering has been studied most extensively for the fluctuations in the optical properties of the material originating from molecular vibrations.

To understand the origin of this phenomenon, we will, therefore consider the following classical description of vibrational Raman effect developed by Placek.

When an electromagnetic wave

$$E(z,t) = E_p(z) \sin \omega_p t \quad (28.1)$$

interacts with a molecule located at the position z , it induces the dipole moment

$$\mu(z,t) = \epsilon_0 \alpha E(z,t) \quad (28.2)$$

$$= \epsilon_0 \alpha E_p(z) \sin \omega_p t \quad (28.3)$$

where α is the second rank polarizability tensor of the molecule. For the sake of simplicity, we will restrict ourselves to the scalar approximation and the case of simple diatomic molecule – more complex molecules can be described by analogous equations by resorting to normal mode analysis. Remember that the constituent atoms of the molecule are in continuous motion i.e. the internuclear distances vary in time. Consequently,

- Change in internuclear distances affects the electronic distribution of the molecule.
- The polarizability α of the molecule is governed by the electronic distribution. Therefore, the polarizability as well as the refractive index of the medium

$$n(t) = (1 + \alpha(t))^{1/2}$$

will be modulated by the internal molecular vibrations. A sketch of the typical variation of polarizability with internuclear distance is shown in figure 28.1.

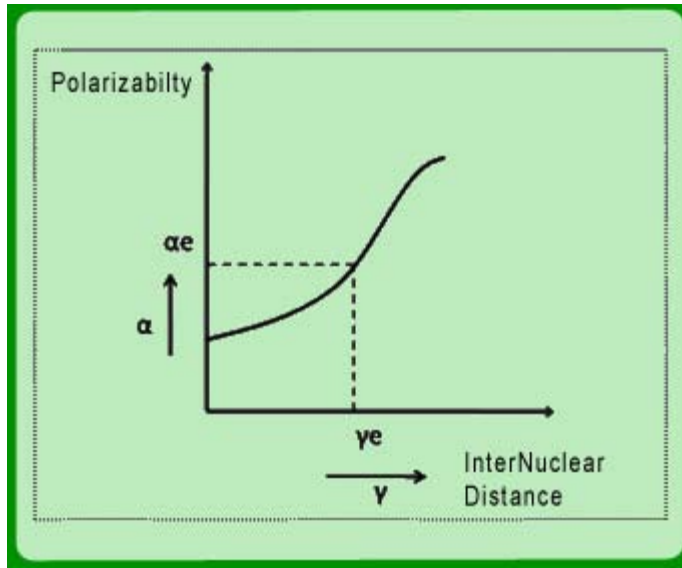


Figure 28.1 Variation of molecular polarizability with internuclear distance

- The resulting refractive index of the medium will impose a time varying phase shift $\phi(t) \propto \frac{2\pi}{\lambda} n(t)$ on the light passing through the medium. It will, thereby, produce new

frequencies as the frequency is given by $\omega = \frac{d\phi(t)}{dt}$

Using Taylor series, we can write α around its equilibrium value as

$$\alpha = \alpha_e + \left(\frac{\partial \alpha}{\partial Q} \right)_e Q + \frac{1}{2} \left(\frac{\partial^2 \alpha}{\partial Q^2} \right)_e Q^2 + \dots \quad (28.4)$$

where $Q = r - r_e$, r and r_e are the instantaneous and equilibrium inter-nuclear distances, respectively; α_e is the polarizability of the molecule at the equilibrium inter-nuclear distance.

If ω_m is the frequency of the molecular vibration, one can express

$$Q = Q_0 \sin \omega_m t \quad (28.5)$$

To the first order approximation one can write

$$\alpha(t) = \alpha_e + \left(\frac{\partial \alpha}{\partial Q} \right)_e Q_0 \sin \omega_m t \quad (28.6)$$

The induced dipole moment can then be written as

$$\begin{aligned} \mu(t) &= \epsilon_0 E_p \alpha_e \sin(\omega_p t) + \epsilon_0 E_p \left(\frac{\partial \alpha}{\partial Q} \right)_e Q_0 \sin(\omega_m t) \sin(\omega_p t) \\ &= \epsilon_0 E_p \alpha_e \sin(\omega_p t) + \epsilon_0 E_p \left(\frac{\partial \alpha}{\partial Q} \right)_e \left[\cos(\omega_p - \omega_m)t - \cos(\omega_p + \omega_m)t \right] \end{aligned} \quad (28.7)$$

