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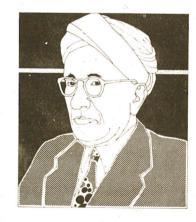


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Step 9: Meaningless made meaningful



A Life Sketch C.V. RAMA

HANDRASEKHARA KATA RAMAN was born on 7 November 1888 in a small village, Thiruvanaikkaval, near Tiruchirapalli in Tamil Nadu. His mother was Parvathi Ammal. His father, Chandrasekhara lyer, was a teacher in a local school. Raman was the second among eight children, five

sons and three daughters.

Raman matriculated at 11, passed his FA (nowadays called PUC or intermediate) at 13, won a scholarship and joined Presidency College, Madras. Very soon, his professors found him so remarkably intelligent that they exempted him from attending all the science classes as they felt he had nothing to learn from them. Raman passed his BA at 15 in the first class, and MA at 18 in 1907.

At the age of 16, while measuring the angle of a prism using a college spectrometer — as thousands of us have done - Raman observed some diffraction bands. He investigated these and they formed the subject of his first publication in The Philosophical Magazine (London) in 1906. This was followed by a note in the same journal on a new experimental method of measuring surface tension. The Presidency College was at that time a teaching institution with no tradition

whatsoever of research.

When he passed his BA, Raman's teachers had suggested that he should go to England for further studies. But the Civil Surgeon of Madras disqualified him medically, saying that



Raman as a student in Presidency College, Madras, in 1903. He was then 141 years

the rigours of the English climate would kill him. Raman is known to have said later, "I shall ever

be grateful to this man". After his MA, Raman, on the advice of his teachers, S. RAMASESHAN

saw a sign which read "The Indian Association for the Cultivation of Science" on Bowbazaar Street. On his way back. Raman knocked on the door. He met Amrita Lal Sircar, the Secretary of the Association, who promptly handed over the keys of the Association to Raman when he heard of his plans to do research there.

The Association had been established in 1876 by Amrita Lal's father, Mahendra Lal Sircar, a man of vision, who wanted to have an institution which was a combination of the Royal Institution of London and the British Association. It had started off well. At every annual meeting, Mahendra Lal advocated the importance of the cultivation of science by original research. There were many popular and scientific lectures in the early days but there was no research of any type. Subsequently the institution had decayed, and, in 1902, a despondent Mahendra Lal had declared, "I do not know how to account for the apathy of our people towards the cultivation of science". Three years later, Raman was to turn the Association into one of the important centres of original research in the world.

Young Lokasundari tells us of the routine - 5.30 am, Raman goes to the Association, returns at 9.45 am, bathes, gulps his food in haste, leaves for office, invariably by taxi so that he may not be late. At 5 pm, Raman goes straight to the Association on his



places, he converted his home into a laboratory and continued his work. In 1911, he was back in Calcutta.

Raman and Ashutosh Dey were the only workers at the Association. Even so, publications poured out. Raman also started the Bulletin of the Indian Association where he published massive monographs. In 1917, the Bulletin became the Proceedings and much later the Indian Journal of Physics. The two together published several papers. Raman was proud when a paper, in which Ashutosh was the sole author, was published in the Proceedings of the Royal Society. Ashu Babu had never entered the portals of a university!

What were the problems Raman tackled? Every one of them was connected with his direct experience, thus arousing his curiosity. He had heard his father play the violin. He had worked with the sonometer and done Melde's experiment in college. So followed his papers on the bowed string, the struck string, the maintenance of vibrations, resonance, aerial waves generated by impact, the singing flames, music from heated metals and many others.

He investigated whether his feeling that the veena produced the most exquisite musical sound was a subjective reaction or has a sound physical basis. He found that the bridge of the veena is so cunningly constructed that the Helmholtz Law, that the position at which the string is plucked cannot be a node, is violated. Thus, this instrument produced innumerable harmonics, making its sound closest in harmonic content to the human voice.

