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Ramifications of Raman Effect

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Introduction:

The year 1988 happens to be the Diamond Jubilee year of the discovery of the Raman effect but also the birth centenary year of Sir C V Raman.

Hence it is fitting occasion to write about The Raman Effect and its ramifications as a fitting tribute to pay homage to the memory of "this titan among Indian Scientists", who strode the world of sciences like a colossus. In the following article though there are several variant techniques of Raman Spectroscopy evolved, only very important findings are highlighted. Certain devices like Spin-flip Raman sources etc., are omitted.

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*A review based on the talk given at CECRI Karaikudi on 28.2.1988 (National Science day).

Raman Effect

While studying the molecular scattering of light at Calcutta Sir C V Raman discovered a new phenomenon known after him as The Raman Effect. The observation of blue opalescence of the Mediterranean sea during his voyage to Europe in 1921 initiated him to have detailed investigation on light scattering at Calcutta later.

When a beam of monochromatic radiation passes through a transparent medium some of it is scattered by the vibrating and/or rotating molecules of the medium. Most of the scattered radiation is of the same frequency (Rayleigh Scattering) and of it changes frequency (new light scattering observed by Raman). The latter observation by C. V. Raman on 28th February 1928 later came to be known as Raman Effect. The frequency shifted spectral lines arise due to the change in polarizability of the molecule and it represents the molecular distortion under the electric field of the incident electromagnetic radiation. Otherwise this is essentially an inelastic scattering of light by molecular vibration and/or rotation arising due to the modulation the electric suscepti-

bility (polarizability) of the above mentioned molecular vibration and/or rotation.

The mechanism of Raman effect can be explained qualitatively as follows. The molecule when irradiated by an electromagnetic radiation (visible or



20.3.1953

Yours sincerely
C. V. Raman

Sir 'C. V. Raman'
1888-1970

uv radiation), two types of emission occur. In one the ground state is completely restored emitting radiation of same wavelength as the incident (exciting) radiation is known as Rayleigh scattering. Another transition on either side of the exciting radiation (frequency shifted) correspond to the inelastic scattering arising from the molecules interacting with the electric field associated with the incident monochromatic radiation. The inelastic contributions are further subdivided; those scattered frequencies smaller than incident radiation known as Stokes components and while the scattered radiation larger than the incident radiation known as anti-Stokes components. Each scattered photon in the Stokes component is associated with a gain in energy by the sample, while the sample losses energy in each scattered photon in the anti-Stokes component.

The above experimental technique is a powerful tool for scientists in elucidating the structure of molecules, biomechanism in biomolecules etc. through the role played by various groups of molecule making the molecular system. The scattered radiation intensity is 10^{-4} times smaller than the incident exciting radiation and hence Raman spectra of molecules are very weak. However, after the advent of lasers, the situation has become more favourable to record the Raman spectra with ease with sample size of a few microgram or microlitre. Moreover the Raman spectra has been made complex due to the linear and nonlinear interactions of molecules with the intense 10^9V m^{-1} electric field associated with the exciting laser radiation. Thus new analytical techniques had been developed to study molecular systems, surfaces etc., in detail giving the scientists a deep insight into various physical and chemical mechanisms and principles involved.

As mentioned earlier when the electric field intensities of the incident

radiation exceeds 10^9 volt m^{-1} , the nonlinear contributions to the induced dipole (polarizability) start to become significant, and that such electric field intensities are associated with the monochromatic radiation produced by giant pulse lasers. Many new phenomena arise from the nonlinear interaction of a system with intense monochromatic radiation. All phenomena involve changes in the wave-number of laser radiation as a result of its interaction with the molecular systems and so are regarded as variants of the Raman effect. This generic relationship is reflected in the names which have been adopted for these new effects; the hyper Raman effect; the inverse Raman effect; the stimulated Raman effect; coherent anti-Stokes Raman scattering (CARS) and Raman induced phase conjugation spectroscopy. Each of these effects involves new principles and hence novel applications are possible and new information can result.

a) Resonance Raman Scattering

In a Raman process from a molecular system, an incident photon is destroyed, a scattering photon is created and the molecular system undergoes a transition from the initial state to a final state. This process is coherent and therefore these events are not independent and resolvable i.e., a process in which three events occur invisibly. If the excitation frequency is close to or in resonance with an available excited state is the process is called Resonance Raman scattering (RRS). By varying the excitation frequency (using tunable lasers or source of light) from off resonance to on resonance condition can be achieved. Thus obtained Raman spectra has striking changes in the intensity, temporal behaviour and frequency distributions.

b) Surface Enhanced Raman Spectroscopy (SERS)

Intense Raman signals were observed from pyridine adsorbed onto

electrochemically roughened silver electrodes. The enhancement of Raman signal is attributed finally to that of the preparation of a microscopically rough surface and was concluded as a necessary prerequisite to observe SERS.

