

THE PHENOMENON OF RAMAN

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RAMAN was one of the greatest experimental physicists of the century, a physicist of light, sound and crystals.

Let me quote Lord Rutherford. While presenting Raman the Hughes Medal of Royal Society of London in 1929, even before Raman got the Nobel prize, Rutherford said, "The Raman Effect must rank among the best three or four discoveries in experimental physics of the last decade". The winners of the Nobel prize for work in experimental physics in the preceding decade were: Millikan (charge and mass of the electron and the photoelectric effect), Siegbahn (X-ray spectroscopy), Frank and Hertz (collisions of electrons with atoms), Perrin (Brownian motion), Compton (for the effect known by his name), C.T.R. Wilson (cloud chamber for making visible the track of very small charged particles) and Richardson (thermionic emission of electrons). So, it was quite a thing for the Raman effect to be among the best three or four discoveries.

Indeed, such is the fecundity of the Raman effect that Raman (scattering) figures more often in current experimental research papers than the names mentioned above including Rutherford's, all put together!

Raman was not only an adept experimentalist with light, in the tradition of Young, Fresnel and Rayleigh, but he also fostered an active school of research in our poor country for almost half a century in the grand manner of German spectroscopists of the nineteenth century—Fraunhofer, Bunsen and Kirchoff. His own work extended to some 360 papers and four books. Among Indians, only the chemist, Prof. Seshadri, F.R.S., excelled him in the number of publications, so far as I know. Raman initiated into research nearly 150 students. He was also a charming speaker, holding his listeners spell-bound.

It is difficult to explain his enormous intellectual development. He was taught by himself alone. He dared to publish his first paper in the year 1906 in the *Philosophical Magazine* of London, then the foremost journal of physics, at the age of 18 years, on diffraction patterns due to a rectangular aperture.

Prof. R.L. Jones who had worked in the Cavendish Laboratory, was Raman's teacher in physics at the Madras University, but Raman recollected: "Professor Jones

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believed in letting those who were capable of looking after themselves to do so.... during the whole of my two years' work for the M.A. degree, I remember attending only one lecture, and that was on the Fabry-Perot interferometer by Prof. Jones himself." Prof. Max Born, a leading physicist of Quantum-Mechanics and a Nobel prize winner, talked of the "European intensity" of Raman. Raman himself recalled at the age of 75 years, "I... do not recollect any time during this long period when I took my mind off from my scientific interests".

Raman was, therefore, a phenomenon, almost in the same class as Ramanujan. Both were completely home-made and self-educated and produced work which will be remembered for centuries.

So, after Raman got the Nobel prize in physics in the year 1930, almost every thinking Indian felt, "We can do it". This spirit must be regenerated, particularly among our scientists.

Raman, the aesthete

Raman loved colour, beauty, form and rhythm in nature. He collected thousands of specimens of butterflies. He purchased after personal inspection, hundreds of diamonds of different forms and fire for his studies. He was so much bewitched by the physical properties of the diamond, that at one time every researcher in his laboratories was working on the physics of this simplest of crystal structures—its properties of absorption, birefringence, Faraday effect, fluorescence, luminescence, magnetic susceptibility, photo-conductivity, specific heat, ultraviolet transparency, etc. But, also, no great secrets of nature were thus revealed, although Raman believed that diamond had "characteristic properties of the solid state in a superlative degree".

He wrote extensively on the colours of foliage and flowers, and of gemstones describing the physics of it all, in words which conjure up the colours and lights of Turner's paintings. He gave a theory of the blue of the sea, correcting Lord Rayleigh's conjecture. This was the starting point and inspiration of his main work, on the scattering of light, as Raman told us in his Nobel Lecture in Stockholm on 11 December, 1930.

Incidentally, he regarded Rayleigh as his "teacher". Works of Rayleigh signed by Raman are, I suppose, still kept in the library of the Raman Institute at Bangalore. (I saw them there about ten years ago.)

He made a scientific study of the drums and the violin. His interests and papers in this field, published in *Nature* and the *Philosophical Magazine* of England went so deep that

he was invited by the editor of the prestigious German *Handbuch der Physik* in 1927 to write an article for the *Handbuch* on musical instruments. It was a singular honour, a salutation to his experimental work in this field.

Matter, light and their interaction

To understand Raman's work one must know something about the structure of matter and the nature of light. The following description should suffice here.