He knew that the normal stretched circular membrane, as found in the Western drum, was "unmusical and just a noise producer". His sharp ear detected musical overtones in the sound of the *mridangam* and the tabla. He discovered that the heterogeneous loading of their membranes could produce harmonics — so that in the hands of the masters, the Indian drum is similar to a stringed instrument. He had become an authority on sound and musical instruments.

Palit Professor

MEANWHILE, Ashutosh Mukherjee, Vice-Chancellor of Calcutta University, offered him the Palit Chair of Physics. Raman decided to accept the offer for a salary less than what he was getting. The decision caused consternation in the establishment. "There may soon be Indianisation of the Department", they told Raman. And as one of the best officers, he may even end up as Member (Finance) in the Viceroy's Council — who knows? But Raman's mind was made up.

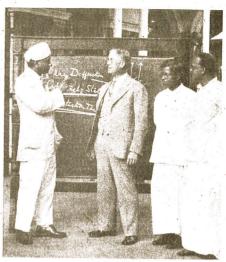
There was a problem, however. One of the requirements for appointment to the Palit Chair was training abroad. Raman refused to go to England to be "trained". Finally, Sir Ashutosh changed the provisions of the endowment. What an administrator!

In 1919, Amrita Lal Sircar died and Raman became the Honorary Secretary of the Association, thus having two laboratories to work in. For the first time, he took research students.

Under pressure from Sir Ashutosh, Raman went to Europe in 1921, as a delegate to the Universities' Congress in Oxford. There he met the most famous physicists of England, J. J. Thomson, Rutherford, William Bragg and others. Later, Raman told a story about how moved he was when Rutherford recognised him sitting in a back bench at a lecture and asked him to come and sit next to him.

Characteristically, even in London he reacted to what he saw. He marvelled at the whispering gallery of St. Paul's Cathedral, did a few experiments, and published two papers — one in Nature and the other in the Proceedings of the Royal Society.

It was on this voyage that Raman saw the grandeur of the Mediterranean, its moods and, in particular, its blueness. The more he saw it, the more did his wonder grow. Lord Rayleigh, who had explained the blue of the sky as due to scattering by the molecules in the atmosphere, had dismissed the blue of the sea with the statement: "The much admired



After a seminar at the Indian Association for the Cultivation of Science, Calcutta

dark blue of the deep sea... is simply, the blue of the sky seen by reflection." Raman demolished this idea by an extremely simple experiment during the return voyage. He quenched the reflection of the sky in the sea by observing at the Brewsterian angle through a polarising nicol prism. Even with the sky reflection so extinguished, he saw the surface of the sea glowing with a vivid blue which appeared to emerge from inside the water, indicating that the blueness of the sea was due to scattering by the water.

Even aboard the ship he felt that the Einstein-Smoluchowski concept of thermodynamic fluctuations—which was developed to explain special optical phenomena near the critical point—could be extended to explain molecular diffraction in liquids. On his return to India, he started three most fruitful lines of investigation: (i) the scattering of light by liquids, (ii) the scattering of X-rays by liquids, and (iii) the vis-

cosity of liquids.

Many may not know that the earliest work on the scattering of X-rays by liquids was done in India. Raman and his group developed an effective theory and confirmed the shapes of many molecules and deduced the nature of their aggregation in the liquid state. Raman once said wistfully, "We were so preoccupied with light scattering that we did not apply the idea of Fourier transforms to X-ray scattering in liquids although we were so close to it ". This was done later by Zernicke and Prins in 1927. The famous Raman-Ramanathan paper was published in 1923. In 1923, he advanced a theory of viscosity which was used by Staudinger, the famous polymer chemist, to explain the viscosity of polymers.

Within a few weeks of his return

from England, Raman (and Seshagiri Rao) had measured the intensity of the molecular scattering of light from water. They established that the Einstein-Smoluchowski concept of thermodynamic fluctuations could be extended to explain molecular scatter-

ing almost quantitatively.

