# Raman Effect: History of the Discovery

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The paper gives a historical account of the discovery of the Raman Effect, starting from Raman's voyage to Europe through the Mediterranean Sea in the summer of 1921 to the observation of modified lines in benzene when illuminated by the 435.8 nm radiations of mercury, through a direct vision spectroscope, on 28 February 1928. The important contributions of Raman and his students during the period which form the progressive stages in the road to discovery have been briefly touched upon. The work of the French group, the Russian group and the theoretical work of Smekal are narrated in sequence.

Although numerous short sketches have appeared on the history of the discovery of the scattering of modified radiation, known as the Raman Effect, during the Golden Jubilee Year of 1978, none of them appears to be either complete or objective. The present author was engaged in the preparation of the bibliography on the Raman effect and during this process had occasion to go through all the original papers. It was considered desirable to present a comprehensive, chronological and objective account of the early work of Raman and his associates in India on the scattering of light which led to the discovery and all other connected work reported in the literature during the same period in other countries.

Professor Joseph Larmor's paper[1] entitled 'Molecular Scattering of Radiation' appears to be the starting point for Raman's interest on the subject of scattering. Unlike most others, Raman was not initiated into research under the guidance of any senior scientist, either Indian or otherwise. His only inspiration was the published work of the Rayleighs (father and son) and his own ever-enquiring mind and intuitive perception of the deepest secrets of nature. His first paper[2] on the Doppler effect in molecular scattering appeared in the same year. Two years later he published a paper on the scattering of light by sulphur suspensions.[3] In 1921 Professor Raman was chosen as a delegate to the Universities Congress held that year at Oxford. This was a turning point in his scientific career, as the foundation to the discovery of the Raman effect was unconsciously laid during his voyage to Europe. While passing through the Mediterranean Sea, Raman was struck by the deep blue opalescence of the seawater. Lord Rayleigh, who had so successfully explained the blue colour of the sky as due to the scattering of sunlight by molecules constituting the gaseous atmosphere, stated as follows while discussing the colour of the sea: 'The much admired dark blue of the deep sea has nothing to do with the colour of water, but is simply the blue of the sky seen by reflection'.[4] On board the SS *Narkunda*, Raman carried out a simple experiment of viewing the surface of the water at the Brewsterian angle through a suitably oriented Nicol prism, thus quenching the reflection, if any, of the sky. In the deeper waters of the Mediterranean and Red Seas, the blue colour, far from being impoverished by suppression of the sky reflection, was wonderfully improved indicating thereby that the blue colour of the deep sea was a distinct phenomenon in itself. Raman later explained this as arising from the scattering of light by water molecules.[5] Immediately after his return, Raman started a series of experimental and theoretical studies on the scattering of light in transparent media of all kinds in the Indian Association for the Cultivation of Science at 210, Bow Bazaar Street, Calcutta, where he was Honorary Director and Professor. These studies were largely inspired by a desire to understand and explain fully such natural optical phenomena as the blue light of the sky, the dark blue colour of the deep sea and the delicate opalescence of ice in glaciers. To clarify his own ideas Raman also wrote in 1922 a monograph[6] entitled *Molecular Diffraction of Light*. In this monograph he considered in detail how energy could be transferred between light quanta and molecules. He had, however, a hunch that the quantum nature of light should reveal itself in scattering. It is interesting to note that the Compton effect was discovered a year later.

During the next six years Professor Raman, along with his brilliant students K. R. Ramanathan, K. S. Krishnan, L. A. Ramdas, A. S. Ganesan, K. Seshagiri Rao, S. Venkateswaran, J. C. Kameswara Rao, I. Ramakrishna Rao and S. Ramachandra Rao, established the various laws of molecular scattering in diverse media with particular reference to the structure of molecules, the state of matter, pressure and temperature and the phase transition at the critical temperature. During this period nearly 56 papers were published on these subjects in *Proceedings of the Royal Society, Philosophical Magazine, Nature, Physical Review, Proceedings of the Indian Association for the Cultivation of Science* etc.

While studying the scattering of light in purified water and alcohols in April 1923, K. R. Ramanathan, the oldest and the most distinguished of Raman's students, came across a new and entirely unexpected phenomenon. When sunlight filtered through a violet glass passed through the liquid, the scattered rays emerging from the track of the incident beam through the substance contained certain rays not present in the incident beam. The observations were made with a system of complementary filters. This was clear proof of a real transformation of light from a violet into a green ray in the process of scattering. Without understanding

its real significance Ramanathan termed the phenomenon 'weak fluorescence'.[7] The most careful purification of the liquid failed to eliminate the weak fluorescence, indicating thereby that the new phenomenon was a characteristic property of the substance. Two years later K. S. Krishnan, another student of Professor Raman, observed the same phenomenon while studying the scattering of light in 65 different carefully purified liquids.[8] He also made another important observation that the new radiation was partially polarized unlike ordinary fluorescence which is unpolarized. The technique used for observing the new phenomenon made use of a beam of sunlight, a condensing lens of large aperture, a flask containing the liquid and a set of complementary filters, i.e. a violet-blue filter in the path of the incident beam and a greenish-yellow filter in the path of the transversely scattered light. S. Venkateswaran continued the work of K. S. Krishnan in the summer of 1925. He attempted to photograph the spectrum of the scattered light using sunlight passed through coloured filters, but was unable to report any decisive results. Raman, under whose guidance all this work was conducted, was not at all satisfied with the explanation that the feeble residual scattering was due to fluorescence appearing in the spectrum in a region different from that of the incident beam. He suspected it was an entirely new type of secondary radiation quite distinct from the usual fluorescence which was normally of high intensity and unpolarized. He did not wish at this stage to commit this idea to publication as the effect was seen only with liquids at that time. Also, he was not aware of any theory which completely accounted for the experimental results.