Matter consists of atoms which can also aggregate into molecules, as the basic bricks of the structure of matter. Each atom consists of a nucleus with a positive electric charge in integral multiples of a unit of charge equal to the charge on an electron which however is negative or opposite (a smaller unit of charge has not been experimentally encountered so far, although fractional charges have been postulated in the quark theory of matter). The nucleus is surrounded by one or more electrons which have the same total electrical charge as the nucleus but opposite in sign. The electrons and nuclei of the atoms, constituting a molecule (such as hydrogen and oxygen in a water molecule), interact in a way such that the atom and the molecule hold together. This model or picture of matter, suffices to explain most of chemistry and much of physics.

The state of the electrons in each atom is determined by the energy of the atom and varies by discrete amounts, i.e., in steps, discontinuously, which are characteristic of each atom. Each of these states corresponds to an equilibrium lasting for a period which may be very short or indefinitely long.

The nature of light is still not fully understood. But an approximate verbal description may be attempted. Light is electromagnetic (em) energy in motion, that is, propagated em energy. It is a travelling electrical field, accompanied by a magnetic field. The intensity of each of these fields varies at any point it traverses, in a periodic fashion like a wave. The fields travel through vacuum with the same constant velocity, and do not require a separate carrier. However, the electromagnetic energy which constitutes light can be absorbed, partly or wholly, by matter in which the same energy is trapped within the atom by a process of change in the state of energy of the electrons. (We need not consider the nucleus for the present purpose.) An atom after absorption of electromagnetic energy, may re-emit this energy, wholly or partly, or it may even part with its own energy and emit more than what it absorbs.

The electromagnetic energy is, however, absorbed or emitted by matter in packets or quanta, not continuously like a flowing stream. Each packet is characterized by just one parameter and that is the frequency of oscillations, ν , of the electromagnetic energy constituting it. (We shall mention later, the spin or the state of polarization of light). The energy of each packet or photon is then $h\nu$, where h is a constant (of action, of dimensions energy \times time), first

postulated in the year 1900 by Max Planck of Germany.

Now consider a highly purified transparent material through which a beam of light of one frequency or colour (monochromatic) is made to pass. Most of the light will pass through but a small amount of it will be scattered in various directions by the atoms and molecules lying in the path of the beam. Lord Rayleigh had studied this phenomenon of scattering in the last century and found that for many liquid scatterers about one-thousandth part of the incident light energy is scattered, and this light has the same wavelength as the incident radiation. (However, the amount of energy scattered varies with the wave-length of the incident light.)

A German physicist, E. Lommel, had shown in 1878 from his theory of scattering, that the scattered light should contain, in addition, some light which combined the frequency of the incident light with the frequency of internal oscillations of the scattering medium but his work received little notice. Another German physicist, A. Smekal in 1923, and H.A. Kramers and W. Heisenberg in 1925 also theoretically predicted that the scattered light would contain other frequencies besides the frequency of the incident radiation and that the changes in the frequencies will be characteristic of the substance of the scatterer. Dirac had theoretically come to the same conclusion in 1927. The resultant frequency was predicted to be the sum or difference of the two frequencies, one external and the other internal. Raman was aware of the work of Kramers and Heisenberg. So were others.

Raman was not only an adept experimentalist with light, in the tradition of Young, Fresnel and Rayleigh, but he also fostered an active school of research in our poor country for almost half a century in the grand manner of German spectroscopists of the nineteenth century

A search was made for these "combination frequencies" by many but without success. In the year 1923, P.A. Ross of U.S.A., using an interferometer of resolving power equal to 360,000, looked for them but failed to detect any shift in the frequencies.

The theory of the Raman effect may now be stated briefly. If $h\nu$ is the energy of the quantum of light falling on a molecule, it may interact with an electron of the molecule in the lowest or ground energy state or a higher stage. By a well known formula of Boltzmann, the number of electrons in a lower energy state is more than the electrons in a higher energy state. So an interaction with the ground-state electrons is the most likely, when the electron will have its energy raised by level $h\nu$. This disturbed state lasts for a short period of time and there is a high probability that the photon will be ejected with the same frequency (ν) and

energy ($h\nu$) by the Rayleigh scattering process. However, if there exists an in-between permitted energy level of the electron $h\nu'$ (ν' less than ν), the electron may release energy equal to $h(\nu-\nu')$, not whole of $h\nu$, absorbing energy $h\nu'$ itself and remaining at level $h\nu'$ above the ground-energy state.