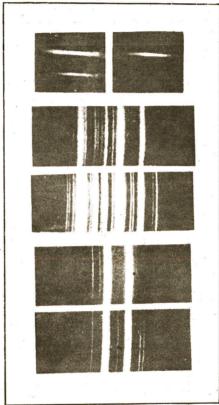
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In April 1923, K. R. Ramanathan, the oldest and among the most distinguished of Raman's students, made a serious study of the scattering of light in water at Raman's suggestion. Sunlight was focused on the liquid and the scattered light was seen as a track in the transverse direction. A system of complementary filters was devised, each filter completely cutting off the light transmitted by the other. When the incident light was passed through one, and the scattered light viewed through the other, no track should have been visible, if there had been no change of colour in the process. But the track could, in fact, be observed. This was attributed to a "weak fluorescence" due to impurities which were believed to be present. This "weak fluorescence" was not completely depolarised (as true fluorescence should have been) and the amount of depolarisation changed with wavelength.

Ramanathan wrote much later: "Raman was not satisfied with the explanation that it was due to fluorescence. He felt that it was characteristic of the substance and wondered whether it might not be akin to the Compton effect in X-ray scattering" (where a change in wavelength of X-rays scattered by atoms had just been discovered that year). Even after repeated slow distillation of the liquids in vacuum, the "weak fluorescence" persisted undiminished. The same effect was also observed later in many organic liquids by K. S. Krishnan, who had just joined him and was later to become one of Raman's distinguished students.

The Compton effect was on Raman's mind. He had calculated that true Compton scattering could not be observed at optical wavelengths. He considered the interaction of X-rays with the electrons of the atom—and

using the concept of fluctuations, which was so successful in explaining the molecular scattering, he derived the relationship now famous as the Compton-Raman formula. The derivation was classical, wherein Raman showed that the coherent scattering (corresponding to Thomson scattering in X-rays and to Rayleigh scattering in light) is proportional to the square of the number of electrons in the atom whereas the incoherent scattering (Compton scattering) is proportional to the number of electrons.



The first Raman spectra

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Raman apparently decided to settle the issue. He asked Krishnan to follow up Venkateswaran's observations. Krishnan set up the experiment for the study of the scattering of light in organic liquids and vapours — but this time he used larger lenses (18 cm diameter) so the intensity of the track was very much greater. He noticed that all his liquids exhibited the famous "weak fluorescence" observed by Ramanathan and, further, the smaller the anisotropy of the molecule, the greater was the polarisation of the "fluorescence" light.

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While the analogy with the X-ray case had been made much closer, it was apparent that the phenomenon was not fully understood. The observations continued. On the evening of 27 February, Raman decided to view the "fluorescence track" through a direct vision spectroscope but by the time Ashu Babu set it up, the Sun had set. Next morning, the first observation was made of what is now known as the Raman effect. The spectroscope showed that the track contained not only the incident colour but at least another, separated by a dark space.

Ashu Babu was immediately asked to set up a mercury arc, a light source known for the sharp monochromatic lines. Using a filter in the incident light which cuts off all the visible light longer than the indigo 4358 AU line, the direct vision spectroscope showed not one but two sharp lines in the blue-green region. The following day, 29 February 1928, the announcement of the discovery was made to the Associated Press.

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Prof. Ramaseshan, a Jawaharlal Fellow, heads the Materials Science Division at the National Aeronautical Laboratory, Bangalore. He was a student of Prof. Raman at the Indian Institute of Science, Bangalore, where he was later a faculty member. He also headed the Department of Physics, IIT, Madras, before he went to the NAL.

The Rise of the Phoenix

- FROM SUNLIGHT TO LASERS

V. B. KARTHA

"HE study of light scattering might carry one into the deepest problems of physics and chemistry,..... The universality of the phenomenon, the convenience of the experimental technique and the simplicity of the spectra obtained enable the effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry."

