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On the Occasion of 90th Anniversary of the Raman Effect

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On February 28, 1928, at the Indian Association for the Cultivation of Sciences, Kolkata (IACS), C V Raman and his associates showed that when monochromatic light is scattered by transparent media, the scattered light contains not only the original colour, but also other colours. This effect was named as Raman effect. In 1930, for the discovery of the Raman effect and work done on light scattering Raman received the Nobel Prize: the greatest award in the whole world. On the occasion of the 90th anniversary of the Raman effect, a brief overview about the discovery and its reception by the scientific community is given here.

The first three decades of the 20th century are considered as the "Golden Period" of "Indian Physics". The well-known facts are: In the beginning of the 1920s; M N Saha gave the Saha ionisation (also known as Saha-Eckert Equation), which explained the structure of stars [1]. On June 4, 1924, S N Bose wrote a letter to Albert Einstein, in which he stated that he (Bose) has derived Planck radiation law by applying his (Einstein's) quantum nature of light. Einstein translated Bose's manuscript, which was published in the German journal "*Zeitschrift für Physik*" [2]. Einstein further developed Bose's idea. Consequently Bose-Einstein emerged [3]. In 1928 C V Raman, K S Krishnan and S Venkateswaran (Fig 1) discovered the Raman effect.

From "a weak fluorescence" to the Raman effect

C V Raman, who was working on acoustic, in the beginning of the 1920s, diverted his attention to observe the scattering of light. In a monograph "Molecular diffraction of light", he reviewed the work in this field [4]. In his publication "On the molecular scattering of light in water and the colour of the sea" in 1922, Raman, as the first person explained the blue colour of the sea [5]. After successfully explaining the blue colour of the sea with the Einstein-Smoluchowski equation, Raman and his student K S Rao observed the polarization of some liquids and gases. Their observed values of the ratio of the weak to the strong components of the polarization for ether, benzene, chloroform and toluene were better than given by Lord Rayleigh [6].

Raman's motivation to continue his work in this field was (i) to check the validity of the Einstein-Smoluchowski equation in broader context; as he was expecting to find the molecular structure of substance by studying the properties of scattered light. (ii) more importantly, he was of the opinion that scattering phenomena might help to find out the nature of light [7]. The latter was important as Albert Einstein, in 1905, gave the concept of the quantum nature of light; which was criticised by his contemporaries, like Max Planck and Niels Bohr, who were not ready to give up the wave nature of light [8].

Raman's student K R Ramanathan derived an expression for the intensity of the transversely scattered light. He compared the theoretical and experimental values of intensity of the scattered light and found the

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results in agreement for moderate anisotropic molecules (water, ethyl alcohol). However, for the strongly anisotropic molecules of ether, benzene, toluene his theoretical results varied than that of experimental [9]. Ramanathan was of the opinion that the imperfection of the polarisation observed in water and alcohol is due to 'a trace of fluorescence' [9]. About five years later, on March 16, 1928, on the occasion of the inaugural meeting of the South Indian Science Association, Bangalore, Raman delivered a lecture on the discovery. Therein he told about the observation of 'a trace of fluorescence' by Ramanathan [10].