If the incident photon ($h\nu$) interacts with an electron in energy state $h\nu'$ above the ground state, it will raise the electron to level $h(\nu+\nu')$ and after remaining in this disturbed state for a very short time, it may fall back into the ground state, emitting a photon of energy $h(\nu+\nu')$. But because the number of electrons at higher energy levels is smaller, the probability of a scattered photon of higher frequency ($\nu+\nu'$) is low.

Naturally, the total energy of all photons of Raman scattering at frequencies ($\nu-\nu'$) and ($\nu+\nu'$) will be less than the total energy of Rayleigh scattering at frequency ν . And within the Raman scattering, the emissions at the lower frequency ($\nu-\nu'$) will have more total energy than those at the higher frequency ($\nu+\nu'$).

The spectral lines of frequency ($\nu-\nu'$) are called Stokes lines and those of frequency ($\nu+\nu'$), anti-Stokes lines. In a laser more electrons can be put in higher energy states within the molecule or the atom, by "pumping" in energy. When this stored energy is released, the laser action takes place in which the light energy emitted is coherent (the waves being in one phase), monochromatic (having almost the same frequency), highly directed (parallel propagation), and concentrated (in a small cross-sectional area with high energy per unit of area). Research with the Raman effect has gone through a renaissance with the use of laser-light.

A word about the polarization characteristic of light or electro-magnetic waves. The electric and magnetic components of these waves at any point lie in a plane at right angles to the direction of propagation or the light-ray path. The electric and magnetic fields themselves stand at right angles to each other in this plane. The direction of the magnetic field of force and the direction of the propagation, then define the plane of polarization of light. The plane of polarization of light from most sources changes irregularly; the light is then said to be unpolarized. As we shall see Raman-scattered light was found to be regular or polarized and this characteristic led Krishnan and Raman to the discovery. We need not go into the details of how the degree of polarization is determined.

Two Indians do it

Let me recall at the outset that the intensities of these combination frequencies are much feebler than even the Rayleigh scattered light. For example, in the case of liquid carbon tetrachloride it is 1/400 and for gaseous oxygen about 1/3300 of the Rayleigh scattering intensity.

The scattering of light by transparent media had been the subject of study in Raman's laboratory since the year 1921. In this year, he himself wrote two papers in *Nature* on the colour of the sea and the molecular scattering of light in liquids and solids. K.R. Ramanathan, then working with Raman, discovered in 1923 that the light scattered even by

purified liquids show, what he called, a "weak fluorescence". Similar results were obtained by K.S. Krishnan while experimenting on 60 liquids in 1924. But this research was abandoned in 1925, to be resumed by Krishnan in January 1928, under the guidance of Raman. Soon, the discovery of what is now known as the Raman effect, was made by Krishnan, who kept a diary, related extracts from which are reproduced below :

7th February (1928), Tuesday

Tried to verify the polarization of fluorescence exhibited by some of the aromatic liquids in the near ultraviolet region. Incidentally, discovered that all pure liquids show a fairly intense fluorescence also in the



Dr. K.S. Krishnan

visible region, and what is much more interesting, all of them are strongly polarized...

When I told Professor (i.e., Raman) about the results, he would not believe that all liquids can show polarized fluorescence and that too in the visible region. When he came in up to the room, I had a bulb of pentane in the tank, and a blue-violet filter in the path of incident light and when he observed the track with a combination of green and yellow filters, he remarked, "You do not mean to suggest, Krishnan, that all that is fluorescence". However, when he transferred the green yellow combination also to the path of the incident light, he could not detect a trace of the track. He was very much excited and repeated several times that it was an amazing result. One after another, the whole series of

liquids were examined and each one of them showed the phenomenon without exception. He wondered how we missed discovering all that five years ago.

In the afternoon, took some measurements on the polarisation of fluorescence.

After meals at night, Venkateswaran and myself were chatting together in our room when Professor suddenly came to the house (at about 9 P.M.) and called for me. When we went down, we found he was much excited and had come to tell me that what we had observed that morning must be the Kramers-Heisenberg Effect, we had been looking for all these days. We, therefore, agreed to call the effect "modified scattering". We were talking in front of our house for more than a quarter of an hour when he repeatedly emphasized the exciting nature of the discovery.

9th February, Thursday

When the Professor came from the college at about three, I announced to him the result (for gases), and there was still enough sunlight at the time; he said that it was a first rate discovery, that he was feeling miserable during the lecture because he had to leave the experiment, and that however he was fully confident that I would not let the grass grow under my feet till I discovered the phenomenon in gases...