These words pronounced by Prof. C. V. Raman, in his Nobel award lecture on 11 December, 1930, have never been so true as they are today, 50 years after the discovery of Raman effect. At the Sixth International Conference on Raman Spectroscopy held in Bangalore this September, about 600 authors presented a total of more than 300 papers in about six days. The papers spanned a wide range of fields in physics, chemistry, biology, biochemistry, medicine, analytical chemistry and related disciplines, providing a dramatic illustration of Professor Raman's prediction. Here we try to look into the growth of Raman Effect to its present status.

What is Raman effect?

ELECTROMAGNETIC radia-tions like visible light, X-rays, and y-rays can interact with molecules in matter, producing a variety of effects. Radiation can be scattered, absorbed and re-emitted, or completely absorbed, leaving behind the molecule unchanged, energetically excited, or even decomposed. In Raman effect, the incident radiation gets scattered by the molecule and the molecule is left in an energy state different from its initial state. If the energy of the molecule is increased in the scattering process, that is, it gains energy from the radiation (with some loss of energy by radiation), it is called Stokes scattering. When there is a loss of energy by the molecule (corresponding gain in energy of the radiation), the phenomenon is called Anti-Stokes scattering. Since the energy of radiation is given by $hv = hc/\lambda$, where \(\lambda \) is the wavelength, \(\nu \) the frequency, and h a constant, the scat-tered radiation has a change in wavelength, depending upon the energy exchange with the molecule.

Raman effect is thus likened to sight-seeing stop-overs of the electrons in the molecule, energised by the photon to what we call a "virtual state". The molecule in its initial state interacts with the incident photon, reaching the virtual state. (The state is called "virtual" because it corresponds to a combined state of the molecule and the photon, and neither of them, when present alone, will have such a state.) Most of the electrons fly back from this virtual state, on express flights, leaving the molecule again in its initial state, and the photon on its own way. This is normal scattering and is called Rayleigh scattering. But a very small fraction of electrons, about one in 106 to 108, return from the virtual state, stopping over at the various energy levels of the molecule, and changing the photon energy in that process. These processes are schematically shown in Fig. 1.

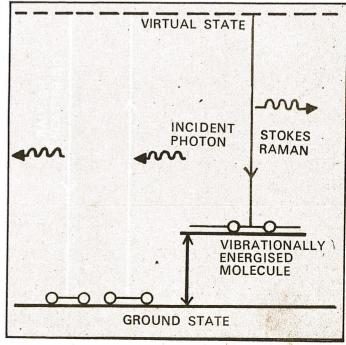
Raman, Smekal, Kramers and Heisenberg

In the hectic 1920's, barely a decade after Niels Bohr had proposed his quantum theory of the hydrogen atom, De Broglie, Heisenberg, Schrodinger, Born, Dirac and others were attempting, and succeeding specta-

cularly, in interpreting various aspects of atomic structure using quantum theory. In spite of these successes, in 1924, Kramers and Heisenberg, while attempting to explain the phenomena of dispersion and scattering of radiation on the basis of the quantum theory, wrote: "The peculiar processes which we describe as transitions from one state to another may be considered as very shortlasting, and no information is given by the optical phenomena as far as they are known and analysed today." Obviously, they were completely unaware of the earlier experiments of Raman and Ramanathan at Calcutta, in which Raman effect had already been observed. The Austrian physicist Smekal, in 1923, had also proposed similar ideas. Generalising the idea of the Compton effect (scattering of X-rays by electrons), Smekal expressed the assumption that in irradiation with light of frequency v, light of frequencies $v + v_k$ or $v - v_l$ will be emitted by the atom, the energy content of the atom decreasing simultaneously by hv_k or increasing by hv_l .

