

FIFTY YEARS OF RAMAN EFFECT—SOME RECENT DEVELOPMENTS

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INTRODUCTION

EXPERIMENTAL studies on the scattering of light carried out by Professor Chandrasekhara Venkata Raman in the Indian Association for the Cultivation of Science at Calcutta, since the year 1921 established the various laws connected with the scattering and finally culminated in 1928 in the discovery of a new scattering phenomenon known as the Raman Effect in which any transparent substance would simultaneously absorb one photon of a certain frequency and emit another of a different frequency. The energies of the two photons differed by an amount corresponding to the energy difference between two quantum-mechanical levels of the medium. The first announcement of the discovery of modified radiation in scattering was made by Prof. C. V. Raman in a lecture delivered under the title "A New Radiation" on March 16th, 1928 at a meeting of the South Indian Science Association at Bangalore.* Raman drew special attention to the universality of the phenomenon and to its principal features. It was realised almost immediately after the discovery, that practically all the data that were till then obtained by studying the near and far infrared absorption spectra of molecules could be collected by studying the Raman spectra. The fundamental and most important aspect of Raman scattering is that it provided a tool for spectroscopic investigation of energy levels of various systems not accessible by the usual absorption and emission techniques. Studies on Raman Effect

established the quantum-mechanical principles and supplied information about the fundamental properties of molecules in gaseous state and of their aggregation in liquid and crystalline states. Although the early interest in this field was confined essentially to physical and chemical problems, with the advent of gas lasers in 1961, the interest began to spread rapidly to other fields. Biology, Biochemistry and Polymer Chemistry are the first sciences to benefit from this renaissance. Even in sophisticated technology and industry, Raman Effect is finding increasing applications.

The development of lasers completely revolutionised the application of Raman spectroscopy and various new types of excitations in transparent, coloured, or even opaque media have been reported. The studies on Raman Effect have increased by leaps and bounds with regard to the range of coverage and the versatility of its applications. Nearly 15,000 original papers have been published, of which more than half have appeared since 1962. Besides many Reviews, Monographs, Books and Treatises have also come out.

In the beginning, the subject was monopolised by some laboratories in India, France, Germany, United States of America, Italy, Japan and Russia, where notable contributions were made. Now it is being investigated in the laboratories of practically every country in the world. On March 16th, 1978 the announcement of the discovery will be completing its golden jubilee and it appears appropriate to publish a historical review of the subject with special reference to the new techniques and recent areas of development and achievements in this Journal which was

* The line spectrum of the new radiation was first seen on 28th February 1928 and the full lecture was published in the *Indian Journal of Physics* on 31st March, 2, 387 (1928),

started under the auspices of the South Indian Science Association.

2. EXPERIMENTAL TECHNIQUES

The equipment originally used by Raman consisted of a quartz mercury lamp, a container for the sample, a condensing lens, and a pocket spectroscope. Later these were replaced by more powerful mercury arcs, large samples with special containers for the same and high dispersion and large aperture spectrographs with photographic recording. The technique is characterised by low signal to noise ratio and hence time consuming. Exposures of the order of hours and even days had to be given. Even the use of mercury resonance radiation together with a Hg filter in the scattered path during the 1940's and 1950's which gave some fillip to the work on Raman spectra of crystals and their interpretation in terms of lattice dynamics, had various limitations. For the first thirty-five years, Raman scattering was a laborious and exotic technique, important more for the quantum mechanical and other fundamental principles it illustrated than for its practical applications.

The laser radiation is characterised by exceptionally high specific intensity, negligible divergence, high monochromaticity, complete polarisation and nearly perfect coherence and hence formed an ideal source for Raman studies. Continuously operating gas lasers began replacing mercury arcs as source of Raman excitation since 1962. Since an almost coherent laser beam can be focussed on to a region whose dimensions are of the order of a few wavelengths, the sample size can be as small as possible. The most commonly used lasers for Raman excitation are the continuously operating He-Ne (6328 Å), Ar⁺ ion (4880, 5145, and 4765 Å) and He-Cd (4415 and 3250 Å) gas lasers and the pulsed and continuously operating forms of the ruby

(6943 Å) and Nd-YAG (1.06 μ) solid state lasers. The very recent development of tunable dye lasers, the wavelengths of whose output radiation are capable of being varied at will, over the entire visible and ultraviolet regions has given a new dimension to the studies on Raman Effect. The use of the frequency doubled laser radiation, obtained by passing a laser beam through a suitably cut and oriented crystal possessing high non-linear optical coefficient such as LiNbO₃, has made it possible to extend the studies on Raman Effect in the far ultraviolet.