Evening was busy and when Professor returned after his walk, he told me that I ought to tackle big problems like that and asked me to take up the problem of the experimental evidence for the spinning electron after this work (was over).

17 February, Friday

Professor confirmed the polarization of fluorescence in pentane vapour. I am having some trouble with my left eye. Professor has promised to make all observations himself for sometime to come.

Apparently, while Raman was checking and confirming the results obtained by Krishnan, a joint letter was drafted and sent for publication to *Nature* on 16 Feb., 1928, which was duly published in its issue of 31 March, 1928 (Vol. 121, p. 501).

On 28 February 1928, Raman announced the discovery to the press and the public.

On 16 March, 1928, Raman delivered an address to the newly formed South Indian Science Association at Bangalore with the title *A New Radiation*. Immediately on return to Calcutta, Raman had this address printed overnight at the Calcutta University Press and reprints of it were posted to thousands of scientists all over the world. I believe that this settled the question of priority of the discovery in favour of Raman. In fact, the Russians, G. Landsberg and L. Mandelstam had made the same discovery (it was later claimed that discovery was made in January 1928) and communicated their finding to the German journal *Naturwissenschaften* on 6 May 1928 (published in the 13 July, 1928 issue, vol. 16, p. 557). The

Russians, working on quartz, a solid, had got quantitative results of the change in wave-lengths and a spectrum, which were published with their article. Raman's and Krishnan's work was done on liquids and they had not given any quantitative results in their first letter to *Nature*

NEW THEORY OF RADIATION

PROF. RAMAN'S DISCOVERY

(ASSOCIATED PRESS OF INDIA.)
CALCUTTA, Feb. 29.

Prof. C. V. Raman, F. R. S., of the Calcutta University, has made a discovery which promises to be of fundamental significance to physics. It will be remembered that Prof. A. H. Compton of the Chicago University was recently awarded the Nobel Prize for his discovery of the remarkable transformation which X-rays undergo when they are scattered by atoms. Shortly after the publication of Prof. Compton's discovery, other experimenters sought to find out whether a similar transformation occurs also when ordinary light is scattered by matter and reported definitely negative results. Prof. Raman with his research associates took up this question afresh, and his experiments have disclosed a new kind of radiation from atoms excited by light.

The new phenomenon exhibits features even more startling than those discovered by Prof. Compton with X-rays. The principal feature observed is that when matter is excited by light of one colour, the atoms contained in it emit light of two colours, one of which is different from the exciting colour and is lower down the spectrum. The astonishing thing is that the altered colour is quite independent of the nature of the substance used. It changes however with the colour of the exciting radiation, and if the latter gives a sharp line in the spectrum, the second colour also appears as a second sharp line. There is in addition a diffuse radiation spread over a considerable range of the spectrum. He will deliver a lecture demonstrating these phenomena first at Bangalore on the 16th March.

The first Raman spectra (From the paper "A New Radiation")
The first newspaper report of the discovery of the Raman Effect (February 29, 1928). It is clear that the observations made with the direct vision spectroscope on 28th could not distinguish the differences in the colour (wavelength) of the new radiation emitted by different liquids. Hence the statement "the altered colour is quite independent of the nature of the substance." The changing of the word "quite" to "approximately" is almost certainly in Prof. Raman's handwriting.

published on 31 March, 1928, although they said that spectroscopic confirmation was available and that modified scattering was demonstrable in the case of high-density gases. Be that as it may, the Russians spoil their claim, by saying at the end of their article of 6 May 1928, "At the moment it is not possible for us to judge if and to what extent, there exists a relation between the phenomenon observed by us and that for the first time briefly discussed by Raman, because of the brevity of discussion". (In those days the date of receipt of a paper by the journal concerned was not usually published.)

