

## Selected papers of Raman: An introduction

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A small selection of papers by Professor C. V. Raman follows this introduction. Some have been selected for their immediate as well as lasting impact, others for their prescience. They illustrate his characteristically direct and incisive approach, his interest in natural phenomena, his concern for basic questions and implications, and his eye (and ear) for beauty.

Raman's writing style is direct, clear and has a characteristic literary flavour. For these reasons annotating his papers is often an undesirable intrusion. However, many of them are very brief, and were written in a certain intellectual milieu for a particular audience. Several papers hint at areas of physics which have seen growth much later. In this introduction, I try therefore to expand on the matter condensed in a few lines, to set out the background, or to point out how the work foreshadows present concerns in physics.

The very first paper [P1] is an extremely brief and incomplete summary of one of Raman's two major contributions to musical acoustics, namely his work on the *Mrdangam* (and the *Tabla*). These Indian drums are true musical instruments, the musical quality being due to the harmonic overtones and their relative intensities, as well as to the clarity, duration and volume of sound. Now in a simple circular drum, the overtones are not integral multiples of a fundamental or lowest frequency mode of vibration. It is therefore not musical. Raman guessed that the Indian drum is designed (with its nonuniform black centre and an auxiliary circular leather strip) to produce harmonic overtones, to damp out high-frequency harmonics and to produce clear long-lasting notes. He showed this by exciting various harmonics, and determined their vibration patterns by noting the places where sand, spread on the drum, collects. (It collects at places which do not vibrate, called nodes; their number and shape are diagnostic of the frequency and nature of the mode of vibration). This note does not detail or even describe these results. They were written up much later, in 1934 [The Indian musical drums, *Proc. Indian Acad. Sci.*, 1934, **1**, 179–188], though all the major results had been obtained before 1921. The reason for this delay was Raman's increasing preoccupation with light and its scattering, the beginnings of which can be seen in the next paper. Anyone interested in the area of musical acoustics should read his 1934 paper. It describes Raman's discoveries in detail, with pictures of the drum in various 'pure' modes of vibration.

The second paper, on 'The colour of the sea' [P2] is a Raman classic. A great scientist, Lord Rayleigh (whom Raman particularly admired) said, perhaps without thinking much about it, that the blue of the sea is just the reflected blue of the sky. Raman, on his first voyage abroad, disposed of this suggestion quickly with a few deckside observations using a Nicol prism analyzer. The idea is the following: the light reflected from water is partially polarized, the polarization being nearly complete for a certain angle of incidence. The Nicol prism, if oriented in a particular direction, will completely block out polarized light. By this simple arrangement, reflected light can be eliminated. Raman found, under these conditions, that the blue of the sky instead of disappearing was 'wonderfully improved'! His belief that the blue of the ocean had the same physical cause as the blue of the sky (explained by Lord Rayleigh!) was reinforced by two observations. The first is that when the reflected light is cut out, the colour of the sea depends on the angle between the incident sunlight and the sea-scattered light reaching the eye. Further, the track of sunlight in water could be seen under certain conditions out to considerable depth. Now, Lord Rayleigh had argued that the blue of the sky is due to scattering of sunlight in the following way. Purely statistically, at a given instant some regions of air are denser, some others rarer. Since the refractive index of air depends on density, these spontaneous density fluctuations mean that the refractive index fluctuates randomly. This scatters sunlight; the extent or intensity of scattering depends on angle as well as on light wavelength, increasing inversely as the fourth power of the latter. Thus the blue part of sunlight is scattered much more than the longer wavelength parts. There is every reason to expect that similar fluctuations in density should occur in water as well and so the same scattering process should be operative. Raman pursued this idea vigorously, and produced a fairly detailed analysis of the colour of the sea rather soon (*Proc. R. Soc.*, 1922, **A101**, 64–80, and a monograph entitled 'Molecular diffraction of light' published by the Calcutta University in 1922). The point is that this scattering is due not to extraneous causes such as dust or other substances, but is due to density fluctuations.

Raman's sustained efforts at observing this Rayleigh scattering in dust-free fluids in the laboratory originate with this experience. These bore fruit in several spectacular ways. Some of these are subjects of the next few reprints.