Kramers, Heisenberg and Smekal were, however, considering scattering by atoms as an extension of the Bohr theory. It may be argued that their ideas could equally well be applied to molecules, but the fact is that no

Fig. 1 An incident photon interacts with the molecule instantaneously a second photon is emitted. In Raleigh scattering, the energies of the molecule and photon are unchanged. In Stokes Raman scattering, the emitted photon has its frequency reduced (vibrational energy of the molecule increased), whereas in Anti-Stokes Raman scattering, the photon has its frequency (the increas⊕d vibrational energy of the molecule lowered)



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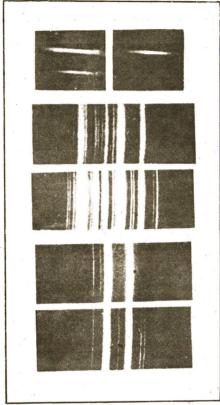
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such detailed quantum principles had yet been applied to molecules at that time. And Raman, unaware of all these predictions, had already started his series of experiments in 1921, convinced that the diffusion of light in liquids "possessed a significance extending far beyond the special purpose. . . and that it offered unlimited scope for research" (Nobel Lecture, 1930, C. V. Raman.)

From sunlight to lasers

THE significant results of Raman scattering were observed by Raman and his collaborators using sunlight and complementary filters to detect the scattered radiation. The Sun as the source of light was soon replaced by a quartz mercury lamp by

Wood published the first laser Raman spectrum in 1962. This opened the flood-gates to a number of theories, techniques and applications in light scattering and Raman effect.

Mechanism of Raman effect

Raman effect with the arrival of lasers, we should look into the fundamental process of interaction of radiation with matter. But the pictorial representation does not give us the mechanism of the process. Nor does it tell us why the laser caused a revolution in Raman effect. To get a clearer picture, we must see how the system of radiation and the molecule couple to each other.

When a molecule is placed in an

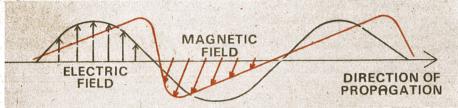


Fig. 2 Electromagnetic waves have electric and magnetic fields that are at right angles to each other and also are at right angles to the direction of propagation. The intensity of the radiation varies as the square of the maximum amplitude of the electric field. In terms of photons, intensity is proportional to the number of photons. The oscillating electric field is along this direction of polarisation

them, and this more powerful monochromatic source made possible the observation of Raman effect for a number of molecules. It should be stressed that the amount of radiation scattered in Raman effect is about ten million times less than the intensity of the incident radiation, and experimental detection of the scattered light at this time required photographic exposures requiring, sometimes, several hours or even days. It is a tribute to the scientific community of that time that they grasped the potentials of Raman effect as soon as it was discovered and produced a vast amount of results of fundamental significance. The rotational Raman spectra of oxygen confirming the zero spin of the 16O nucleus, and the nitrogen spectrum, showing that the nitrogen nucleus obeys Bose-Einstein statistics, are just two examples of such fundamental results.

The application of Raman effect in this early period, thus, mainly consisted of the study of vibrational-rotational spectra of simple molecules, and vibrational spectra of liquids or crystals, by a staunch few, who kept Raman spectroscopy alive during the period 1930 to 1960. Then came the laser. The first pulsed ruby laser was built by Maiman in 1960. This was followed by the heliumneon continuous gas laser by Javan and co-workers in 1961. Porto and

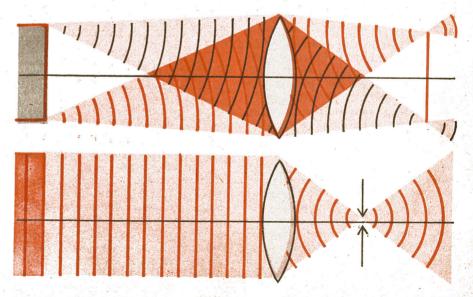
electric field, the equilibrium distribution of the negative and positive charges is disturbed, causing a separation of the charge centres and producing a dipole moment which is equal to charge separation multiplied by their magnitude. The molecule is said to be polarised. In light scattering, the applied field is the electromagnetic field of the radiation, which is characterised by two quanti-

ties, the wavelength λ (or frequency $\nu = c/\lambda$), and the polarisation of the field, as shown in Fig. 2.