Towards the end of 1927 Raman himself observed the phenomenon in optical glasses and in a crystal of ice.[9] In January 1928, S. Venkateswaran, working under Raman, made a very remarkable observation that the colour of sunlight (filtered through Corning glass G 586) scattered by pure dry glycerine was a brilliant green instead of the usual blue, and was found to be strongly polarized. Tests were made with a series of filters transmitting narrow regions of the solar spectrum placed in the path of the incident beam, which showed that in every case the colour of the scattered light was different from that of the incident light and was displaced from its position towards the red. The real significance of these observations became clear to Raman when he was occupied with the development of the classical theory of the Compton effect during that period. He immediately conceived the idea that the phenomenon which had puzzled him ever since 1923 was in fact the optical analogue of the Compton effect.

Raman decided to find a satisfactory solution to the problem and asked his student K. S. Krishnan to stop his work on theoretical problems and to start more intensive experimental studies on the anomalous scattering in liquids and vapours. Raman himself took an active part in setting up the experiment and making observations. They used a powerful beam of sunlight focused by an 18 cm telescope objective lens combined with a short focus lens. This was passed through a blue-violet filter and then through the liquid contained in a sealed flask purified by repeated double distillation *in vacuo*. When a second filter of green glass which was complementary in

colour to the blue-violet filter was placed in the path of the incident beam, no track of the scattered light was visible in the transverse direction. When the same was placed between the bulb and the observer, the opalescent track within the liquid continued to be visible, though less brightly. Nearly 80 different aromatic, aliphatic and inorganic liquids were examined and the effect was seen in all cases indicating thereby the universal character of the phenomenon. It was shown to be distinctly different from the usual fluorescence because of its feebleness and strong polarization which was nearly the same as that of the unmodified scattered light. As K. S. Krishnan noted in his diary, on the night of 7 February Professor Raman rushed to Krishnan's residence to tell him that their observations made that morning were related to the Kramers–Heisenberg process for which they had been looking all these years. They christened the effect 'modified scattering'. Two days later, Raman and Krishnan detected the new radiation in vapours of ether and amylene. They soon realized that they were dealing with a new phenomenon of a fundamental character and communicated their conclusions by cable to *Nature* on 16 February 1928 in a letter entitled 'A New Type of Secondary Radiation', which was published on 31 March 1928.[10] In this note they repeated the arguments used in Raman's classical derivation of the Compton effect and suggested that the modified radiation could arise from the fluctuations of the molecules from the normal state. Raman and Krishnan succeeded in detecting the new radiation and observing its partial polarization in a number of organic vapours and also in the gases $CO_2$ and $N_2O$. The modified scattering was easily detected in vapours such as ether and pentane at higher temperature and consequent higher vapour pressure. Its polarization was quite strong and was comparable with the polarization of ordinary scattering.

While continuing further studies on the subject, Raman and Krishnan proceeded to examine the influence of the wavelength of the incident light on the phenomenon, in the afternoon of 28 February 1928. Using a narrower range of transmission of the incident radiation brought about by a combination of blue-violet filter and a piece of uranium glass, they examined the scattered track through a direct vision spectroscope and found to their great surprise that the modified scattering was separated from the scattering corresponding to the incident unmodified light by a dark space. Further work carried out on that day is described by Raman in an extract from his address on 'New Radiation' given to the South Indian Science Association at Bangalore on 16 March 1928:[11]

This encouraged me to take up observations with a monochromatic source of light. A quartz mercury lamp with a filter which completely cuts out all the visible lines of longer wavelength than the indigo line 4358 AU was found to be very effective. When the light from such a lamp was passed through the bulb containing a dust-free liquid, and the spectrum of the scattered light was observed through a direct vision spectroscope, it was found to exhibit two or more sharp bright lines in the blue and green regions of the spectrum. These lines are not present in the spectrum of the incident light or in the unfiltered light of the mercury arc and are thus manufactured by the molecules of the liquid.

There has, as yet, not been sufficient time for photographing the spectra from a large number of liquids, or even for measuring the photographs already obtained. Visual observations have, however, been made with a large number of liquids. There is an astonishing similarity between the spectra obtained with different liquids. When only the 4358 lines was used, most liquids showed in the spectrum of the scattered light, a bright line in the blue–green region of the spectrum (about 5000 AU), whose position was practically the same for chemically similar liquids such as pentane, hexane and octane for instance. There was, however, a recognizable difference in the position of the modified line when other liquids such as benzene or water were used. When the 4047 line of the mercury arc was let in by removing the quinine sulphate solution, a second modified line in the blue region of the spectrum was seen with most liquids . . . .