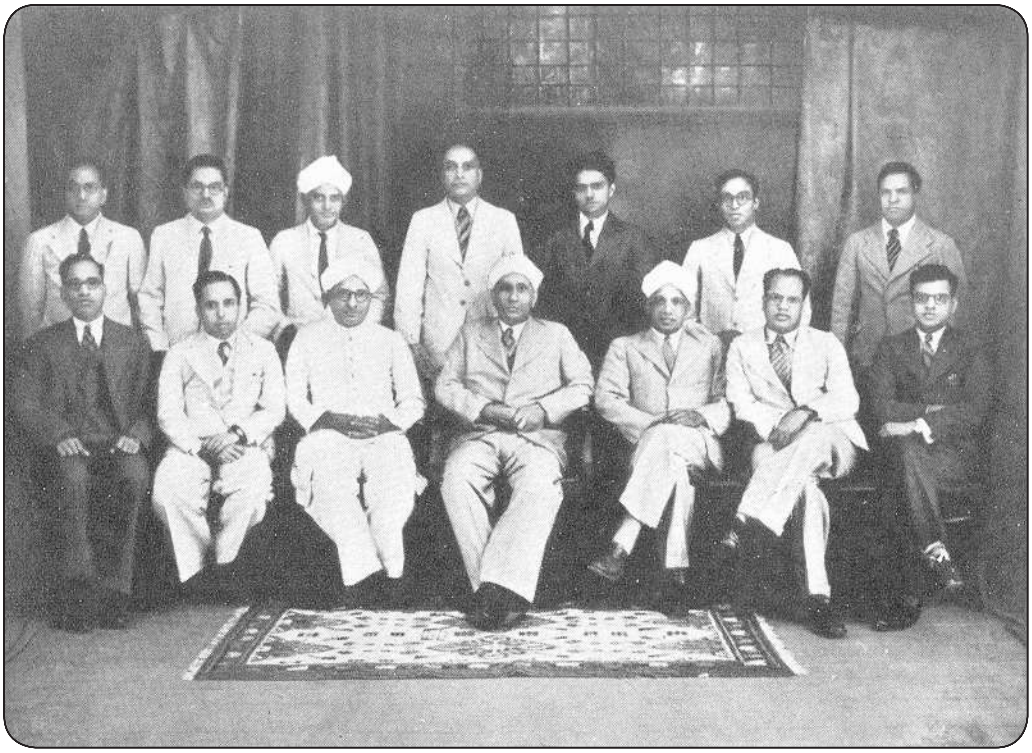

Fig 1. C V Raman and some of his scholars at the IACS. Sitting (left to right): A S Ganesan, L A Ramdas, K S Krishnan, C V Raman, K R Ramanathan, S Venkateswaran, and S S M Rao. Standing (left to right): C Ramaswamy, S Bhagavantam, S Paramasivan, S Rao, N S Nagendranath, A Ananthakrishnan and C S Venkateswaran. (Courtesy: IACS.)

The scientific work on the intensity and depolarisation of the light scattered by liquids was continued by K S Krishnan. He studied 65 liquids. In order to check the effect of wavelength on the depolarisation, Krishnan used blue, green and orange glass filters. He observed that in some of the liquids, the imperfection is changed when the filter is transferred from the incident to the scattered beam and this may be considered as *a very feeble kind of fluorescence* (emphasis in original) [11].

After 1925, being quite unsuccessful, Raman discontinued his research in this direction. According to Raman, the impetus to restart the work in this direction came, after Arthur Holly Compton, in 1927 was awarded the Physics Nobel Prize for the discovery named Compton Effect after him. Raman was convinced that analogue to the change in wavelength in x-rays, as was the case of the Compton effect, similar effect must also exist in the visible light.

According to Raman's lecture on the discovery: "The chemical importance of the subject led to Mr S Venkateswaran attempting to make a fuller study of it in the summer of 1925, but without any special success. The research was discontinued at the time but was resumed by him later in the current year (1928).

The remarkable observation was made that the visible radiation which is excited in pure dry glycerine by ultraviolet radiation (sunlight filtered through Corning glass G. 586) is *strongly polarised* (emphasis in original) [10].