The second important innovation is the use of grating double and triple monochromators with efficient stray light elimination and the use of high speed and reproducible scanning mechanisms in place of the prism spectrographs. The third important factor for the rapid revival of interest in Raman spectroscopy is the parallel development of sophisticated photon counting techniques (photomultiplier and associated electronic equipment, counters and recorders) and Raman-computer interfaces and their use in spectral scanning.

High quality Raman spectra can now be obtained in minutes even from micro-samples (~ 10⁻⁹ g) which no longer need be transparent or colourless. A new vista of micro Raman spectroscopic analysis has already begun enabling one to extend such studies to biological and biomedical samples, available only in very small quantities or concentration either by themselves or in solution. With the modern techniques it is possible to count the individual scattered photon and thereby one can get an accurate estimate of the intensities of Raman lines and hence cross-sections for Raman scattering.

With the use of an intense exciting source, the main limitation, in getting satisfactory Raman spectra of opaque, coloured or absorbing materials is the localised overheating and consequent decomposition of the sample. To

overcome this difficulty a few effective techniques have been developed recently based on the principle of relative motion between the sample and the focussed laser beam. The most commonly used ones are the spinning or flowing sample arrangements. In the former case the sample can be rotated keeping the incident beam fixed or the focussed laser beam can be made to scan rapidly linearly or circularly over the surface of the sample, keeping the sample fixed. Highly coloured solids (crystals or powders) which would decompose instantly in a static beam, yielded good Raman spectra when either of these two techniques is used.

Among the other notable improvements in experimental techniques, mention may be made of the following :

(A) *Difference Raman Spectroscopy* : The principle idea is to use a rotating cell which is divided into two equal parts one containing the solution and the other the solvent. The signals from both halves of the cell are fed to the same photometer-electronic system with a differential amplifier which allows the cancellation of the Raman lines of the solvent from the spectrum of the solution. Difference Raman spectra of solid samples (e.g., doped versus undoped materials) can also be scanned directly.

(B) *Addition Raman Spectroscopy* : A divided rotating cell is used to superimpose spectra from the sample and the standard without the necessity of mixing sample and standard together. The two spectra are mixed and scanned electronically.

(C) *Automatic Scanning of Depolarisation Ratio* : In this technique the intensities of the two scattered spectra with vibrations vertical and horizontal respectively and the depolarisation ratio ρ can be scanned as a function of the Raman shift one after another. This is specially useful for the study of spectra of single crystals and for unequivocally classifying the observed Raman lines, and for the study

of molecular orientations in polymers and biopolymers.

(D) *Raman Circular Intensity Differential Technique* : The quantity actually measured is the circular intensity differential (CID) which is given by.

$$\Delta = \frac{I_R - I_L}{I_R + I_L}$$

where I_R and I_L are the scattered intensities for right and left circularly polarised incident light. This factor is related to the vibrational (Raman) optical activity which in turn provides stereochemical information about the substance under examination. Using a magnetic beam parallel to the incident laser beam, magnetic Raman CID has been demonstrated which brings in, additional structure into the vibrational spectra.

(E) *Derivative Raman Spectroscopy* : In this technique, one plots the $dI/d\nu$ versus ν . The resultant curve enables one to recognise the multiple structure caused by overlapping bands.

(F) *The Optical Fibre Raman Spectroscopy* : This has been developed using liquid filled optical fibres. The advantages of high collection efficiency and intensification of spontaneous Raman scattering are made use of.

(G) *Time Resolved and Space Resolved Raman Spectroscopy* : Before concluding this section, it is necessary to refer to another important technique called the time resolved and space resolved Raman spectroscopy which finds application for the study of a variety of problems in physical chemistry, namely fast chemical reactions in gas, liquid and solid phases, photochemical processes, phase transitions in solids, defects in solids, etc. The main characteristics of the new technique are the ability to focus the energy of the laser beam on a very tiny spot on the sample, whose dimensions may be limited by the wavelength and the ability to deliver a large number of photons in a pulse of a very short duration, without the energy density exceeding the

limits at which the sample gets destroyed and the limit at which non-linear phenomena begin to show up.

Multichannel Raman spectroscopy has also been developed, which has high sensitivity, no reciprocity effect and short response time of a few pico seconds and high storage capacity. It can analyse simultaneously 10^5 channels of information. Space resolution enables one to conduct Raman micro analysis and Raman microscopic examination of heterogeneous samples.

Compared to the very simple equipment used by Raman for the discovery of the effect, the developments over the last fifteen years have led us to the necessity of using more and more sophisticated and expensive equipment for unveiling the various ramifications of Raman Effect.