Krishnan and Venkateswaran were with Raman at the time of the discovery and thus had the distinction of knowing about the discovery first. Most of the other scholars in the laboratory subsequently had the opportunity of seeing this phenomenon on that day. By this observation, the discovery of a new effect which was later christened the 'Raman effect' was complete. The line spectrum of the new radiation was first seen on 28 February 1928 and the same was given publicity through the Associated Press of India on the following day. The above results were published by Raman in a letter to *Nature* sent on 8 March 1928 which appeared on 21 April 1928.[12] It is said that Sir Richard Gregory, who was then Editor of *Nature*, took the responsibility of publishing this note although it was rejected by the referee. The scattered spectra in the case of benzene and toluene were photographed and measured and new lines were observed on either side of the exciting line. The shift in frequency of each new line from the incident one was identified with the change in the energy of the vibrational state of the molecule.

The first detailed announcement of discovery before a scientific audience with a description of the principal features of the new effect was made by Raman under the title 'A New Radiation' on 16 March 1928, while inaugurating the South Indian Science Association at Bangalore. The full text of the lecture was subsequently communicated and published as a special number of the *Indian Journal of Physics* on 31 March 1928, along with photographs of the scattered spectrum of benzene.[11]

In this historic paper the following characteristics of the new effect were clearly stated. Each incident radiation produced its own set of modified lines which were markedly polarized. Normally, modified lines were of lower frequency compared to that of the incident radiation. In some cases modified lines of increased frequency but of less intensity were also observed. In the spectrum of benzene which was reproduced in the paper both sets of lines are visible. The frequency differences between the incident and scattered radiations represented the absorption frequencies of the medium which normally lie in the IR region. The effect was observed in a large number of liquids, gases and vapours and also in a crystal of ice and in optical glasses, thereby indicating its universality. In the case of ice, the lines were sharp and approximately in the same positions as in pure water. In optical glasses the scattered spectrum consisted of diffuse bands. In the case of liquids there was a continuous spectrum or wing accompanying the modified line.

The wing was found to be very prominent in the case of carbon disulfide and was depolarized to a great extent. In the language of quantum theory, part of the incident energy was absorbed by the molecule for raising it to an excited state and the balance was scattered. A possible relationship between the new phenomenon and Kramers's and Heisenberg's quantum theory of dispersion was also indicated. These observations of Raman established and emphasized the fundamental character of the new effect. The spectra were recorded with a Hilger Baby Quartz Spectrograph of very low dispersion and hence the modified lines for chemically similar substances appeared with nearly the same shifts.

Professor Raman concluded this epoch-making paper with the following words:

> We are only on the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out . . . . I owe much to the valuable cooperation in this research of Mr K. S. Krishnan and the assistance of Mr Venkateswaran and other workers in the laboratory.

The *Indian Journal of Physics* was started by Raman in 1927 and did not have much of a circulation in 1928. In order to give maximum publicity to his discovery Raman obtained 2000 reprints of his historic paper after publication in the *Indian Journal of Physics* and posted it to all physicists of importance including those working on the scattering of light in France, Germany, Russia, Canada and the USA, and to scientific institutions all over the world, thus ensuring Raman's priority to the discovery, for once announced many other scientists began to work on it. In a note entitled 'The Optical Analogue of the Compton effect' sent to *Nature* on March 22 and published on 5 May 1928,[13] Raman and Krishnan reproduced the scattered spectrum of toluene taken with a mercury arc showing the modified lines very clearly, the diminution in frequency being of the same order of magnitude as the frequency of the molecular IR absorption and the shift being different for different molecules.

Immediately following the announcement, Raman and Krishnan carried out further experiments and established the following:[14]

1. Each substance displays a characteristic Raman spectrum which can serve to identify it unambiguously.
2. For a given substance the difference in frequency between the Raman lines and the exciting line is constant and independent of the frequency of the incident light. It is in this crucial respect that the Raman effect is distinguished from fluorescence for which the frequency and not the frequency shift is independent of the frequency of the exciting line.
3. The new lines are sharp and often occur in pairs uniformly separated in frequency units from the exciting line. Those appearing on the lower frequency or higher wavelength side are called 'Stokes' lines and are generally more intense than their counterparts on the higher frequency side called 'anti-Stokes' lines. (Professor R. W. Wood was responsible for the terms Stokes and anti-Stokes.)

4. The observed range of frequency shifts in any Raman spectrum extends from a few $cm^{-1}$ to about $3800 \, cm^{-1}$.

5. The frequency shifts observed in the Raman effect are the frequencies of oscillation of the chemically bonded atoms of the molecule, which in turn depend on the geometry of the molecule and the forces binding the atoms together. They correspond to the frequencies of absorption of the molecule in the IR region of the spectrum.