So far we were discussing the linear interaction of the electromagnetic radiation with the molecular system. Let us now devote our attention to what type of result oriented phenomena occur when the electric field intensity of the incident radiation exceeds $10^9 \text{ volts m}^{-1}$. It is found that new phenomena arise from the nonlinear interaction of the molecular system with intense monochromatic radiation akin to the normal Raman effect. Hyper Raman; inverse Raman; stimulated Raman (SRS) and coherent anti-Stokes Raman Scattering (CARS) involve changes in the wave number of Laser radiation as a result of its interaction with a molecular system and so are to be regarded as variants of the normal spontaneous Raman effect. This generic relationship is reflected in the names which have been adopted for the new effects.

Hyper Raman Effect

This effect arises when focused ν_0 (6943.3Å) laser beam (pulsed nanosecond duration) interacts in any direction of the samples gives rise to lines at $2\nu_0$ (3471Å) and at $2\nu \pm \nu_M$ where ν_M is the molecular vibrations. This method provides a novel tool to observe weak Raman lines arising from poor scatters like water molecules.

Stimulated Raman Effect (SRS)

When monochromatic radiation from a giant pulse laser of sufficiently large irradiance is incident upon a scattering system hyper Raman scattering is superceded by a new phenomenon viz., stimulated Raman Scattering. SRS depends on the direction and manner of illumination. The giant pulse laser radiation is focused into

sample and the scattering observed along the laser beam direction in the forward direction at a small angle.

- (1) SRS differs from the normal Raman scattering not only in its wave number pattern and angular dependence but also to its intensity.
- (2) In SRS only selective excitation of molecular vibration occurs viz., Raman active modes.
- (3) The first stokes line in SRS rapidly grows in intensity to act as a power source and chain reaction occurs for the formation of further lines.
- (4) The generation of the anti stokes line does not arise as a result of downward transition from a populated upper state as in normal Raman effect but created at the expense of laser photon.
- (5) High conversion efficiency and hence new laser lines can be generated using suitable molecular media thus increasing the number of laser lines in the electromagnetic spectrum for resonance absorption studies.

Inverse Raman Effect

If a molecular system is illuminated with a giant pulse laser beam of wave number $\bar{\nu}_0$ and a continuum covering the wave number range $(\bar{\nu}_0 + 3500)$ cm^{-1} , absorption bands are observed in the continuum at wave numbers $\bar{\nu}_0 + \bar{\nu}_M$ etc; where $\bar{\nu}_M$ is a Raman active vibration mode of a molecular system. This method offers a method of recording Raman spectra of short lived molecular species of the order of 10^{-8} to 10^{-11} seconds. There is no restriction in the direction of observation as in SRS and hence it has great promise to study short lived species, but the experimental procedure is not easy.

Coherent Anti-Stokes Raman Scattering (CARS)

If a coherent radiation of wave number $\bar{\nu}_1$ is mixed in a molecular medium with coherent radiation of wave number $\bar{\nu}_2$ and the irradiances of the two radiations are sufficiently

large, then inter alia coherent radiation of wave number $\bar{\nu}_3$ can result.

$$\bar{\nu}_3 = \bar{\nu}_1 + (\bar{\nu}_1 - \bar{\nu}_2) \quad \text{—————} \quad (1)$$

Here mixing implies spatial and temporal coincidence of the two beams. If $\bar{\nu}_1$ is kept fixed (say monochromatic) and $\bar{\nu}_2$ is varied so that the condition

$$\bar{\nu}_1 - \bar{\nu}_2 = \bar{\nu}_M \quad \text{—————} \quad (2)$$

is achieved where $\bar{\nu}_M$ is some molecular wave number of the system then

$$\bar{\nu}_3 = \bar{\nu}_1 + \bar{\nu}_M \quad \text{—————} \quad (3)$$

Thus $\bar{\nu}_3$ is coincident in wave number with stokes Raman Scattering associated with the molecular wave number $\bar{\nu}_M$ when excited by radiation of wave number $\bar{\nu}_1$. Radiation produced in this way is termed as coherent anti-stokes scattering (CARS) to emphasize its different origin and properties. The usefulness of the techniques are highlighted as below.