3. RECENT DEVELOPMENTS

Using laser excitation, Raman spectra of many substances have been reinvestigated and the spectra of many new compounds including coloured or opaque substances, polymers, nucleic acids, proteins, enzymes and other biomolecules have been studied for the first time and considerable information has been accumulated about their structure. New types of excitations such as electronic Raman Effect, inverse Raman Effect, resonance, etc. have been discovered.

In normal Raman Effect, vibrational and/or rotational energy levels of the systems take part. With the aid of the appropriate laser excitation, transitions in low-lying electronic levels especially in rare earth salt can be induced by Raman Effect. The electronic Raman spectra of many substances including semimetals and semiconductors have been recorded for getting information about their electronic levels.

With the availability of powerful lasers which now provide a large number of different

excitation frequencies in well collimated beams, it has been possible to build up vast data on the frequency dependence of the intensity of Raman lines, as the exciting frequency approaches that of an electronic absorption band of the scattering system. When the exciting line coincides with that of the allowed broad electronic absorption band of the molecule, it leads to a rigorous resonance Raman scattering (RRS). This is characterised by an enormous increase in the intensity of the corresponding Raman line. It is the development of RRS with the ingenious sample handling techniques that has made possible the structural studies of heme proteins and other biological systems containing chromophors. Although the phenomenon of RRS was predicted by Plazcek's theory of Raman scattering (1934) and experimentally observed as early as 1958, it is only with the availability of powerful tunable dye lasers, the usefulness of RRS for structural studies has been fully exploited. A phenomenon called inverse Raman Effect has also been reported. In this process Raman scattering appears as absorption lines in a continuum on the anti-Stokes side instead of the normal emission lines.

4. RAMAN SCATTERING OTHER THAN BY PHONONS

In polar crystals electromagnetic waves and optical phonons interact strongly when their energies and wave vectors are nearly equal. This interaction removes the intersection of the uncoupled dispersion curves and results in upper and lower branches which have mixed electromagnetic and mechanical nature. The crystal excitations in this mixed region have been called polaritons which give rise to Raman scattering when excited. The frequency of the polariton appearing as Raman shift varies with angle of scattering. Polariton Raman scattering enables us to understand the nature of the electric field

inside the crystal and its interaction with lattice vibrations. Spontaneous Raman scattering of polaritons provides a tunable source of visible and infrared radiation. Stimulated Raman scattering of polaritons would provide an intense coherent and variable source of infrared and visible radiation.

The existence of spin orbit interaction in magnetic crystals leads to a mechanism of Raman scattering from spin waves. Such magnon or collective excitations have been observed both in the first and the second order, Raman spectra of the transition metal fluorides below the Neel temperature using laser excitation. Raman spectroscopy is a valuable tool for studying spin-orbit interactions in magnetic materials.

Spin-flip Raman scattering has been observed from magnetically split ground states of donors and acceptors, *i.e.*, bound electrons and holes in CdS and other semiconductors. Raman scattering from plasma, *i.e.*, from single particle electron and hole excitations in semiconductors such as GaAs and GaP have also been recorded. Some exciting new applications of Raman Effect in the area of electronic processes in semiconductors namely *p*-type cubic crystals are in the offing. Raman Effect has been found to be demonstrably superior to EPR for the determination of gyro-magnetic ratios and spin temperature for mobile holes and shallow acceptors in semiconductors.

5. NON-LINEAR EFFECTS

When giant pulses of short duration and high peak power from a ruby or Nd-YAG laser are used for excitation, various non linear optical phenomena are observed. Of the many non-linear effects, the important ones as regards Raman scattering is concerned are the stimulated Raman Effect, the Hyper Raman Effect and coherent anti-Stokes Raman scattering (CARS) of which the last one

holds greater promise for future development and applications.

In stimulated Raman scattering the incident light wave of frequency ν_0 induces a gain in the scattering medium at another frequency $(\nu_0 - \nu_R)$ where ν_R is the frequency of some Raman active vibration. If the incident intensity is above a threshold value, the gain can exceed the losses and the scattered beam with the frequency $(\nu_0 - \nu_R)$, gets amplified. A good fraction of the incident light is thrown as coherent stimulated Raman scattering close to the forward direction. Only a couple of Raman modes are studied in this process. This effect has been studied in many liquids and some solids.

In hyper Raman Effect, (HRE) Raman lines appear on either side of the octave of the laser excitation frequency. It is a very feeble phenomenon and hence difficult to record. All the vibrational modes of a system will be active in HRE unlike in ordinary Raman Effect and infrared absorption.