6. The intensity and the depolarization ratio are different for different Raman lines.

7. According to the quantum theory of radiation, exchange of energy can take place between the molecule and the incident light quantum as follows:

$$molecule + h\nu_1 \leftrightarrows molecule^* + h\nu_2$$
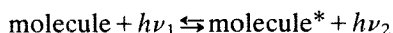
The exchange can take place in either direction. From left to right the molecule is receiving energy and goes over to the excited state indicated by the asterisk, and $\nu_2$, the frequency of the Raman line, is less than the frequency $\nu_1$ of the incident radiation. From right to left the molecule, already in an excited state, is giving up energy and $\nu_1$, the frequency of the Raman line, will be more than $\nu_2$, the frequency of the incident light. In the former case one observes Stokes Raman lines, while in the latter case one observes the anti-Stokes Raman lines. Thus, Raman was the first person to demonstrate that the energy of a photon can undergo partial transformation within matter. The ratio of the intensities of the corresponding Stokes and anti-Stokes Raman lines is proportional to the ratio of the populations of states in terms of the Boltzmann distribution. Thus, the processes giving rise to the Raman effect are a striking demonstration of the corpuscular aspect of radiation.

8. The Raman scattering is in general much feebler than Rayleigh scattering. The intensity of Raman scattering, like Rayleigh scattering, increases as the fourth power of the incident frequency except in the neighbourhood of an absorption band.

9. The effect is universal in character as it was observed in the widest variety of physical conditions, namely gas, vapour, liquid, crystal and amorphous solids and in many different compounds.

In short, 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 tool for the solution of a wide range of problems in various branches of science and technology. It is these reasons which constitute the principal significance of Raman's discovery.

It is interesting to point out that, at almost the same time as Raman was carrying out his crucial experiments, work on similar lines was going on in Paris and Moscow. On 14 November 1927 Brillouin presented a paper by Rocard entitled 'On the role of atomic vibrations of molecules in the phenomenon of light scattering'[15] to the French Academy of Sciences. He had investigated theoretically the effect of an oscillating dipole moment on the intensity of scattering. He pointed out that there should be an additional term in the expression for the scattering intensity, which would be appreciable only in the case of molecules with high anisotropy. In continuation of this work, Rocard had come to the conclusion that this additional scattering should have a spectral structure different from that of the incident light. He delayed the publication of this theoretical result pending experimental verification. Since, unlike the Indian group who initiated the work with liquids which were good scatterers, the French group, including Cabannes and Rocard, was working with gases which were poor scatterers, experimental verification of Rocard's theoretical prediction was delayed. In the meantime Raman's two notes in $Nature$[10,12] were seen by Rocard and the reprint of his address at Bangalore[11] was duly received by him. This immediately prompted him to publish his theoretical results. His paper[16] entitled 'Les nouvelles radiations diffusies' was presented before the French Academy on 23 April 1928, again by Brillouin. In this paper Rocard interpreted the frequency-shifted scattered light as an optical modulation caused by the various vibrational frequencies of the electric dipole moment of the oscillating molecules. If $\nu_I$ is the frequency of the incident light wave and $\nu_R$ is one of the characteristic frequencies of oscillation of the molecules, the scattered light should contain radiations of frequencies $\nu_I + \nu_R$ and $\nu_I - \nu_R$. Raman's observation of a strong Raman line at about 500 nm in pentane, octane etc. when scattered by the 435.8 nm mercury line was accounted for by Rocard as arising from the modulation of the C—H stretching vibration in saturated hydrocarbons having a wavelength of 3.4 $\mu$m or a frequency of $\sim 3000 \, cm^{-1}$. In benzene the corresponding C—H line was at about 505.3 nm and in water the modified line arising from O—H vibrations was at 508.7 nm.

A week later, on 30 April 1928, Fabry presented a paper[17] by Cabannes to the French Academy of Sciences. This paper was prepared after seeing the reprint of Raman's paper.[11] Cabannes discussed the effect of optical beating in the case of anisotropic molecules which were in rotation and vibration. Cabannes had been trying to observe such beatings in gases since 1924 without success. His main drawback was that he worked with gases which are essentially of very low scattering power under normal conditions. One important point in Cabannes' favour was that he had recognized the condition for the existence of pure rotational lines, namely the finite optical anisotropy of the molecules. Cabannes and his students were the first to make a detailed study of Raman wings in liquids and its relationship to molecular anisotropy.

During the same period, Landsberg, who was working in the Institute for Theoretical Physics in Moscow under the guidance of Mandelstam, was carrying out investigations on the scattering of light in solid bodies using a Point-O-lite lamp as a continuous source of illumination. He found that the intensity of scattering in crystalline quartz was directly proportional to absolute temperature. He communicated two papers on the subject to $Zeitschrift \, für \, Physik$ on 10 May and 1 August 1927. They were published on 12 July[18] and 18 October 1927[19] respectively. While looking for a change of wavelength in scattering on the basis of Debye's theory of specific heat, Landsberg and Mandelstam reported on 6 May 1928 the independent observation of a modified line in the scattered spectrum of a crystal of quartz when excited by the radiations from a quartz mercury arc.