When this radiation is incident on the molecule, the electric component of the field radiation induces a charge separation, producing an induced dipole moment. The direction of the latter is determined by the relative orientation of the molecule and the electromagnetic field. In a gas or liquid, all orientations of molecules are possible and, therefore, the induced dipole moment also will have all orientations. The magnitude of the induced dipole moment depends on the details of the charge distribution in the molecule. This is determined by a property called the "polarisability of the molecule".

Since the radiation field is an alternating field oscillating with the frequency of the radiation, the induced dipole moment also oscillates at this frequency. An oscillating dipole emits electromagnetic radiation of its oscillation frequency, which in this case is the frequency of the incident light. Hence, the scattered light will consist mostly of radiation of the same frequency as the incident light, giving Rayleigh scattering. Now, the molecule is itself executing certain internal motions like rotation about its axis or vibration about its equilibrium structure, which means the equilibrium charge distribution in the molecule is also being modulated in the same fashion. The polarisability and the induced dipole moment will thus be changing with these internal frequencies, and, hence, the oscillation of the induced dipole moment caused by the incident radiation is modified by the rotational and vibra-

Fig. 3 In an ordinary source like a mercury lamp, light is emitted in all directions resulting in a low intensity in a given direction (below). The laser beam is highly directional and the intensity decreases negligibly with distance (bottom)



tional frequencies. Thus, a small part of the radiation is emitted at these modified frequencies. This gives rise to Raman effect.

Let us go a step further. The induced dipole moment which depends upon both the polarisability of the molecule and the strength of the field applied can be given by an equation of the form

 $\overrightarrow{P} = \chi(^1) \overrightarrow{E} + \chi(^2) \overrightarrow{E}^2 + \chi(^3) \overrightarrow{E}^3 +$ higher terms,

where P is the induced dipole moment, E the electric field of the radiation, and the x's are terms determining the molecular polarisability. The x's decrease by several orders of magnitude with each step higher up in the series. For example, we can roughly say that $\chi(^1):\chi(^2):\chi(^3)=1:10^{-8}:10^{-16}$. Normally, therefore, the second and higher terms can be neglected when the electric field is small. With increasing field strength, the contribution of the higher terms increase tremendously, since they go up as the square, cube, etc of the field strength. It is here that the laser brings in new phenomena. Whereas a high-power mercury arc disperses its power of a few watts over a volume of several hundred cubic centimetres, the laser beam, which can be focused to a volume of the order of 10-3 cubic centimetres or less, produces energy densities and fields which are several orders of magnitude larger. With lasers, it has thus become possible to observe the simple Raman effect arising from the first term proportional to E as a routine technique, because of the high scattered intensity and the small sample size required. Furthermore, there are several other unique properties of laser radiation which make it an ideal source for Raman spectroscopy. In Fig. 3, we compare a conventional source of light with laser radiation.

The conventional sources of light give broad-band radiation (spread over different wavelengths) which is incoherent and the photons are emitted randomly in all directions and with all polarisations. In contrast, laser radiation is coherent, all individual photons have the same wavelength, travel in phase in the same direction and have the same polarisation. Whereas ordinary light can be focused, without loss of energy, to only a big image, the laser source can be focused to a very small area. The extremely high directionality, monochromaticity and polarisation make the laser ideal for new kinds of Raman spectroscopy, some of which we describe below. The use of the laser has brought in a wide