Coherent anti-Stokes Raman spectroscopy (CARS) is a relatively new kind of Raman spectroscopy which is based on non-linear conversion of two laser beams into a coherent laser-like Raman beam of high intensity in the anti-Stokes region. The technique consists in mixing two collinear laser beams of frequencies ν_1 and ν_2 ($\nu_1 > \nu_2$) in a medium which possesses a Raman active mode of frequency ν_R such that $\nu_R \simeq (\nu_1 - \nu_2)$. New waves are generated in the forward direction at frequency ν_3 , $\nu_3 = (2\nu_1 - \nu_2)$ which corresponds to the anti-stokes Raman line of vibration ν_1 . The emission is often many orders of magnitude greater than normal scattering and because of the coherent and anti-Stokes character of the radiation, the CARS is potentially a powerful technique for obtaining analytical and spectroscopic information pertaining to Raman active resonance in gases, liquids and solids even if they are fluorescent. It is widely used to take Raman spectra of gases in discharges,

plasmas, combustions and atmospheric chemistry. CARS techniques may be expected to be useful for studying fluctuations phenomena, reaction dynamics, photochemistry, kinetics, relaxation, and energy transfer.

In the CARS experiment if ν_1 is less than ν_2 the analogous technique is called Coherent Stokes Raman spectroscopy (CSRS—pronounced “sissors”). Besides CARS and CSRS, several advantages of observing Raman spectra by means of non-linear optical mixing have been realised in a variety of other coherent Raman spectroscopic techniques. Acronyms and neologisms such as RIKES (Raman induced Kerr Effect), HORSES (Higher Order Raman Excitation Studies), “Submarine”, “Helicopter”, and so on, have been invented to designate each variation of the basic four photon parametric mixing process. Continued technological innovation and development of more powerful tunable lasers may ultimately make the coherent Raman techniques as accessible as spontaneous scattering is to day. This will eventually lead to a second revolution in the history of Raman Effect.

6. APPLICATIONS

A. Chemical Applications :

One of the very first applications of Raman spectroscopy was for the solution or understanding of many physicochemical problems. Raman Effect served as an aid for the analysis of unknown structures of molecules and also for the identification and estimation of the quantity of any substance present in any stationary state or during any transient process. Raman data of various molecules and ions have led to vibrational assignments and evaluation of their force constants and other thermodynamical properties. Chemical problems such as molecular interactions, nature of the chemical bond, constitution, tautomerism, isomerism, molecular rotations, hindered

rotation, electrolytic dissociation, association, polymerisation, solvent effect exchange interactions, hydrogen bonding, spectra structure correlation, kinetics of fast reactions, catalysis adsorption, phase transitions, etc., have been successfully solved. Recently Raman spectroscopy has been applied for the determination of potential functions governing puckering and internal torsional modes and for getting information on intramolecular forces.

In the past, Raman spectroscopy of gases was limited to the study of molecular structures only. The availability of powerful lasers, scanning spectrometers and new techniques has greatly enlarged the scope of Raman spectroscopy of gases in recent years. More than 61 different molecules in the gaseous state have been examined for high resolution Raman spectroscopy and their molecular constants have been determined very accurately. Laser Raman spectroscopy of gases is now being applied to a variety of scientific and technological problems including the detection of molecular hydrogen in planetary atmospheres and interstellar space, determination of temperatures, particle densities, reaction kinetics and air pollution studies.

B. Physics of the Solid State :

In the earlier days, a number of Indian and French workers investigated the changes in the intensities of Raman lines arising from changing orientations of the crystal axes with reference to the directions of incidence and observation and with reference to the direction of polarisation of the incident electric vector. From group theoretical analysis they had worked out the Raman active vibrational symmetries and Raman tensors for the 32 crystal symmetry classes. Only after the advent of laser Raman spectroscopy, precision measurements of polarisation characteristics and orientation effects could be carried out in a variety of crystals and all the theoretical

predictions including splitting of Raman modes in the crystalline field predicted by group theory could be satisfactorily verified.