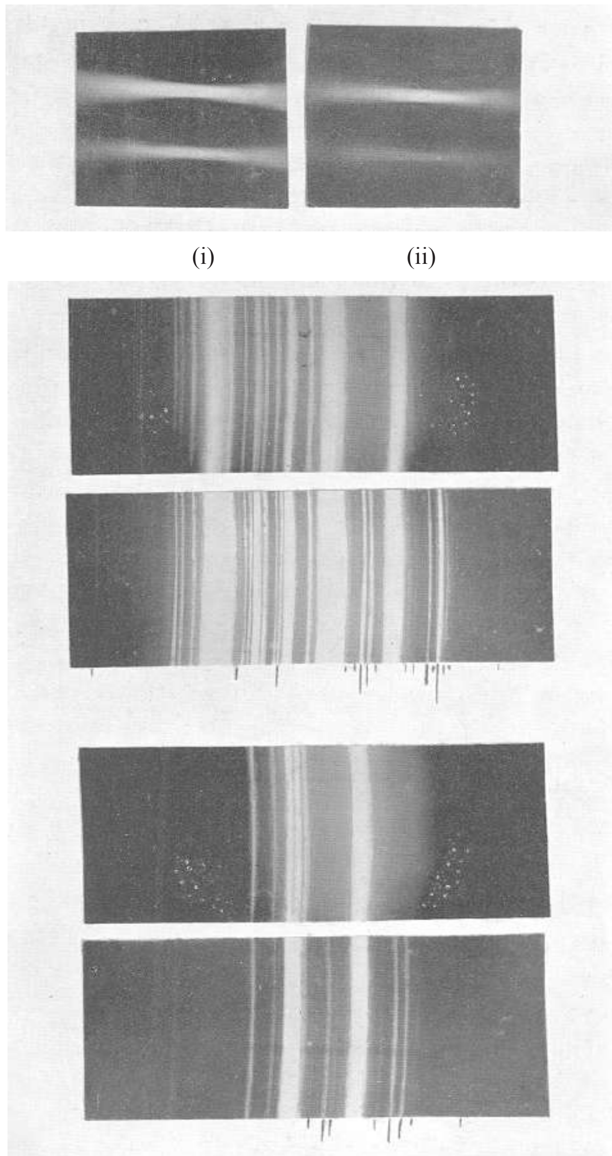

Fig 2. Top: Polarisation of scattered light in toluene: (i) Unmodified and (ii) Modified. Middle-upper: Mercury arc light filtered through a blue glass with transmission range from 350 to 440 Nanometer. Middle-lower: Scattered spectrum of benzene with additional lines. Bottom-upper: Mercury arc incident light filtered with potassium permanganate solution. Bottom-lower: Scattered spectrum of benzene with additional lines. (Courtesy IACS. Indian Journal of Physics.)

Unfortunate for Venkateswaran who could not devote whole time for researches; Raman asked K S Krishnan to reconfirm Venkateswaran's observations. Krishnan not only reconfirmed, but also at the suggestion of his Professor observed the effect in other liquids and vapours.

On Feb 16, 1928, Raman and K S Krishnan sent a paper to the British journal "*Nature*", which was entitled as: "A new type of secondary radiation." Thereafter the authors reported the observation of a new effect, that is, a modified scattered radiation of degraded frequency, in the case of dust free liquids and gases. They argued that it is not fluorescence, which is also an effect associated with change of wavelength, because: (i) the effect is feeble. (ii) The polarisation of the scattered light is quite strong and comparable with the polarisation of the ordinary scattering [12]. The next paper, signed by Raman alone, sent on March 8, 1928, was published in "*Nature*" on April 21st, 1928. In it, Raman draw a wrong conclusion: "The preliminary visual observations appear to indicate that the position of the principal modified lines is the same for all substances, though their intensity and that of the continuous spectrum does vary with their chemical nature." [13]. Other paper, entitled "The optical analogue of the Compton Effect" was sent by Raman and Krishnan to "*Nature*". This was the first spectrogram published by Raman in a western journal. Therein Raman corrected his results by stating "It is found that the shift of wavelength is not quite the same for different molecules, …" [14]. The most convincing results were presented by Raman, in a lecture, which he delivered in Bangalore, on March 16, 1928. It was published by Raman in the "Indian Journal of Physics, 2, 1928", where he presented the first "Raman Spectrum" (Fig 2). Qualitative and quantitative results, which match with theory, were given, in a paper, which was communicated in the beginning of May 1928 to *Indian J Phys* [10]. With his work, C V Raman proved the correctness of theories of A Smekal [15]; and H A Kramers and W Heisenberg [16]; which in 1925 predicted that when monochromatic light is scattered by a transparent media, the scattered radiation contains not only the original frequency, but also lower- and higher frequencies.