Their letter, 'Zuschrift' was published in *Naturwissen-schaften* on 13 July.[20] A similar communication was also sent to the *Russian Journal of Physical Chemistry* on 10 May.[21] The frequency shifts arising from Debye's elastic waves should be much less than a wavenumber and could not therefore be resolved by an ordinary spectrograph. The observed frequency shift was of an entirely different order of magnitude and they explained its appearance in the following words: 'When light is scattered by quartz, some of the infra-red frequencies of the crystal can be excited at the expense of the energy of the scattered light and the scattered quanta; hence their frequencies decrease by the amount of the respective infra-red quanta'. Although their letter was communicated well over two months after the publication of Raman's detailed paper,[11] a reprint of which should have been sent to them also, there is no reference to this paper. They did, however, refer to Raman's two notes in *Nature*[10,12] with the following remark; 'Whether and how far the phenomenon observed by us is related to that described by Raman in brief, we are not able to decide at the moment as his description is too terse'. The use of monochromatic radiation from a mercury arc for excitation was indicated in Raman's second note to *Nature*[12] which they had seen. This might have given them the necessary clue. Rocard and Cabannes had received the reprint of Raman's detailed paper[11] in April and it was most likely that the Russian physicists also would have received their reprints either before or immediately after sending their *Zuschrift.* They had, however, introduced some additions concerning the observations with calcite at the proof stage. Their detailed paper describing the observations with quartz and calcite was sent on 12 July 1928 and published in *Zeitschrift fur Physik.*[22] Even in this paper they gave only a passing reference to Raman's detailed paper, and failed to give due recognition to Raman's discovery. Isolated observation in one or two substances like the one reported by Landsberg and Mandelstam certainly failed to demonstrate the fundamental character and significance of the phenomenon unlike the wide-ranging observations of Raman and Krishnan in gases, liquids and solids. In spite of this fact, the Russian scientists refused to use the phrase 'Raman effect' for quite a long time. Most of the papers published from Russia until a few years ago still used the phrase 'combination scattering'.

Let us now pass on to an interesting theoretical publication which followed immediately after the discovery of the Compton effect. In 1923 an Austrian physicist, A. Smekal, published a short note in *Naturwissenschaften*[23] on the quantum theory of dispersion. While discussing the interaction of radiation with matter quantum mechanically, he indicated the possibility of change in the energy of the radiation during such interaction. He pointed out that the energy of the incident radiation might be lowered by an amount equal to the energy difference between the normal and excited energy states of the system. In the process of scattering, therefore, the frequency of the incident radiation would decrease. Smekal's paper was often quoted as indicating a prediction of the Raman effect.† It is interesting to note that

† The Austrian scientist, K. W. F. Kohlrausch, published a book entitled *Der Smekal-Raman-Effekt* in 1931 and a supplementary volume with the same title in 1939.

letters (*Zuschrift*) appearing in *Naturwissenschaften* were never abstracted in *Science Abstracts A* in the 1920s and as such Smekal's paper did not appear to have been noticed by any experimental physicist working in the field of light scattering, including the group working under Raman. However, Kramers and Heisenberg took notice of Smekal's idea and further developed it in their treatment of the quantum theory of scattering[24] in 1925. They showed how the origin of a modified scattered radiation could be understood classically and later derived the quantum theoretical scattering formula by combining the correspondence principle with the classical theory of electromagnetic radiation. Their contribution is important because it formed the origin of modern quantum mechanics. In 1927 Dirac[25] developed the quantum mechanical scattering theory from which he derived the formulae for the intensity of scattered radiation. Although the appearance of modified lines were implicit in the dispersion formula the existence of the effect remained obscure and their significance was not understood until they were discovered quite independently by Raman in 1928, based entirely on laboratory observations and deductions. Thus, although the theory of the Raman effect was fully established nearly a year before its experimental discovery, it is only after Raman's discovery that the full implications of the dispersion theory came to be recognized.[26] An important observation later derived from Smekal's note is the fact that the Raman effect corresponded to a transition between two discrete levels and all elementary excitations which are associated with quantized excitation energies could give rise to a Raman effect. This idea became significant when Raman effects by phonons, polaritons, magnons, excitons, Landau levels etc. in solids were experimentally demonstrated.

In a note entitled 'On the Theory of Raman Effect' published in *Naturwissenschaften* of 24 August 1928, Max Born[27] said that Raman's discovery had been predicted by quantum mechanics in all its entirety and could be thought of as proof for the same.

L. A. Ramdas,[28] working in Raman's laboratory, was the first to photograph the scattered spectrum successfully from ether vapour. The Raman lines appeared in approximately the same positions as in the liquid. While communicating his results to *Nature* on 29 May 1928, Ramdas called the effect the 'Raman effect'.

