

## INTRODUCTION

Chandrasekhara Venkata Raman—familiarily known to most as Sir C V Raman—was born on the 7th of November 1888 and died on the 21st of November 1970. During his scientific career which extended over 66 years he published more than 450 original research papers and monographs. Almost three times that number of scientific papers was published by his students, based on the work done under his direction. This volume presents 94 of the papers published by C V Raman either by himself or along with his students, on the general subject of the scattering of light. In it there are papers on colloid scattering, molecular scattering, surface scattering, Raman scattering and Brillouin scattering, as also his pioneering publications on molecular anisotropy. The celebrated monograph he wrote in 1922 on the *Molecular Diffraction of Light* as also his investigations on X-ray scattering and Compton scattering have been included as these played a significant role in his discovery of the Raman effect in 1928. The classical papers he wrote on magnetic, electric and flow birefringence along with his gifted student K S Krishnan also find a place in this volume. The titles of papers published by his students and collaborators from his laboratory on light scattering have been given at the end of this volume.

In early 1904 at the age of 16, C V Raman as an undergraduate at the Presidency College, Madras, commenced his experimental researches on sound and light. Lord Rayleigh's *Scientific Papers*, his *Treatise on Sound* and the works of Helmholtz were familiar to him. At eighteen he became an officer in the Finance Department of the Government of India. He did his scientific researches after hours at home or mostly in the Indian Association for the Cultivation of Science in Calcutta. His investigations were largely in the fields of acoustics, musical instruments and wave optics. The exquisite sensations of tone and the beauty of the colours arising from interference and diffraction of light fascinated him.

His first paper on the scattering of light appeared only in 1919. It was on the Doppler effect in molecular scattering. At that time he had also begun to take interest in the phenomenon of the scattering of light by sulphur suspensions. The paper on this subject makes interesting reading now, as one can see many elements in it that were to be introduced later into the Raman-Nath theory (Vols II and III) of the diffraction of light by ultrasonic waves.

It is definite that the intense interest he developed in the scattering of light was due to the visual impact that the blue of the Mediterranean sea made on him during his first voyage to Europe in 1921. It was not, however, the first time he saw

the blue of the waters. Almost every day he must have seen the panoramic view of the famous Madras beach from his college—the Bay of Bengal in all its glory with colours ranging from a greenish yellow near the shore to an intense blue in the distance.

That he was puzzled by the problem of the colour of the sea is clear from the fact that even on his onward journey he had prepared himself well for experimental observations; for he carried in his pocket nicol prisms, a small telescope to which polarisers and analysers could be attached, a slit and even a diffraction grating.

He wrote two papers on board the ship (s.s. Narkunda) on which he returned to India. The one entitled 'The Colour of the Sea' questioned the validity of the view expressed by Lord Rayleigh that the much admired dark blue of the deep sea was—simply the blue of the sky seen by reflection. While on the Mediterranean and the Red seas Raman quenched the surface reflection by a nicol prism and noticed that the colour of the sea was by no means impoverished by this, but actually improved wonderfully. Using the diffraction grating he showed that the maximum spectral intensity differed in the case of the blue sky and that of the blue sea. He suggested that the local fluctuations in density postulated by Einstein and Smoluchowski should not only explain the scattering of light in liquids but also in solids. He proceeded to make measurements on water and crystalline quartz and showed that this was indeed true. He also examined amorphous substances and proposed that the intense scattering of light by these was due to the *permanent* local fluctuations in density similar to those that arise transitorily in liquids. He climbed the summit of Mount Doddabetta in the Nilgiris (to avoid the dust haze), measured the depolarization of light scattered by the sky and ascribed the residual depolarization to molecular anisotropy.

To clarify his own views he wrote a monograph on the *Molecular Diffraction of Light*. He dedicated it to the enlightened Vice-Chancellor of the Calcutta University Sir Asutosh Mukherjee who had made Raman a full-time scientist by offering him the Palit Chair of Physics. The monograph bristles with ideas, but it is obviously hastily written. It is said that it was written, printed and published during the course of seven weeks. In this volume Raman examines the molecular scattering of light by gases, by the atmosphere, and by liquids. The colour of the sea, the albedo of the earth, scattering of light in crystals and in amorphous solids occupy his attention. He deals with the problem of the Doppler effect in molecular scattering—a topic to which he was to come back to in later years.

In the concluding chapter of this essay entitled 'The Scattering of Light and the Quantum Theory' he tries to understand the mechanism of light scattering. By imagining molecular scattering to take place in a black body enclosure Raman convinced himself that Rayleigh scattering must also occur in a discontinuous manner.