Raman was probably the first person to appreciate the implications of light scattering from glassy or amorphous solids, and viscous liquids. Glasses are generally made by rapidly cooling melts or liquids, the cooling rate being large enough to prevent crystallization or formation of the crystal. If the arrangement of atoms in the glass is just the same as in the melt, but is frozen-in, then light would be scattered from the frozen-in density fluctuations appropriate to that for the melt *i.e.* the liquid. Another possibility is that atoms in a glass are positionally well ordered, almost as in the corresponding crystal, but that the constituent anisotropic molecules are not orientationally ordered, *i.e.* there are considerable orientational fluctuations (frozen-in again). A third possibility is that especially in chemically complex glasses (*e.g.* optical or window glass) there are sizeable compositional fluctuations. In general, things tend to separate out at low temperatures (entropy is less at lower temperatures!) so that these compositional fluctuations tend to increase on cooling. In a particular glass, all these effects could be present to different degrees at different length (and time) scales.

In the very first brief paper on the subject [P3] Raman argued, from the rather large Rayleigh-like scattering of light in glasses, that there are sizeable frozen-in density fluctuations in them, comparable to those in liquids. Thus a quasicrystalline model for the glassy state, with sizeable crystallites, is ruled out. To confirm for himself the hypothesis that the scattering of light from glasses is due to intrinsic fluctuations and not accidental 'inclusions' and inhomogeneities, Raman took a dozen optical glasses with graded refractive indices and studied the intensity and the depolarization of light scattered from these [P11]. He found that the former increases and the latter decreases as the refractive index increases. This systematic dependence suggests that the scattering process at work is intrinsic, related to their 'optical density' and is not extrinsic. These contributions mark the beginning of a powerful way of probing a class of systems and phenomena not fully understood yet.

Glasses are strange systems which have fallen out of thermal equilibrium in regard to some degrees of freedom (or configurations) and are in equilibrium as far as other degrees of freedom (*e.g.* local atomic vibrations) are concerned. That is, the distribution of energy in some arrangements of atoms or molecules cannot be described by a temperature, while for some other arrangements it can be! The dynamics of this process, *i.e.* how it occurs, is an area of great current interest. Light-scattering techniques are much more sophisticated now and time-dependent processes are routinely studied. Fascinating very slow relaxation processes have been uncovered. However, one still does not have a deep understanding of these phenomena which are common to all glasses.

Another contribution in the same general area is light scattering from viscous liquids [P9]. Raman was fascinated by the following idea, due primarily to Brillouin. The thermal (temperature-induced) agitation of atoms in a liquid (more clearly in a solid) can be thought of a sum (or superposition) of sound waves of different wavelengths, amplitudes and directions of propagation. Scattering of light from one such wave will lead to a light wave with a slightly different (shifted) direction of propagation and nearly the same frequency just as happens when light is incident on a diffraction grating. This Brillouin line was looked for by Raman and coworkers. Now if the sound wave damps out quickly, such a distinct line won't be seen. The damping is due to viscous friction in a liquid, and will thus decrease as temperature increases (and fluid viscosity decreases). Thus on increasing the temperature of a liquid, the Brillouin line should appear; this was exactly what Raman and Raghavendra Rao found. This also is an active current area of research; one would like to probe and understand the way the Brillouin line disappears as one approaches the glass transition marked by a catastrophic viscosity increase.

The paper on optical behaviour of protein solutions [P5] is again well ahead of its time. Whereas large protein molecules in solution were thought of as particles of dust leading to haze or light scattering, Raman considered them to be a gas of particles with a temperature, compressibility, etc. It turns out that this gas or fluid changes its nature (*e.g.* from gas to liquid) as its density, or the medium in which the molecules are suspended, changes. At such a transition point, fluctuations in density are very prominent, and we expect the same excess scattering of light as occurs for example at the

liquefaction point of carbon dioxide. The study of phase changes in polymers, colloids and gels has emerged as a major field and light scattering is an important tool for monitoring molecular movements, arrangements and cooperative changes. This was probably the first paper in which one such object (protein solution) was thought of as a thermodynamic system.