The importance of Raman's discovery was immediately recognized by the authorities in optics and scattering, namely Rocard, Fabry, Cabannes and Daure of France, J. C. McLennan and W. H. Martin of Canada, P. Pringsheim of Germany, A. E. Ruark and R. W. Wood of the USA and A. Carrelli of Italy. They confirmed Raman's findings. In a review paper entitled 'The Raman Effect, a New Radiation Effect Discovered by C. V. Raman', Pringsheim[29] gave a detailed report on the new scattering effect covering its various aspects. He compared Raman scattering with the Tyndall effect, fluorescence and the Compton effect and concluded that the effect discovered by Raman was an entirely new phenomenon and should therefore be designated as the 'Raman Effect' and the spectrum of new lines as the Raman spectrum. He further showed how a study of the Raman spectrum enabled one to record the characteristic molecular frequencies more conveniently in the visible region. He concluded the paper with the

following words: 'With the increasing number of new researchers coming into this field, new problems will show up in increasing proportions. One can state without doubt that through his discovery Raman has opened up a big and completely new field of spectroscopy'. R. W. Wood[30] sent a cable to *Nature* in August, the first and last sentences of which are quoted below:

> Professor Raman's brilliant and surprising discovery that transparent substances illuminated by very intense monochromatic light scatter radiations of modified wavelength and that frequency difference between the emitted radiation and one exciting the medium is identical with frequency of the infra-red absorption bands, opens up wholly new field of study of molecular structure. I have verified this discovery in every particular . . . it appears to be that this very beautiful discovery which resulted from Raman's long and patient study of phenomena of light scattering is one of the most convincing proofs of quantum theory of light which we have at present time.

In a detailed paper communicated to *Philosophical Magazine* on 8 September 1928, Wood[31] described a new type of cell for holding any liquid for Raman spectroscopic studies. This container is now commonly known as 'Wood's tube'. He also reported the results obtained with six liquids, quartz and calcite, but obtained negative results with rock salt.

The apparatus used by Raman for the discovery consisted of a mirror for deflecting sunlight, a condensing lens, a pair of complementary glass filters, a flask containing benzene and a pocket spectroscope, the total cost not exceeding $25. It could also be inferred from the above account that the discovery was not the result of an accident, but was the culmination of seven years of systematic and sustained work carried out with devotion by Raman and his band of students. The achievement is all the more creditable when one considers the fact that scientific research in India was not liberally supported by the Government as it is today.

The history of the discovery of the Raman effect teaches us many lessons. Firstly, hardly any discovery appears immediately in its clear and final form. The truth is approached step by step. Secondly, it is the calibre of the scientist that matters for scientific progress and not the provision of very costly equipment. Thirdly, sustained effort in a single field only will ultimately lead to success and fame. Fourthly, great discoveries always appear incredibly simple, but only after some devoted person has made the discovery.

Professor Raman was awarded the Hughes Medal of the Royal Society of England in 1930 and the Nobel Prize for Physics in the same year for his discovery. While presenting the Hughes Medal, Lord Rutherford of Nelson, then President of the Royal Society, made the following observation: 'Raman effect must rank among the best three or four discoveries in experimental physics of the last decade. It has proved and will prove an instrument of great power in the study of the theory of solids'. This prophecy has been fully vindicated by recent progress in Raman spectroscopy of crystals.

The account of the early history of the effect would not be complete without a reference to an important theoretical contribution made by G. Placzek[32] in 1934.

In this article Placzek had developed the bond-polarizability theory of Raman scattering. Although the quantum mechanical theory of scattering was proposed a year before Raman's discovery, it remained a curiosity for a long time as the numerical calculation of the intensity of scattering required the knowledge of all eigenstates of the scattering systems, i.e. a molecule or a crystal, in order to calculate the first and second derivatives of the molecular polarizability. Quantum chemical methods are not so far developed as to make the calculation of such derivatives easily possible. It is in this context that Placzek's semi-classical bond-polarizability theory became handy for physicists and chemists as a practical proposition.

In order to calculate Raman intensity Placzek considered the nuclei of the molecules as being fixed. He concluded that the polarizability was a function only of the position of the nuclei, and not of their velocity when the following conditions were satisfied. Firstly, the frequency of the exciting light must be far away from all electronic transition frequencies. This conclusion excludes the so-called resonance Raman effect which has come into prominence recently. Secondly, the exciting frequency should be large compared to the nuclear frequency of the electronic ground state. Thirdly, the electronic ground state should not be essentially degenerate.

With these assumptions Placzek derived an expression for the intensity of Raman scattering in terms of the parameters related to the electronic ground state only. The influence of all other states is contained in a term called the polarizability tensor and its derivatives with respect to nuclear coordinates. This tensor is of rank two and is symmetric except for special cases. The main advantage of the polarizability theory was that group theoretical methods could be applied for deriving the selection rules for Raman effect from the symmetry behaviour of the polarizability. On the basis of Placzek's theory all the details of molecular Raman effect could be quantitatively accounted for. His theory is even now finding applications in the derivation of formulae for the hyper, stimulated, inverse and electronic Raman effect and other non-linear phenomena which have come to prominence with the development of high power lasers and tuneable dye lasers.

Immediately following the discovery, the Raman effect began to be used by physicists and chemists alike for solving a wide range of problems, and many important contributions to our knowledge in physics and chemistry were reported in a short span of five years. This upsurge can be attributed to the fact that the data obtained from the Raman effect depend essentially on the structure of the molecules of the scattering substance. It is thus possible to obtain information of great value to physicists and more so to chemists by a single observation of the Raman spectrum instead of a whole series of difficult experiments in the IR region. More than 2500 chemical compounds were studied by the Raman effect during the first decade following its discovery.