He then points out that if the process of scattering could be regarded as a collision between a light quantum localized in space and an individual molecule,

the observed laws of light scattering would be different from that anticipated on the classical principles of an electromagnetic theory of light. He makes reference to cases in which the classical wave theory seems to fail to explain the facts relating to molecular scattering in a satisfactory manner. In fact Raman was convinced that accurate measurements on the scattered light would bring out these contradictions. The review of the monograph in *Nature* (1922) 110 505 mentions: "Prof. Raman makes the interesting suggestion that the failure may mean that the continuous wave theory of light does not strictly represent the facts and that we may perhaps find experimental support for the Einstein conception that light itself consists of quantum units".

To the historian of science, there is one paragraph in this monograph which is of interest

"The belief in the validity of Newtonian dynamics applied to the ultimate particles of matter has, however, received a rude shock from the success of the quantum theory as applied to the theory of specific heats, and there seems no particular reason why we should necessarily cling to Newtonian dynamics, in constructing the mathematical framework of field-equations which form the kernel of Maxwell's theory. Rather, to be consistent, it is necessary that the field-equations should be modified so as to introduce the concept of the quantum of action. In other words, the electrical and magnetic circuits should be conceived not as continuously distributed in the field but as discrete units each representing a quantum of action, and possessing an independent existence."

These words were written in early 1922. The programme suggested here of quantizing the electromagnetic field was commenced by Dirac in 1928.

Students, many of whom were university teachers (who came as vacation workers) were put on problems connected with the scattering of light. In 1923 the study of the scattering of light in water was taken up by K R Ramanathan. Sunlight was focussed on the liquid contained in a flask and the scattered light was seen as a track in the transverse direction. Even from the beginning, Raman's intuition seems to have told him to look for a change in colour in scattering. By the proper use of a system of complementary filters a 'weak fluorescence' was detected in the scattered track. This was attributed to impurities in the liquid. 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" (which had just been discovered that year). At the insistence of Raman, the liquid was purified again and again but the effect persisted. The "weak fluorescence" also showed polarization effects but Raman did not, for some strange reason, follow up this important clue as he did later in 1928. In 1924 the "weak fluorescence" was again observed by K S Krishnan and in 1925 Raman asked S Venkateswaran to try to obtain a spectrum of this "weak fluorescence" but no spectrum could be recorded. Raman saw this "feeble fluorescence" as a *disturbing effect* superposed on the classical scattering of light. It is interesting that Compton too attributed the softening of X-rays by scattering to what he

called a "general fluorescent radiation" almost in the manner Raman labelled the phenomenon he observed as "a special type of feeble fluorescence". Because of the close analogy with the Compton effect Raman became interested in X-ray scattering again.

Raman (along with Ramanathan) had broken new ground in the field of X-ray scattering in liquids in 1923. He showed that scattering at very low angles was governed by the Einstein-Smoluchowski fluctuations. For explaining the scattering at larger angles the discrete structure of the medium must be taken into account. For this the distribution of matter in the fluid must be analysed into a continuous "structural spectrum" which has its peak of intensity at a wavelength equal to the mean distance between the neighbouring molecules. Raman once said, "We were so preoccupied with light scattering that we did not apply the idea of Fourier transforms to X-ray scattering of liquids although we were so close to it". This was done later in 1927 by Zernicke and Prins.

Raman attempted to understand the Compton effect from the point of view of the classical wave theory. In this process he derived what is now known as the Raman-Compton formula. It was then that the true nature of the "feeble fluorescence" phenomenon became evident to him. The Compton effect could be considered as due to a kind of "fluctuation" in the state of the scattering atom in the field of the radiation. If much milder fluctuations were possible they should give rise to a change in wavelength in the light scattered by the molecule. He was more convinced than ever that the "weak fluorescence" phenomenon was the optical analogue of the Compton effect.

So he pressed on with the experimental study of this phenomenon. S Venkateswaran, a part time worker in his laboratory succeeded in purifying many organic liquids by slow distillation *in vacuo* and observed a greenish blue track in pure glycerine and the fluorescence was *strongly polarized*. This clearly indicated to Raman that the phenomenon could not be the conventional fluorescence—a point of view he had always taken and for which he was seeking proof. Venkateswaran was a part-time worker who could only work after working hours and on holidays. Raman wanted some one to use the sunlight available all through the day, particularly as he himself had lecturing commitments at the University. And so he persuaded K S Krishnan, the best student he had at that time, to get on to these experiments. With K S Krishnan, Raman observed that all the pure organic liquids available in the laboratory showed this "feeble fluorescence" and he was convinced that this was the modified scattering of altered wavelength corresponding to his "milder fluctuations" in the state of the scattering molecule and in fact due to the Kramers-Heisenberg process. The real discovery of the Raman Effect took place on the 28th of February 1928 when Raman pointed a direct vision spectroscope on to the scattered track and saw that the scattered light contained not only the incident colour but at least one another, separated by a dark space.