Raman's interest in understanding the arrangement of molecules in dense systems such as liquids led to the pioneering use of X-ray scattering (diffraction) for probing their structure. Raman and Ramanathan had realized in 1923 that since X-rays have wavelengths of molecular dimensions, small-angle scattering is related to the statistical density fluctuations described earlier but large-angle scattering is a direct probe of local molecular arrangement. This large-angle scattering shows up as haloes [P4]. Raman and Sogani compared the haloes for two organic compounds, hexane and cyclohexane, and argued that the differences are due to specific differences in molecular shape. This is the first work on X-ray diffraction as a structural tool in liquids. The work would have been complete if the authors had realized that the Fourier transform  $g(r)$  of the observed intensity  $S(q)$  (as a function of wavevector change  $q$ ) gives the two-particle correlation function or the probability of finding two molecules a distance  $r$  apart, a quantity of direct physical appeal. This was done by Zernicke and Prins in 1927.

The papers P6, P7 and P12 describe the most celebrated contribution of Raman to science, namely the Raman Effect. Raman, his students, and coworkers had been investigating the scattering of light from liquids since 1921 or so. Most observations, some of which have been described above, could be explained by assuming light to be a classical wave scattered by spontaneous fluctuations in the medium. However one persistent phenomenon did not fit into this pattern; it was dubbed 'weak fluorescence' to begin with. Clues about its nature and evidence for its general occurrence, were obtained over the years. One such is the following. By using a pair of complementary filters, *i.e.*, filters such that one filter blocks the colours that the other transmits, Raman and Krishnan found the following: When both the filters are placed in the path of the beam incident on the pure fluid no scattered light is seen. However, if one filter is placed in the path of the incident beam and the other in the path of the scattered beam, some weak fluorescence could be seen. This clearly means that the colour (or wavelength) of the light transmitted by the first filter changes on scattering by the fluid so that it is no longer exactly complementary to the other filter and is therefore not fully blocked by it. Raman was reinforced in this belief by the then recently discovered Compton Effect in which the wavelength of X-rays hitting a 'free' electron is changed. He reasoned that there could be an optical analogue of the Compton Effect, namely that a light wave changes its wavelength (or frequency or energy) on being scattered by an atom or molecule. To check this, a source emitting light of a single colour or wavelength is needed. An intense mercury vapour lamp with proper filters is such a monochromatic source. When the scattered light was viewed by a spectroscope (in which light of different wavelengths shows up as differently placed lines) Raman found, in addition to the line corresponding to the original wavelength, another line with a shifted (increased) wavelength. In some substances, more

than one line was seen; there were also lines with reduced wavelength. The spectra were recorded, and the papers reprinted here show some of them.

Why is this 'new radiation' important? With his uniquely well-prepared mind, Raman understood it all. Firstly, it is striking evidence for the quantum nature of light. A light quantum hits a molecule, and excites one of its internal modes. The remaining electromagnetic energy comes out as a light quantum or photon of reduced energy or increased wavelength. If the light quantum absorbs a quantum of internal molecular excitation, the outgoing photon has higher energy or shorter wavelength. Thus Einstein's ideas (put forward to explain the photoelectric effect) that light energy is carried in quanta, and that this energy is equal to  $(hc/\lambda)$  where  $h$  is a constant called Planck's constant,  $c$  the velocity of light and  $\lambda$  the wavelength, are strongly supported. At a more detailed level, Raman realized that the polarizability of the molecule was involved in the mechanism. (This is the same property which causes the refractive index of the liquid to differ from unity and to depend on light wavelength). Indeed, he realized that a detailed theory of molecular and atomic polarizability, due to Kramers and Heisenberg, suggested the possibility of such an effect.

The other major implication, clear to Raman, was that here was a tool of great convenience, precision and power for studying internal excitations of molecules, *e.g.* their vibrations, rotations, and electronic-excited states. Instead of studying the former by direct absorption in the infrared and far-infrared, one could conveniently investigate them in the optical region, as energy differences. Now molecular structure and binding are the backbone of chemistry, so he foresaw that this new branch of spectroscopy would be important for chemistry. With the advent of lasers (monochromatic light sources of great intensity and coherence) Raman spectroscopy became a standard physico-chemical technique.