Although with the use of mercury resonance radiation as exciter, it was possible to record the first and second order Raman spectra of simple crystals, like diamond, alkali halides, etc., which led to the progressive development of the theory of the dynamics of crystal lattices, very little work could be done on temperature dependence of Raman frequencies in crystals and on other types of excitations in crystals. With the advent of laser Raman spectroscopy, great insight has been obtained regarding the mechanisms responsible for Raman scattering in the solid state. Much activity has been directed towards the study of phase transitions and polaritons. It is well known that many structural phase transitions in solids are accompanied by a so called soft mode. As the transition temperature is approached, the frequency of this mode decreases. It is found that in many cases, the soft mode tends to a hard core frequency at the phase transition. As this soft mode is a normal mode of lattice vibration, the dynamic and static properties can be investigated by measuring soft mode response using Raman technique. The two important categories of soft mode transitions that are being extensively studied are in ferro-electric and ferro-elastic crystals, the order parameter in the former being spontaneous polarization and that in the latter being spontaneous strain. By monitoring the intensity of Raman active phonon, through transitions as a function of temperature and pressure, one would be able to say whether the transition is of first or second order. Thus one gets greater insight into the mechanism of phase transitions.

C. Bio-Chemical, Biological and Polymer Sciences :

Recent developments in techniques of Raman spectroscopy have established that it

is an invaluable tool for gaining information concerning molecular conformation and inter-molecular interactions in nucleic acids and proteins, as well as the corresponding homopolymers, poly nucleotides and polypeptides. In the 300–1700 cm^{-1} spectral region, pure nucleic acid or protein gives about 30 to 40 Raman lines, some of which are strong and some weak. They are mostly identified even in a Raman spectrum of a complex system containing more than one kind of molecule. Some of the lines are useful for conformation and/or interaction studies.

The Raman lines characteristic of α -helix, β -form and random coil or non-helical portion have been catalogued in the literature. Comparing the observed Raman spectrum of any protein with the above catalogue, one can estimate the extent of each portion and thereby make a conformational analysis of the protein under study. Such an analysis is extremely useful for interpreting any change in the structure of the proteins, brought about by certain physical or chemical reactions.

Some typical problems for which Raman spectroscopy is capable of giving solutions are concerned with the conformation of RNA or DNA in the native virion types of interactions between the nucleotides, dynamics of the conformation due to viral infection and a host of such related ones. Greater speed, simplicity and versatility, ease with which spectra can be obtained equally well with amorphous solids, aqueous suspensions or solutions and the fact that the Raman spectrum of a virus contains resolvable features due to different molecular sub-groups of both nucleic acid and protein components render the technique of Raman spectroscopy superior to and more useful than many other physicochemical methods of investigation.

Observation of the changes in the various Raman lines, as the conformation of a biological macromolecule is changed from the order to disordered form, by raising the

temperature has been termed Raman-T jump experiment. It can be used for determining the kinetics of order-disorder transition as a function of time in nucleic acids and proteins. Biological importance of such studies is very well known.

Another interesting area of application is in polymer characterisation. Elucidation of chemical structure and compositions, study of stereoregularity of monosubstituted vinyl polymers $(CH_2 \cdot CHX)_n$, geometrical isomerism of repeat units, chain conformation in solid state, melt and in aqueous and other solutions and packing of polymer chains in a crystal are the major areas in polymer chemistry where Raman spectroscopy offers considerable scope. Underlying all these applications is the identification of certain intense scattering by nearly homo nuclear single and multiple bonds of carbon-carbon, sulphur-sulphur, and nitrogen-nitrogen.

Physicists, chemists, and particularly spectroscopists everywhere owe Professor Raman a great debt of gratitude for his revolutionary contribution to physics. Without his vision and initiative it would have taken many more years for his effect to have been discovered and physics would not be what it is today.

In conclusion, it is necessary to point out that quite a few scientists from all over the world have made notable contributions to

various aspects of Raman Effect. The list is too long to be enumerated here. At the completion of fifty years after the discovery, one finds that the field of activity on Raman effect is widening both in scope and in utility. Nobody including the discoverer would have ever dreamt about this vista of activity for the Effect nearly sixteen years ago. On behalf of the Raman spectroscopists all over the world who number well over four hundred and on behalf of myself I wish to pay our homage and respect to our beloved Professor, the late Chandrasekhara Venkata Raman, for this brilliant discovery.

For further information the reader may refer to any of the following books :

1. *Raman Spectroscopy*, H. A. Szymanski, (Ed.), Vols. 1 and 2, Plenum Press, New York.
 2. *The Raman Effect*, Vols. 1 and 2, A. Anderson (Ed.), Marcel Dekker Inc., New York.
 3. *Laser Raman Spectroscopy*, T. R. Gibson and P. J. Hendra, Wiley (Interscience), New York.
 4. *Advances in Infra-red and Raman Spectroscopy*, Vols. 1, 2 and 3, R. J. H. Clark and R. E. Hester (Eds.), Heydon and Sons, Ltd., London.
 5. *Advances in Raman Spectroscopy*, Vol. I, J. P. Mathieu (Ed.), Heydon and Sons, Ltd., London.
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