Filtered sunlight, which till then had been used as the incident light, was

replaced by a quartz mercury arc and sharp modified Raman lines were recorded. The shift in the frequencies were identified with some of the characteristic infra-red frequencies of the molecule. Not only the degradation but the enhancement of the frequency of the scattered radiations was also observed. Scores of papers were published by his students on Raman scattering. Before long many laboratories round the world also took up the study of the Raman effect particularly in simpler molecules. But in Raman's laboratory the accent was on the study of more fundamental problems connected with the physics of the solid and liquid states.

This volume also includes the texts of (a) the lecture entitled "The New Radiation" delivered by Raman to the South Indian Science Association at Bangalore on the 16th of March 1928, where he first announced the discovery to a scientific audience, (b) the lecture at the Bristol meeting of the Faraday Society in the fall of 1929 and (c) the Nobel lecture, "The Molecular Scattering of Light", delivered by him at Stockholm on the 11th of December 1930.

Even in their earliest photographs, Raman and Krishnan noticed an asymmetric nebulosity accompanying the spectral line of the incident radiation when scattered by liquids. This they suggested was the effect of those collisions of the incident light quanta with molecules which result in a change of their rotational state. We include in this volume four later papers by Raman and Bhagavantam, on the experimental and theoretical investigations of the wings of the Rayleigh line. They found that, even on increasing the spectral resolution as far as possible, the depolarisation ratio of the central line to the entire Rayleigh line did not fall to the value of one fourth predicted by the Kramers-Heisenberg formula. The authors were of course aware that stray light, instrumental polarization, imperfect spectral resolution would all tend to increase the measured depolarization of the central component. Nevertheless, Raman and Bhagavantam attributed the discrepancy to a new effect arising from the spin of the photon which (they felt) was not included in the semi-classical radiation theory.

However, we now know that the search for an effect lying entirely outside the province of the semi-classical theory did not end till the late 1940's when the Lamb shift and the deviation of the electron  $g$ -factor from 2 were discovered.

Raman's interest in optical anisotropy led him on to study magnetic anisotropy, and then to the magnetic properties of molecules. He was amongst the earliest to explain the anomalous diamagnetic susceptibility in graphite and the high diamagnetic anisotropy of aromatic organic compounds as due to electron orbits of large area including several atoms within their radius. The lecture at the Physical Society, London summarises much of the work done in Calcutta by Raman's school on magnetism and magnetic properties.

The Doppler effect in molecular scattering intrigued Raman even in 1919. He was attracted by the theory of Brillouin that the medium which scatters radiation can be treated as a continuum filled with moving high frequency sound waves of various wavelengths which reflect the light rays in the same manner a moving

crystal would give Bragg reflections of X-rays. Raman showed that (as in Compton scattering) Brillouin scattering can only take place when both the energy and the momentum equations are satisfied. Even in the monograph of 1922 Raman had suggested an experimental technique for studying the Doppler effect in light scattering. Using a similar set-up with a Fabry-Perot etalon, the Brillouin scattering was observed in many liquids, and Raman discussed the paradox of the appearance of the central component. The velocities of the "hypersonic" waves in these liquids were determined. Perhaps the most exciting result obtained by Raman and his collaborators in the field is that viscous liquids at these high frequencies behave like amorphous solids capable of sustaining both longitudinal and transverse waves.

His studies in Brillouin scattering made Raman reconsider the thermodynamic theory of light scattering. Einstein considered the density fluctuations to be static and isothermal while in the theory of Brillouin they are considered to be dynamic stratification of sound waves and therefore presumably adiabatic in character. To test this, the adiabatic piezo-optic coefficients of some common liquids were measured. Using these experimental values and assuming the density fluctuations to be adiabatic in character, the intensity of scattering was calculated. The observed intensities were found to support the adiabatic hypothesis.

Raman (together with Nedungadi) published a beautiful paper on 11 December 1939 on the alpha-beta transformation of quartz. As the temperature is raised it was noticed that  $220\text{ cm}^{-1}$  line in the Raman spectrum behaves in an exceptional way, spreading out greatly towards the exciting line and becoming a weak diffuse band as the transition temperature is approached. On the other hand the other intense lines having both larger and smaller frequency shifts continue to be easily visible, though appreciably broadened and displaced. Raman conjectured that "the binding-forces which determine the frequency of the corresponding mode of vibration of the crystal lattices diminish rapidly with rising temperature". He inferred that "the increasing excitation of this particular mode of vibration with rising temperature and the deformations of the atomic arrangement resulting therefrom are in a special measure responsible for the remarkable changes in the properties of the crystals already mentioned, as well as for inducing the transformation from the alpha to the beta form". Almost twenty years later this effect was rediscovered and is now known as the "soft mode".

We have contented ourselves, in this introduction, with making a few historical comments, and now leave the vigour and lucidity of Raman's papers to speak for themselves.