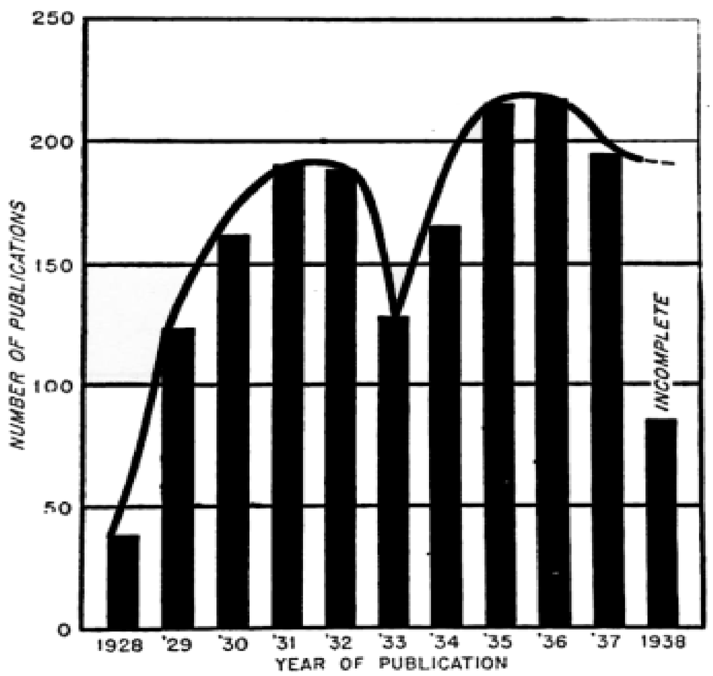

Fig 3. Number of publications per annum on the Raman effect. The number of publications on the Raman spectroscopy amounts to over 1700 within 10 years of its discovery [18]. (Courtesy: Indian Academy of Sciences, Bangalore).

After Raman's discovery spectroscopists all over the world became interested in this new technique. As most of the laboratories possessed the required instruments for "Raman spectroscopy", within a year after the discovery, 160 articles and monographs were published, as given in a bibliography of Raman effect, which was published by Raman's student, A Ganesan in 1929 [17]. The publication trend in the next ten years is shown in Fig 3 [18]. Already in 1929, in the "*Handbuch der Experimentalphysik*", G Joos, wrote a complete chapter: "The Raman Effect" in German "Encylopaedia of Experimental Physics" [19]. In 1929, in the monograph "*Forschritte der Chemie, Physik und Physikalische Chemie*" the importance of the effect in relevance to chemistry was given by C Schäfer and F Matossi [20]. In 1931, K W F Kohlrausch published "*Der Smekal-Raman-Effekt*", in which he gave 417 references, which include many monographs and articles [21].

In 1928, same effect in crystals was discovered by the Russian physicists G S Landsberg and L I Mandelstam [22, 23]. For the Physics Nobel Prize for the year 1930, they were also nominated. Why the Nobel Committee decided in Raman's favour? This will be discussed in a separate article in next issue of AJP.

As most of the discoveries and inventions; also the discovery of the *Raman effect* was the result of hard work of many years by Raman and his students.

Raman was aware of the potentialities of his fundamental discovery. In his Nobel lecture on December 11, 1930 he said,: *It follows that the new field of spectroscopy, has unrestricted scope in the problems, relating to the structure of matter. We may also hope that it will lead us to a further understanding of the nature of light and of the interactions between light and matter"*

Recent developments and celebrations

Recent advances in electronics, lasers, optics and instrumentation have made Raman spectroscopy suitable in many areas of applications and it has now established itself as an indispensable technique of investigating the molecular species in all phases of matter. Many applications have been developed during the past decade. As a result, Raman Spectroscopy is being used today in almost all walks of life. Its applications range from ancient archaeology to advanced nanotechnology [24], including biological systems, geological as well as planetary science. In the last few years Raman Spectroscopy has been identified as a possible method for *in situ* planetary analysis. Raman measurements on samples originating from one of the Martian SNC meteorites have been reported in literature [25]. Applications of Raman Spectroscopy in Agricultural Products and Food Analysis have been reviewed by Yang and Ying [26]. Many excellent review articles and monographs dealing with the basic principles and applications of Raman spectroscopy have appeared in literature. A Raman spectrometer coupled with a fiber optics probe has great potential in applications such as monitoring and quality control in industrial food processing, food safety in agricultural plant production, and convenient inspection of pharmaceutical products, even through different types of packing [27]. Also, recent studies have illustrated the diversity of potential applications of Raman spectroscopy ranging from monitoring cataract formation *in vivo* to the precise molecular diagnosis of atherosclerotic lesions in coronary arteries and suggested that Raman spectroscopy can be used to diagnose the evolution of precancerous and cancerous lesions in human tissues *in vivo*. The application of Raman spectroscopy has been reported recently for the detection of different types of pathologies, including cancer. Recently, a review on "Current Advances in the Application of Raman Spectroscopy for Molecular Diagnosis of Cervical Cancer" has been published by Ramos *et al* [28]. Biomedical applications of Raman spectroscopy has been very recently reviewed by Das *et al* [29.]. A very good overview of the discovery of Raman Effect has been described by Kiefer and Cinta-Pinzaru in a recently published book by Springer[30].