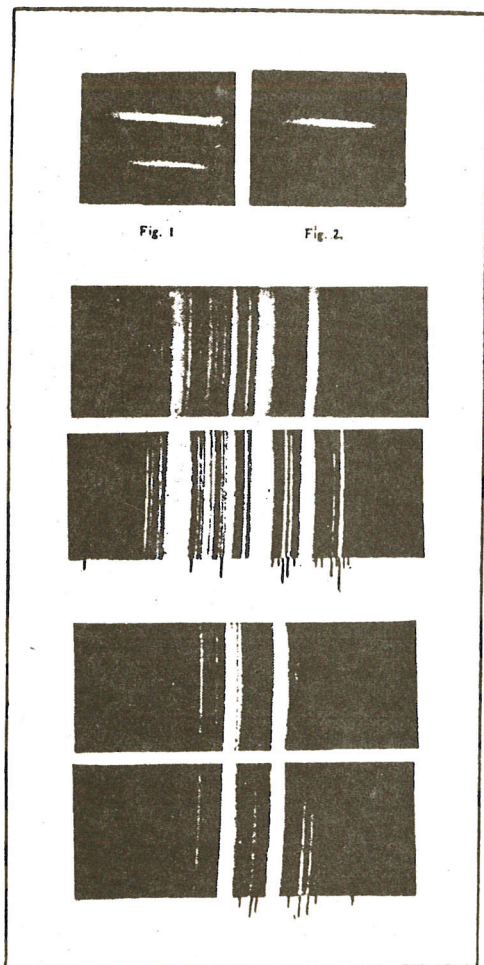
Raman moved on. He wrote another Letter to *Nature*, now in his own name only, on 8 March, 1928, in which he made the following statement: "The preliminary visual observations appear to indicate that the position of the principal modified lines is the same for all substances...." He seemed to believe for some time after the discovery that it was a "new radiation" with a constant shift in frequency, which had been discovered, and that the shift was therefore independent of the material of the scatterer. Indeed, in the report filed by the Associated Press of India, published on 29 February 1928, based on Raman's announcement, the

Luminescence and Raman Scattering

THE discriminating characteristics of the new scattered radiation, in terms of the physical ideas current in those days (1920s) were: a decreased frequency of the scattered radiation (initially only decrease was observed) and the strongly polarized nature of the radiation as observed by Krishnan and Raman. The decrease in frequency was known to occur also in the case of fluorescence but this was ruled out because fluorescent radiation was then known to be not strongly polarized.

It can now be said that light scattering in the Raman (Rayleigh, Compton and Brillouin) interactions, might be distinguished from various luminescent processes (which are legion), including fluorescence, by the period elapsing between the excitation of, and emission by a molecule, compared to the period of one oscillation (reciprocal of frequency, $1/\nu$ in sec), of the incident light. This period is of the order of 10^{-14} sec for visible light. The time between excitation and emission has a magnitude of this order, viz. 10^{-14} second, for Raman scattering. But in the case of luminescence it is much longer, being usually in the range 10^{-14} sec to 10^{-10} sec. This is the crucial difference between the two phenomena. Also, Raman excitations are far more universal than luminescence which is markedly exhibited by only some substances.

G.H.K.



The first Raman spectra (From the paper "A New Radiation")

following corroborative line occurs, "The astonishing thing is that the altered colour is quite independent of the nature of the substance used."

However, this astonishing statement of Raman's was corrected in a joint letter written by Raman and Krishnan on 22 March 1928, to *Nature* (third in the series) in which it was stated that "it may be assumed that an incident quantum of radiation may be scattered by the molecules of a fluid either as a whole or in part, etc." Incidentally, there is no mention even at this stage, of so-called anti-Stokes lines of reduced wave-length and increased frequency (or energy), as shown by the theory of Smekal (1923), Kramers and Heisenberg (1925) and Dirac (1927), although Raman was aware of the work of Kramers and Heisenberg, at least. Being a fellow of the Royal Society of London, he should have seen Dirac's 1927 article in the proceedings of the Society.

There is no doubt that the observation and measurements of the modified frequency were most difficult. Krishnan and Raman had available only sunlight and filters, and a pocket spectroscope; that is all. The total cost of the equipment was a lordly sum of Rs. 200/-. Even the mercury-vapour lamp—Alladin's lamp as Raman called it—came after the discovery was made.

Nonetheless, the theory of the effect known to Raman, predicted changes in frequency characteristic of the molecular structure of the scatterer and its internal energy

levels, which varied from substance to substance. As Einstein put it in a message for the Jubilee celebrations of the Raman effect in 1953, this effect for the first time showed experimentally that a photon undergoes a partial transformation within matter. The atoms and molecules leave their individual fingerprints, so to speak, on the interacting photons. That is why Raman effect is, perhaps, the best technique for studying the internal structure of matter (leaving other methods behind after the development of the Laser Raman Spectroscopy).

Raman's statement that the position of the modified spectral lines, after scattering was "the same for all substances", cannot be understood. This is not even approximately true, and if it was, the Raman effect would become magic.

I shall return to the role of Krishnan presently but before I do that, I may mention a meeting I had with Prof. S. Chandrasekhar in Chicago in October, 1980. He wanted to know what I had said in my biography of Raman and I told him, among other things, what I have said above. He then went up to one of his filing cabinets and brought out a sealed envelope. He bid me to open it and read some parts which I did. I think, I can say here, that Prof. Chandrasekhar had himself come to similar views regarding the origins of the discovery.