The development of lasers nearly two decades ago and their first successful use as the exciter for Raman spectra by Porto and D. L. Wood[33] in 1961 completely revolutionized the practice of Raman spectroscopy. Various new types of excitations in transparent,

coloured or even opaque media have been reported. No other discovery in science has shown such a dramatic rejuvenation and renaissance. Nearly 23 600 original papers were published up to the end of 1978. A complete bibliography has been prepared and will be published in due course. Nobody, including the discoverer, would have ever dreamt about this vista of activity on Raman spectroscopy that we witness today.

## Acknowledgement

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8. K. S. Krishnan, *Philos. Mag.* **50**, 697 (1925).
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17. J. Cabannes, *Compt. Rend.* **186**, 1201 (1928).
18. Gr. Landsberg, *Z. Phys.* **43**, 773 (1927).
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20. Gr. Landsberg and L. Mandelstam, *Naturwissenschaften* **16**, 557 (1928).
21. Gr. Landsberg and L. Mandelstam, *Russ. J. Phys. Chem.* **60**, 335 (1928).
22. Gr. Landsberg and L. Mandelstam, *Z. Phys.* **50**, 769 (1928).
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24. H. A. Kramers and W. Heisenberg, *Z. Phys.* **31**, 681 (1925).
25. P. A. M. Dirac, *Proc. R. Soc. London Ser. A* **114**, 710 (1927).
26. A. Smekal, *Naturwissenschaften* **16**, 612 (1928).
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29. P. Pringsheim, *Naturwissenschaften* **16**, 597 (1928).
30. R. W. Wood, *Nature London* **122**, 349 (1928).
31. R. W. Wood, *Philos Mag.* **6**, 729 (1928).
32. G. Placzek, 'Rayleigh-Streuung und Raman-Effekt in E. Marx.' *Handb. Radiol.* **6**, Part 2, 205 (134).
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## APPENDIX: LIST OF PAPERS ON THE RAMAN EFFECT PUBLISHED IN 1928

(The papers are arranged in the chronological order of the date of communication given within brackets at the end of each paper.)

1. C. V. Raman and K. S. Krishnan, 'A new type of secondary radiation.' *Nature London* **121**, 501, 31 March 1928 (16 February).
2. C. V. Raman, 'A change of wave-length in light scattering.' *Nature London* **121**, 619, 21 April 1928 (8 March).
3. C. V. Raman, 'A new radiation.' *Indian J. Phys.* **2**, 387, 31 March 1928 (16 March).
4. C. V. Raman and K. S. Krishnan, 'Optical analog of the Compton effect'. *Nature London* **121**, 711, 5 May 1928 (22 March).
5. Y. Rocard, 'New diffused radiations.' *Compt. Rend.* **186**, 1107, May 1928 (23 April).
6. J. Cabannes, 'Un nouveau phenomene d'Optique: les battements qui se produisent lorsque des molecules anisotropes en rotation et diffusent de la lumiere visible ou ultraviolette.' *Compt. Rend.* **186**, 1201, May 1928 (30 April).
7. Gr. Landsberg and L. Mandelstam (Univ. Moskau), 'A novel effect of light scattering in crystals.' *Naturwissenschaften* **16**, 557, 13 July 1928 (5 May).
8. C. V. Raman and K. S. Krishnan, 'A new class of spectra due to secondary radiation. Part I.' *Indian J. Phys.* **II**, 399, 5 June 1928 (7 May).
9. Gr. Landsberg and L. Mandelstam, 'Eine neue erscheinung bei der Lichtstreuung.' *Russ. Phys. Chem. Soc.* **60**, 335, July 1928 (10 May).
10. C. V. Raman and K. S. Krishnan, 'The negative absorption of radiation.' *Nature London* **122**, 12, 7 July 1928 (15 May).
11. L. A. Ramdas, 'The Raman effect and the spectrum of the zodiacal light.' *Nature London* **122**, 57, 14 July 1928 (29 May).
12. Y. Rocard, Les Modèles moleculaires de la théorie classique et quantique de la diffusion. Leur lieu avec le nouvel effect Raman. *J. Phys. Radium* **9**, 1045, June 1928 (1 June).
13. C. H. Fabry, 'A remarkable phenomenon in the scattering of light by transparent substances discovered by Raman.' *J. Phys. Radium* **9**, 92s, June 1928 (June).
14. A. Cotton, 'Remarques a propos de la note de MM. Cabbannes et Daure sur la diffusion moléculaire.' *Compt. Rend.* **186**, 1475, June 1928 (4 June).
15. J. Cabannes and P. Daure, 'Spectroscopic analysis of the light obtained from the molecular scattering of a monochromatic radiation by a liquid.' *Compt. Rend.* **186**, 1533, June 1928 (4 June).
16. C. V. Raman and K. S. Krishnan, 'Polarization of scattered light quanta.' *Nature London* **122**, 169, 4 August 1928 (14 June).