Recently a conference was jointly organised by Christian College Chengannur and, Indian Spectroscopy Society, Ghaziabad (Oct 4-7, 2017, Hotel Haveli, Alappuzha, Kerala, India) focusing on the Spectroscopy of Biomolecules and Advanced Materials, under the chairmanship of Prof Wolfgang Kiefer, a world-renowned pioneer in the field of Raman spectroscopy.

Fig 4. Prof V K Rastogi (left) honoring well-known Raman Spectroscopist Prof Wolfgang Kiefer (right) by presenting shawl on October 6, 2017 during ICSBAM-2017, Hotel Haweli, Alappuzha, jointly Organized by Christian College, Chengannur and Indian Spectroscopy Society, Ghaziabad, India.

Fig 5. Prof V K Rastogi (left) honoring Prof Young Mee Jung (right) by presenting shawl on October 6, 2017 during ICSBAM-2017, Hotel Haweli, Alappuzha, jointly Organized by Christian College, Chengannur and Indian Spectroscopy Society, Ghaziabad, India.

Fig 6. Prof V K Rastogi (left) honoring Prof Dongho Kim (right) by presenting shawl on October 6, 2017 during ICSBAM-2017, Hotel Haweli, Alappuzha, jointly Organized by Christian College, Chengannur and Indian Spectroscopy Society, Ghaziabad India.

The range of applications of Raman Spectroscopy in conjunction with Infrared Spectroscopy is very wide. A Raman spectrum can be interpreted as a type of characteristic "molecular fingerprint" of an examined species like e.g. biological cells and tissue. Spectral contributions are assigned to proteins, lipids, nucleic acids and carbohydrates. As cancer and other pathologic anomalies are accompanied by changes in the biochemical composition and structure of biomolecules, the Raman spectrum provides a sensitive and specific fingerprint of the type and state of the specimen. During the last years Raman based (micro) spectroscopy has been recognized as an extremely powerful tool for bioanalytical and biomedical applications. Advantages of the technique for biomedical problems include (i) it is label-free and (ii) non-destructive. Within the last years number of research groups worldwide developed and applied a broad range of different Raman approaches to characterize biological cells and tissues according to unmet medical needs of e.g. pathology, oncology, and infection/ sepsis. In addition , through the use of optical spectroscopic methods like e.g. Raman spectroscopy, it is possible to obtain qualitative and quantitative biochemical information in addition to morphological information that can be correlated with clinical results [31].

Over the past decade, Raman spectroscopy has also proven its importance as a tool for analyzing and characterising objects of cultural and archaeological interests. Because of the basic non-destructive nature of the technique, studies have flourished with applications in analyzing paints and pigments, glazes, precious stones, glasses and porcelains [32] .

The importance of Raman Spectroscopy in modern world can be judged by the fact that an International conference on Raman Spectroscopy is being organised once in two years since 1969 ; the 26th ICORS will be organised in Korea during Aug 26-31, 2018 at ICC JEJU, Jeju, Korea, under the chairmanship of Prof Dongho Kim (Fig 6) and Prof Young Mee Jung (Fig 5). ICORS 2018 aims to bring together experts from different fields to discuss the recent progress in Raman Spectroscopy. To celebrate the 90th Anniversary of discovery of Raman effect an International conference " 90 Years of Raman Effect : Current Status and Future Directions" was organized at Indian Institute of Science, Bangalore during 27th February - 2nd March 2018, Many leaders of the field from all around the world actively participated in this four days conference, where Prof Raman had joined as Director in 1933.

Fig 7. The two awardees for longtime contributions to Raman spectroscopy, Prof Hiro-o Hamaguchi (left) and Prof. Wolfgang Kiefer (right); middle: Prof Siva Umapathy, chair of conference, on the occasion of International conference on "90 Years of Raman Effect : Current Status and Future Directions" at Indian Institute of Science, Bangalore during 27th February - 2nd March 2018. (Photograph by Prof Tony Parker)

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