The expression above reveals that

1. the oscillating dipole moment μ will radiate at three different frequencies.
2. The first term that oscillates with the driving field frequency corresponds to the Rayleigh scattering.
3. The next two terms serve as source terms for the Raman scattered photons - one with the down shifted frequency

$$\omega_s = \omega_p - \omega_m, \quad (28.9)$$

called the Stokes Raman frequency and the other with the up shifted frequency for the anti-Stokes Raman scattering

$$\omega_{as} = \omega_p + \omega_m$$

Also note that

- The intensity of the Rayleigh line is proportional to α_e
- Intensities for the Stokes and anti-Stokes Raman lines are proportional to $\left(\frac{\partial \alpha}{\partial Q} \right)_e$. This is incorrect as experimentally Stokes lines are observed to be much stronger than the anti-Stokes lines.

Thus the classical description of the Raman effect is unsatisfactory.

Like all spontaneous emission processes, the Raman effect requires full quantum mechanical treatment for its correct theoretical description. Detailed quantum theoretical treatment is outside the scope of this lecture. We will, therefore, present below a simple qualitative quantum mechanical picture.

Quantum Mechanical Picture:

In the Raman scattering process, an incident photon of energy $\hbar \omega_p$ interacting with the scattering center is annihilated, a scattered photon of energy $\hbar \omega_{scat.}$ is created and the difference in their energy, $\Delta E = (\hbar \omega_p - \hbar \omega_{scat.})$ is exchanged with the scattering center to change its quantum state.

We consider here that the incident photon energy is

- nonresonant with the internal resonances of the medium and
- it is much larger than the energy difference between the initial and final quantum states of the scattering system i.e.

$$\hbar \omega_p \gg \Delta E$$

To understand how this process is facilitated we consider the following facts.

A quantum system such as a molecule in a given state $|m\rangle$, even without getting any energy from outside, performs incessant transitions to its other states $|n\rangle$ (n represents any other eigen state of the system) with an inevitable return every time to the starting state. Such transitions $|m\rangle \rightarrow |n\rangle \rightarrow |m\rangle$ are called virtual transitions in contrast to real transitions and are possible due to quantum uncertainty principle when the duration of the journey is such that $\frac{\hbar}{\Delta t} \gg \Delta E$, the energy

difference between the states $|m\rangle$ and $|n\rangle$. During the interaction of quantum system undergoing virtual transitions with an electromagnetic field, resonant or nonresonant, the changes in the state of the quantum system and the mode of the electromagnetic field are liable to occur such that the initial photon energy is shared between the excitation of quantum system and resulting mode of the electromagnetic field to conserve energy.

In Raman scattering process the initial and final eigen states of the system $|i\rangle$ and $|f\rangle$ are coupled upon excitation with an a photon of energy $\hbar\omega_p$ via such virtual transitions to and from an intermediate state, $|j\rangle$ with the creation of scattered photon with energy $\hbar\omega_s$ and annihilation of the initial photon.

To put it in an other way, a quantum system in a given eigen state interacting with radiation field ceases to be in the eigen state of the unperturbed system. The new quantum state called a virtual state can be expressed as the superposition of the eigen states of the unperturbed system.

The mixed state character to its original state is produced by the virtual transitions. This new state serves as the intermediate state $|j\rangle$.

In light of the above discussion, Raman scattering can be viewed as illustrated in figure 28.2. Quantum system under consideration makes a transition $|i\rangle \rightarrow |j\rangle$ to the virtual state by annihilating a quanta $\hbar\omega_p$ from the incident field with a simultaneous transition $|j\rangle \rightarrow |f\rangle$ from the intermediate state to the final state creating the scattered photon with energy $\hbar\omega_{scat}$, so as to satisfy the energy conservation

$$\hbar\omega_p = \hbar\omega_{scat} + \hbar\omega_m \quad (28.10)$$

where $\hbar\omega_m = E_f - E_i$ is the excitation energy exchanged with the molecule.