- (1) Conversion efficiency of $\bar{\nu}_3$ is several orders greater than the normal Raman effect.
- (2) $\bar{\nu}_3$ from CARS is highly collimated and hence the collection efficiency is very high.
- (3) Fluorescence and thermal radiation from hot samples can be eliminated using spatial filtering technique.
- (4) No dispersion device is needed.
- (5) The power associated with CARS depends on the (a) square of the normal Raman scattering cross section (b) square of the number of molecules.
- (6) (i) Useful in flame diagnostics as a spatial probe.
- (ii) In the study of biological chromophores through pure rotation spectra.
- (iii) An important tool for molecular structural studies.

Raman Induced Phase Conjugation Spectroscopy

In order to study optical Raman spectra of transient media, hot media, or static media exhibiting strong fluorescence, or to obtain, spectral resolution greater than 1 cm^{-1} , one generally employs some form of cohe-

rent Raman spectroscopy (CRS). Most widely used CRS techniques employ two coherent sources, whose frequencies are separated by nearly the Raman excitation frequency. As explained earlier SRS, CARS, and Raman induced Kerr effect (RIKE) are of the above category. RIKE is a version Raman spectroscopy that makes use of defined input and output polarizations. When a Raman-active medium is simultaneously irradiated by two exciting radiation sources, namely an elliptically polarized wave and a linearly polarized stokes wave or anti-stokes wave, the nonlinear-linear third order interaction gives rise to a new stokes wave or anti-stokes wave that is polarized perpendicularly to the wave originally incident on the medium. This phenomenon exhibits resonance if the difference in two exciting radiation frequency is near one of the Raman active molecular frequency. The signal in the spectral region of nonlinear resonance is determined on the one hand by the polarization properties of the elliptically polarized laser light and on the other hand by the resonant and nonlinear resonant terms in the nonlinear susceptibility. A circularly polarized laser beam leads to a background free Raman spectrum if one of the exciting radiation sources is being tuned or if broad band irradiation is used. The first studies of this "pure" RIKE were performed with organic liquids. Compared with other methods of active Raman scattering, the advantage of RIKE is that the phase matching condition in isotropic media is satisfied in a broad band spectrum so that under fixed excitation geometry, spectral tuning can be achieved. RIKE with an elliptically polarised laser beam proves to be an appropriate polarisation-spectroscopic method for determining optical material parameters.

Another new CRS technique employing coherent sources at only two frequencies is known as Raman in-

duced phase conjugation technique (RIPC). This is a form of four wave mixing in which two beams at ν and $\nu - \nu_1$ (or at $\nu + \nu_1$) mix with a third beam at ν to generate a fourth beam at $\nu - \nu_1$ or at $\nu + \nu_1$. The generated beam is nearly phase conjugate to one of the beams at ν .

The effect so studied has the following characteristics

1. The Raman signal is generated as a coherent beam which is nearly phase conjugate to one of the incident beam
- (2) Upto 16 independent combinations of beam polarisations are possible
- (3) The Raman signal beam is not coincident with any input beam
- (4) Phase matching among the four beams can be achieved for excitation frequencies in a wide range many hundreds of cm^{-1} for a given beam geometry
- (5) Phase matching among

the four beams can also be achieved for given beam frequencies, for a wide range of input or image beam angles, thus allowing an enhanced or altered phase conjugate image at Raman resonance. This spatial resolution can be used to enhance spectral resolution or to focus on a particular region of the sample (6) The wave vectors of the excitations observed in RIPC are nearly $(2\nu \pm \nu_1) n/c$ where n is the refractive index (7) If the input beam containing $\nu \pm \nu_1$ is broadband, and beam polarisation are properly adjusted, only Raman-shifted frequencies will be conjugated and the usual nonlinear-resonant component will be absent. These properties allow Raman spectra to be recorded with single nanosecond pulses. RIPC is the latest very useful Raman technique in special situations such as for hot, birefringent and slightly tremulous media.