17. A. Carrelli, 'Raman diffusion.' *Accad. Lincei Atti.* **8**, 155, August 1928 (17 June).

18. J. Cabannes, 'Experimental laws of the Raman effect and theories of light.' *Compt. Rend.* **186**, 1714, June 1928 (18 June).

19. A. Bogros and Y. Rocard, 'Quelques precisions au sujet des effets Raman et Cabannes-Daure.' *Compt. Rend.* **186**, 1712, July 1928 (18 June).

20. P. Daure, 'Secondary radiations in the molecular diffusion of light by liquids.' *Compt. Rend.* **186**, 1833, July 1928 (25 June).

21. P. Pringsheim, 'Der Raman-effekt: ein neuer von C. V. Raman entdeckter Strahlungseffekt.' *Naturwissenschaften* **16**, 597, 3 August 1928 (25 June).

22. A. Smekal, 'The quantum theory of scattering and dispersion.' *Naturwissenschaften* **16**, 612, 3 August 1928 (26 June).

23. C. V. Raman and K. S. Krishnan, 'Molecular spectra in the extreme infrared.' *Nature London* **122**, 278, 25 August 1928 (5 July).

24. L. A. Ramdas, 'Raman effect in gases and vapours.' *Indian J. Phys.* **3**, 131, 30 September 1928 (7 July).

25. Gr. Landsberg and L. Mandelstam, 'Diffusion of light in crystals.' *Compt. Rend.* **187**, 109, July 1928 (9 July).

26. Gr. Landsberg and L. Mandelstam, 'On light scattering in crystals.' *Z. Phys.* **50**, 769, 19 September 1928 (12 July).

27. A. E. Ruark, 'Wavelength shifts in scattered light.' *Nature London* **122**, 312, 1 September 1928 (20 July).

28. P. Pringsheim and B. Rosen, 'Raman effect.' *Z. Phys.* **50**, 741, 19 September 1928 (20 July).

29. C. E. Bleeker, 'Raman effect in xylol.' *Z. Phys.* **50**, 781, 29 September 1928 (23 July).

30. H. Kornfeld, 'Bemerkung zu der Mitteilung von Landsberg und Mandelstam uber eine neue Erscheinung in der Lightzerstreuung in Krystalle.' *Naturwissenschaften* **16**, 653, 17 August 1928 (27 July).

31. M. Born, 'Zur theorie des Raman effektes.' *Naturwissenschaften* **16**, 673, 24 August 1928 (2 August).

32. I. R. Rao, 'Raman effect in crystals.' *Indian J. Phys.* **3**, 123, 30 September 1928 (2 August).

33. S. Venkateswaran, 'Raman effect in glycerine and glycerine–water mixtures.' *Indian J. Phys.* **3**, 105, 30 September 1928 (3 August).

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35. A. Carrelli and P. Pringsheim and B. Rosen, 'Raman effect in aqueous solutions.' *Z. Phys.* **51**, 511, October 1928 (9 August).

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38. R. W. Wood, 'Wavelength shifts in scattered light.' *Nature London* **122**, 349, 8 September 1928 (20 August).

39. W. H. Martin, 'Wavelength shifts in scattered light.' *Nature London* **122**, 506, 6 October 1928 (20 August).

40. K. S. Krishnan, 'Influence of temperature on the Raman effect.' *Nature London* **122**, 650, 27 October 1928 (6 September).

41. R. W. Wood, 'The Raman spectra of scattered radiation.' *Philos. Mag.* **6**, 729, October 1928 (8 September).

42. O. Oldenberg, 'Uber ein Zusammen wirken von Stoss und Strahlung.' *Z. Phys.* **51**, 605, 2 November 1928 (10 September).

43. J. Cabannes, 'Depolarisation of the secondary radiations in the complex light resulting from molecular diffusion of a monochromatic radiation.' *Compt. Rend.* **187**, 654, October 1928 (15 October).

44. C. V. Raman and K. S. Krishnan, 'Rotation of molecules induced by light.' *Nature London* **122**, 882, 8 December 1928 (18 October).

45. S. Venkateswaran and A. Karl, 'The Raman effect in alcohols.' *Z. Phys. Chem. B* **1**, 466, 18 November 1928 (18 October).

46. K. S. Krishnan, 'Raman effect in X-ray scattering.' *Nature London* **122**, 961, 22 December 1928 (25 October).

47. G. I. Pokrowski, 'Light scattering in water.' *Z. Phys.* **52**, 448, 4 December 1928 (30 October).

48. R. M. Langer, 'Light scattering in liquids.' *J. Opt. Soc. Am. Supplem.* **17**, 24, December 1928 (2 November).

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55. V. Posejpal, 'Fluorescence du benzène et son absorption infrarouge.' *Compt. Rend.* **187**, 1046, December 1928 (3 December).

56. M. Kimura and Y. Uchida, 'The Raman spectra of certain substances.' *Jpn J. Phys.* **5**, 97, December, 1928 (5 December).

57. J. C. McLennan and J. H. McLeod, 'Raman effect with liquid oxygen and nitrogen.' *Trans. R. Soc. Can.* **22**, 413, December 1928 (10 December).