There are two possible scenarios

1. If the initial state $|i\rangle$ of the system is the ground state, then as shown in figure 28.2(a), it can only go to the higher energy state $|f\rangle$. Consequently,

$$\hbar\omega_{scat} \equiv \hbar\omega_s = \hbar\omega_p - \hbar\omega_m \quad (28.11)$$

This is the Stokes Raman Scattering.

2. If the system is initially in the higher energy state $|i\rangle$, it is de-excited to the lower energy state $|f\rangle$ and the scattered photon has higher energy than the incident photon as illustrated in figure 28.2(b).

$$\hbar\omega_{scat} \equiv \hbar\omega_{\alpha} = \hbar\omega_p + \hbar\omega_m \quad (28.12)$$

This process is called the anti-Stokes Raman scattering.

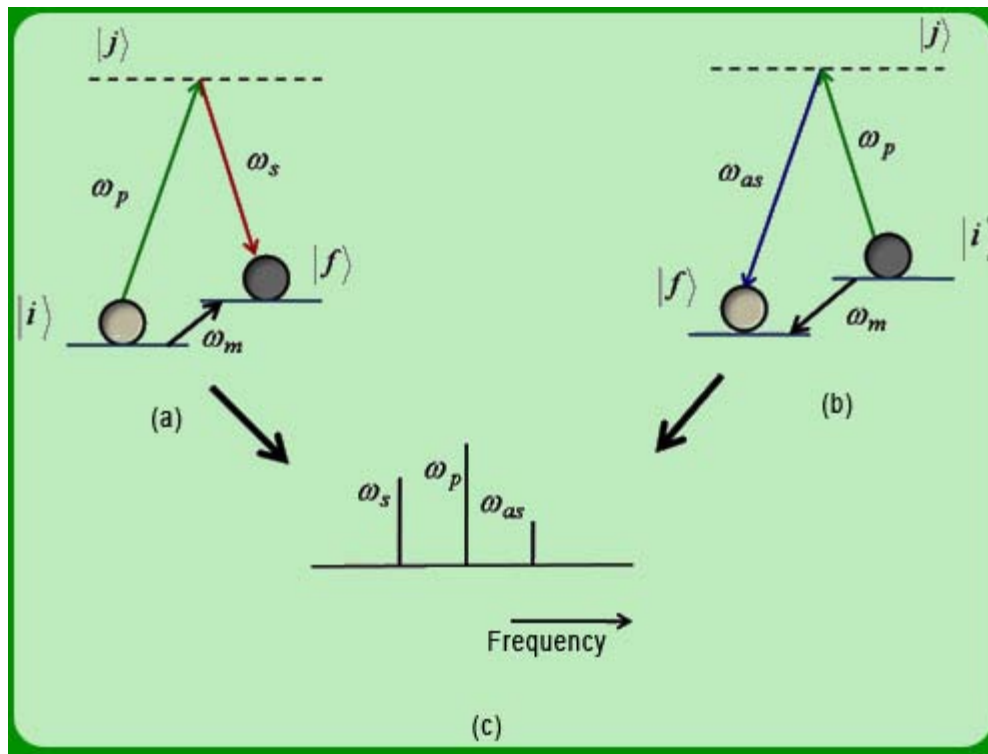


Figure 28.2 Quantum picture describing (a) Raman Stokes scattering (b) Raman anti-stokes scattering (c) Raman Frequency spectrum

Important!

- Raman scattering involves two transitions $|i\rangle \rightarrow |j\rangle$ and $|j\rangle \rightarrow |f\rangle$ for the annihilation and creation of photons and is thus a two photon process.
- Both these transitions should be allowed by the selection rules for this process to take place. That is to say, the matrix elements $\langle j|\hat{\mu}|i\rangle$ and $\langle f|\hat{\mu}|j\rangle$ should be nonzero. Here $\hat{\mu}$ is the transition dipole moment operator.

As an example, in a material with inversion symmetry ($\alpha_e = 0$ and $\left(\frac{\partial \alpha}{\partial Q}\right) \neq 0$), these are

nonzero only if the states $|i\rangle$ and $|j\rangle$ as well as $|j\rangle$ and $|f\rangle$ are opposite parity states.