ADVANTAGES OF RAMAN SPECTROSCOPY	
1. Sampling	Remote or laboratory
2. Sample type	Gas, liquid, solid, solution, melt, matrix, vacuum, stationary or flowing, surface or bulk;Low or high temperatures
3. Sample damage	Non-destructive (unless very high laser powers are used)
4. Sample quantity	Micro-macro
5. Sample concentration	Trace or major components
6. Time resolution	Instantaneous; Time-resolved; Time-averaged, transient species; East reactions
7. Spatial resolution	Few microns in lab, few metres in remote samples
CHEMICAL AND ANALYTICAL APPLICATIONS	
Molecular structure, Molecular parameters	Vibrational spectra; Vibration-rotation spectra; Rotational spectra
2. Surface chemistry Catalysis, Electrochemistry	Raman spectra of surface species; Adsorbed gases; Electrode reactions
3. Flames, Combustion studies, High-temp - erature chemistry	Routine Raman spectral studies possible for jet engines; Gas turbines; Fuels; Rockets
Solid state chemistry, Phase transitions, Corrosion	Phase transitions can be followed through changes in Raman spectra; Solid state properties, Phonons; Plasmons; Magnons, Polaritons; etc observed
5. Photochemistry, Fast reactions, Reactions, Energy transfer	Instantaneous spectral information on inter- mediate species; Excited states; Transient Pro- ducts
Aqueous and Non-aqueous solutions, Liquids	Ion-ion and ion-solvent interactions; Inter- molecular interactions; Molecular motions in con- densed systems
7. Polymers, Biological systems	Structure; Conformation; Active groups; Aqueous systems
Microanalysis, Trace analysis, Remote analysis	Small samples; Inaccessible areas; Air pollutants; Radioactive samples
9. Minerals, Geological samples	Inclusions; Surfaces; Microcrystallites in minerals

range of applications in various fields in conventional Raman effect itself. Some of these are indicated in Tables above.

New Raman processes

EVEN without any other developments, lasers have made Raman spectroscopy an extremely important technique in several fields of modern science. But the high-power lasers of today have also brought about an entirely different revolution in Raman spectroscopy. This is because of the extremely high fields of the radia ion that could be produced by a pulsed laser or a focused laser beam. In this article, however, we shall highlight only some of the new

Raman processes which, in our opinion, will contribute to fundamental knowledge in physics and chemistry.

As mentioned earlier, with the extremely high fields produced by a laser, higher terms of the polarisation expansion have to be taken into account and we get effects associated with the quadratic, cubic and higher-order terms in the field. Each of these terms gives rise to a new Raman process. Thus, we have hyper Raman effect from the $\chi(^2)$ terms, inverse Raman effect, stimulated Raman effect, etc coming from $\chi(^3)$ and so on. Series of spectroscopic techniques have now been generated from these effects. Stimulated Raman Gain Spectroscopy (SRS), Coherent Anti-Stokes Raman

Spectroscopy (CARS), Higher-Order Raman Spectral Excitation Studies (HORSES) and Raman Induced Kerr Effect (RIKE) are examples of this. To indicate the capabilities of these new techniques, we will briefly describe two of them, SRS and CARS.

In SRS, two lasers are used in such a way that the difference in frequency corresponds to the Raman frequency of the system under study. One of these is called the "pump beam"

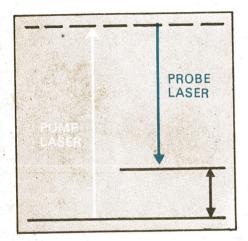


Fig. 4 The probe laser beam at frequency v_2 gains intensity whenever $v_1-v_R=v_2$, where v_R is a vibrational Raman mode. The photons are taken from the pump beam and transferred to the probe

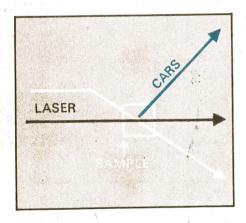


Fig. 5 A new laser beam of frequency $2\nu_1 - \nu_2$ is obtained when two laser beams of frequencies ν_1 and ν_2 are focused onto the sample at an appropriate angle.

and the other the "probe beam". The two beams are superposed on the sample, when, through the third-order non-linear term, the pump beam induces a gain (Stokes) or loss (anti-Stokes) in the probe beam, which is detected. Physically, the Stokes process can be visualised as stimulated gain in the probe beam by pumping the molecules under investigation with the pump beam, the system acting as a Raman amplifier. By tuning the pump beam over the various energy levels

of the system, we get the complete Raman spectrum (see Fig. 4).