The availability of lasers has brought about an explosive increase in the number of light-scattering experiments, as several articles in this volume describe. In his Nobel lecture, Raman said: "The universality of the phenomenon, the convenience of the experimental technique and the simplicity of the spectra obtained enable the effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry. Indeed, it may be said that it is this fact which constitutes the principal significance of the effect. The frequency differences from the spectra, the width and character of the lines appearing in them, and the intensity and state of polarization of the scattered radiations enable us to obtain an insight into the ultimate structure of the scattering substance. As experimental research has shown, these features in the spectra are very definitely influenced by physical conditions, such as temperature and state of aggregation, by physico-chemical conditions, such as mixture, solution, molecular association and polymerization, and most essentially by chemical constitution. It follows that the new field of spectroscopy has practically unrestricted scope in the study of problems relating to the structure of matter. We may also hope that it will lead us to a fuller understanding of the nature of light, and of the interactions between matter and light". The prophecy has been fulfilled, I think even beyond the dreams of its visionary discoverer.

The paper in this collection on anomalous diamagnetism [P8] is an example of the quickness and richness of Raman's scientific imagination. Diamagnetism is due to electrons circulating in closed (atomic) orbits. Ehrenfest had suggested that the large diamagnetism of bismuth implied that in crystalline Bi electron orbits are specially large. Raman argues in this paper that many facts *e.g.* large change of electrical resistance in magnetic field, anomalous Hall Effect, large change of size in a magnetic field, change of these properties with temperature, are all connected with this. Now with hindsight (as well as the idea of holes and an extremely detailed knowledge of electronic states in Bi) it appears that many of the suggestions are not correct, but let us just look at the quick reach!

The paper with Nagendra Nath [P13] is one of a series of five, in which a phenomenon first observed by several others, was analyzed in a characteristically direct fashion. A high-frequency sound wave propagates in a liquid, and on being reflected by a plane boundary wall, forms stationary waves, or fixed sinusoidal patterns of lower and higher liquid density (and hence refractive index). Now suppose a plane light beam is incident on this. It will be diffracted. The pattern of intensity of diffracted light is observed to be very complex, with a large number of maxima and minima, and considerable wandering of their relative intensities as the angle of light incidence or sound wavelength are varied. Raman and Nath assumed to begin with that the periodic change in refractive index affects only the phase of the plane wavefront sinusoidally. Thus the outgoing wavefront is no longer planar, but corrugated. They calculated diffracted beam intensities, and showed that the complex observations are explained simply. In further work, the assumption that only the phase changes (valid if the light wavelength is much shorter than the sound wavelength) was given up, and amplitude modulation also considered. This whole work is remarkable for its perfection (a well-defined, interesting and rich phenomenon was completely explained theoretically), for its prototypical nature, and because it is a primarily theoretical contribution from a great experimenter. (Contrary to popular belief Raman not only had a sure and creative grasp of theoretical concepts and principles, he was also conversant with theoretical methods, and of course in detail with the great masters *e.g.* Rayleigh, Helmholtz, as well as with the theoretical papers of relevance to his interests).

The latest paper reprinted here [P10] reports a discovery: the soft mode. Many crystalline solids change their structure as a function of temperature, pressure, or both. If the change or transition is continuous, one can imagine a particular distortion or movement of atoms leading to the new structure. Now in a crystalline, harmonic solid, all arrangements of atoms can be described in terms of normal modes of atomic oscillations about a mean position. Thus as the point of transition is approached, that mode of oscillation which corresponds to the displacements leading to the new structure becomes soft, *i.e.* easily excited or of low frequency. This was exactly what Raman and Nedungadi observed in quartz. The particular lattice-vibration mode corresponding to the symmetry change ( $\alpha \rightarrow \beta$  quartz) was seen to become softer and softer as the transition temperature  $T$  is approached. In the 1960s Cochran as well as Anderson showed that the square of the soft mode frequency is proportional to  $(T - T_c)$ . The subject of structural transitions and

soft modes saw considerable activity in the two decades 1960–1979; the pioneering work of Raman and Nedungadi was noted to be the beginning of it all.

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