\Rightarrow the states $|i\rangle$ and $|f\rangle$ have the same parity and direct single photon electric dipole transition will be forbidden between these two stationary states making such states inaccessible to one-photon spectroscopic techniques such as absorption spectroscopy. However, these can be investigated using Raman spectroscopy.

Example: the symmetric stretching mode of vibration in CO_2 molecule will not show in IR spectroscopy but will be Raman active.

- The transition $|i\rangle \rightarrow |j\rangle \rightarrow |f\rangle$ cannot be factored in time and is to be treated as one single quantum mechanical event.

NOTE:

Usually, the quantum states involved here are vibrational or rotational states of the molecule but in principle, the initial and final states of the system can even be electronic. It is also not necessary that the incident light be nonresonant with the medium. In that case, it will lead to the resonant Raman effect which we have excluded from the present discussion

If we assume that only two modes of radiation fields, namely the Stokes mode with initial number of photons n_s and the incident field with initial photon number n_p , take part in the process, the transition probability can be calculated using second order perturbation theory by representing the initial and final states of the combined photon and the quantum system to be

$$|E_i\rangle = |i\rangle |n_s, n_p\rangle \quad (28.13)$$

$$|E_f\rangle = |f\rangle |n_s + 1, n_p - 1\rangle \quad (28.14)$$

Evidently it is a two-photon process. Omitting the details of the calculation which are similar to two-photon absorption, transition rate(probability per unit time) can be written as

$$P_{ind}(\hbar\omega_s) = Dn_p(n_s + 1)N_0 \quad (28.15)$$

When $n_s = 0$, transition probability corresponds to spontaneous Raman effect and when $n_s \neq 0$ it refers to stimulated Raman scattering which we will discuss in the next lecture.

Thus in a way the spontaneous Raman scattering can be viewed as the process stimulated by the vacuum field fluctuations.

The transition rate for the spontaneous emission of Stokes photons is given by

$$P_s(\hbar\omega_s) = Dn_p N_0 \quad (28.16)$$

Where D is a constant of proportionality and N_0 is the number density of the molecules initially in the ground state.

The transition rate for the spontaneous emission of the anti-Stokes photons is accordingly

$$P_{as}(\hbar\omega_{as}) = Dn_p N_1 \quad (28.17)$$

where N_1 is the number density of the molecules in the initial excited state.

Intensities of the Stokes and anti-Stokes Raman lines are determined by their respective transition probabilities. Hence

$$\frac{I_{as}}{I_s} \propto \frac{N_1}{N_0} \quad (28.18)$$

Considering the population densities to be in thermal equilibrium at absolute temperature T , their ratio according to Boltzmann distribution is given by

$$\frac{N_1}{N_0} = \exp\left(-\frac{\hbar\omega_m}{k_B T}\right) \ll 1 \quad (28.19)$$

Thus, the anti-Stokes lines are much weaker than the Stokes lines at thermal equilibrium. It is obvious from equations (28.16 and 28.17) that the intensities of the Stokes and anti-Stokes lines depends upon the intensity of the incident radiation field.

Applications:

The vibrational frequency of the constituent atoms of a molecule or solid is characteristic to the specific nature of the chemical bonding. A study of their vibrational modes can provide valuable information on the chemical structure.

As explained above, not all vibrational modes can be accessed in IR absorption spectroscopy. Those modes which are not seen in IR spectroscopy are found to be Raman active. Raman spectroscopy thus complements the IR spectroscopy and both together form indispensable tool in the study of matter.

Intensity of Raman lines depends on the density of molecules in the initial state and on the Raman scattering cross section. Intensity of anti-Stokes Raman lines can be used to measure the population densities from the knowledge of the predetermined scattering cross section. From these measurements the temperature profiles of the sample can be obtained using Boltzmann distribution. Raman spectroscopy thus proves to be invaluable tool in the fuel combustion studies.

Further, Raman spectroscopy forms powerful noninvasive and in-situ probe for biological studies and medical diagnosis.

A typical experimental set-up for Raman spectroscopy is shown in figure 28.3 which is self explanatory. Right panel shows the Raman spectrum of MoS₂ film. The observed shift with respect to that in MoS₂ in single crystal is an indication of its bi-layer character and demonstrates the importance of Raman scattering for the study of the structure of the matter.