The advantages of this technique over conventional Raman spectroscopy are many. First of all, because of the coherence of the probe beam, non-coherent background effects like fluorescence and luminescence can be easily removed, thus making the technique applicable to a variety of samples, which may fluoresce under irradiation. Similarly, the coherence also makes it unnecessary to have large double monochromators for elimination of stray light. Since the process involves only stimulated scattering, the line width of which is determined by the laser sources, extremely high resolution is possible without the use of high resolution monochromators or Fabri-Perot interferometers. With dye laser systems available commercially, resolutions of the order of a few MHz could be obtained, making this technique comparable to high resolution infrared spectroscopy with semiconductor diode lasers.

In the Coherent Anti-Stokes Raman Spectroscopy or CARS, once again we make use of the third-order non-linear polarisability. When two beams having frequencies v_1 and v_2 are sent into the sample, the Raman mode of the system is strongly excited, if $v_1 - v_2 = v_R$. The polarisability of the system is thus being strongly modulated at this frequency and an incident beam of frequency v_1 will generate a coherent beam of frequency $v_1 + (v_1 - v_2) = 2v_1 - v_2$. The beam, being coherent, will be very well collimated and look like a laser beam (Fig. 5).

Thus, while in the SRS one of the two laser beams itself is used to measure the Raman spectra, in CARS an entirely new beam is generated in a different direction.

Raman repays lasers

T is only in the fitness of things, that having gained so much through lasers, Raman effect should contribute to the production of lasers themselves. Stimulated Raman Lasers, Spin-Flip Raman Lasers, Polariton Lasers, Dye-Laser Pumped Raman Lasers, and Stimulated Electronic Raman Scattering Lasers are examples of how Raman effect has been used in the fabrication of tunable lasers for various investigations.

The versatility and usefulness of such systems are magnificently illustrated by the Spin-Flip Raman Laser developed by C. K. N. Patel and collaborators at the Bell Telephone Laboratories (USA).

The Spin-Flip Raman Laser is based on stimulated Raman scattering of an incident fixed-frequency laser

radiation by the spin states in a solid. The scattered photons lose or gain energy by an amount proportional to the magnetic field, H, applied to the crystal. The beauty of the process is that by varying H, the energy of the scattered photon and, hence, its frequency can be continuously altered. By using polished crystals forming a laser cavity, the scattered beam comes out as a laser beam and we get a tunable laser. At present this process has been observed at 5 µm and 10 µm in the infrared. Patel and his collaborators have used this device in a variety of investigations involving the detection of pollutants in atmospheric and stratospheric regions at concentrations of parts per billion.

Raman effect today

ET us now go back to the Sixth International Raman Conference. The Conference was divided into 11 plenary sessions and 32 contributory sessions. The fields covered Chemical Applications, included Molecular Relaxation, Resonance Raman, Liquids and Solutions, Polymers, Ionic Crystals, Molecular Crystals, Gases and Flames, Biochemistry and Biology, Non-linear Effects, CARS, New Techniques, Electronic Raman Effect, High Resolution Spectroscopy, Stimulated and Coherent Raman Scattering, Spin-Flip Raman Lasers, Raman Intensities, Semiconductors, Ion-Ion and Ion-Solvent Interactions, Free Radicals, ordered Solids, Micro Analysis, Organo-metallic Complexes, Thin Films and so on. Applications of Raman spectroscopy to medical diagnosis, electrochemical interfacial analysis, adsorbed molecules, turbulent flow, time-resolved spectroscopy, optical fibres and Raman microprobes were some of the new developments. In short, it can be said that there is hardly any branch of physics, chemistry, or biology in which Raman effect has not become a tool for analytical and fundamental investigations. As scientists try to probe deeper into the problems of interaction of radiation with matter using advanced laser technologies, we can be sure of many more novel and significant developments in Raman effect and light scattering.



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