Let us resume our narrative regarding Krishnan's role. After talking about Krishnan's work of 1924, Raman said, in his Bangalore address of 16 March, 1928, "The research was discontinued at the time but was resumed by him [that is, Krishnan] later in the current year (January, 1928). The remarkable observation was made (by whom first ?) that visible radiation which is excited in pure dry glycerine by ultraviolet radiation (sunlight filtered through Corning glass G. 586) is *strongly polarized*". (Words in square brackets are added but italics occur in the original.)

He said in the same address after mentioning award of the Nobel prize to Compton, "I immediately undertook an experimental re-examination of the subject in collaboration with Mr. K.S. Krishnan and this has proved very fruitful in results".

And later, "A more satisfactory proof was, however, forthcoming when Krishnan and myself examined the polarization of this new type of radiation and found that it was nearly as strong as that of the ordinary light scattering in many cases, and is thus quite distinct from ordinary fluorescence which is usually unpolarized."

And at the end, "I owe much to the valuable cooperation in this research to Mr. K.S. Krishnan".

The crucial point is as to who observed the strong polarization of the scattered light, first, and thus set the phenomenon apart from fluorescence which is what it had been considered earlier by everyone involved in it, in Raman's laboratory. Let me quote in this context from the Nobel Lecture of Raman delivered at Stockholm in 1930:

"Krishnan, who *very materially* assisted me in these investigations, found at the same time that the phenomenon could be observed in several organic

vapours, and *even succeeded in visually determining the state of polarization of the modified radiations from them*". (Emphasis added.)

The observations on which the first letter to *Nature* announcing the discovery, were based; used ordinary sunlight. As the above passage shows, Krishnan had the extraordinary ability to determine *visually* the state of polarization using ordinary sunlight (and filters and condensers). The mercury vapour lamp giving an intense beam in a narrow band, came later.

It will be correct to say, therefore, that it was the seeing eye of Krishnan, which made the discovery in Raman's laboratory. It was Raman's experience, imagination, inspiration and status which made it possible for the discovery to be known and immediately acknowledged. And, of course, he had intimations of it and toiled for years over the phenomenon of scattering of light. Raman and Krishnan whose names rhyme, formed an excellent pair, for the observation and understanding of the phenomenon.

It would, therefore, be just to call it Raman-Krishnan effect. I might say here that many knowing authors now attribute the discovery to Raman and Krishnan jointly. I may mention the latest edition of the *McGraw Hill Encyclopedia of Science & Technology* (1986) and *Encyclopedia of Physical Science and Technology*, Academic Press (1987).

So while we remember Raman today, with all our heart, we should equally remember his most able and inspired collaborator K.S. Krishnan. No doubt, as the French historian of science, Taton, has said, both chance and reason play a part in discovery. One is tempted to add that chance meets the prepared mind.

Further reading

1. Keswani, G.H., *Raman and his Effect*, National Book Trust, India, 1980. K.S. Krishnan's diaries were with Dr. Ramanathan. Also see R.S. Krishnan's (no relative of K.S. Krishnan), *K.S. Krishnan Memorial Lecture*, 1978, National Physical Laboratory, New Delhi.
2. Kramers, H.A. and Heisenberg, W., *Z. Physik*, **31**, 681 (1925).
3. Landsberg, G. and Mandelstam, L., *Z. Physik*, **50**, 769 (1928); *Die Naturwiss.*, **16**, 557/772 (1928); *Comptes Rendus*, **187**, 109 (1928).
4. Lommel, E., *Wiedem. Ann.*, **3**, 251, (1878).
5. Raman, C.V. and Krishnan, K.S., *Nature*, **121**, 501 (1928).
6. Raman, C.V., *Nature*, **121**, 619 (1928).
7. Raman, C.V. and Krishnan, K.S., *Nature*, **121**, 711 (1928).
8. Raman, C.V., *Nobel Lecture*, reproduced in: Keswani, G.H., *Raman and his Effect*, National Book Trust, India, 1980.
9. Ross, P.A., *Nat. Acad. Sci. Proc.*, **9**, 246 (1923).
10. Rutherford Lord; see *Nature*, **126**, 898 (1930), for his remarks at the time of presentation of the Hughes medal to Raman.
11. Smekal, A., *Die Naturwiss*, **11**, 875 (1923).