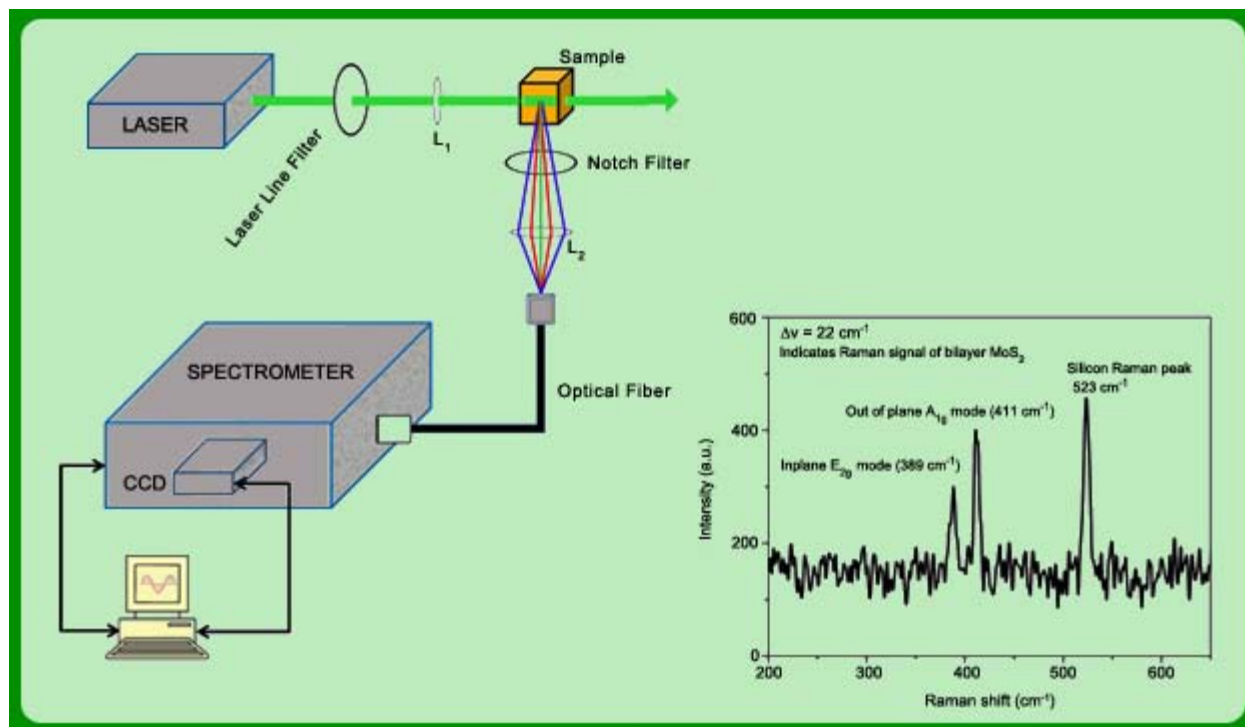


Figure 28.3 Left panel Raman spectroscopy setup; Right panel-Raman spectrum of MoS₂

Recap

In this lecture you have learnt the following

- We have pointed out the spatial and temporal inhomogeneities of the optical properties of the matter to be the cause of light scattering processes.
- We have described spontaneous Raman effect as an example of the inelastic light scattering.
- In the classical description of the Raman effect, it has been shown that it originates from the modulation of the polarizability by the molecular vibrations.
- We have shown the inadequacy of the classical picture to account for the Stokes and anti-Stokes Raman line intensities.
- In terms of the quantum mechanical picture, it has been described qualitatively as a two-photon process.
- Cause of the experimentally observed unequal intensities of the Stokes and anti-Stokes Raman line has been traced to the difference in the population densities of the excited and ground states of the molecule at thermal equilibrium.
- It has been shown that the intensity of the Raman line will increase with the intensity of the incident field. Does the scattered light intensity increase linearly always with the incident intensity or something different will happen if a strong source of light like a Q-switched laser is employed? We will explore this question in our next lecture.
- It has been shown that it provides access to those vibrational states of the molecule which cannot be addressed in IR absorption spectroscopy and hence complements the later. Various application of the Spontaneous Raman spectroscopy has been pointed out.