NUMBER 3



Sir C.V. Raman birth centenary issue





A quarterly journal of higher education sponsored by the University Grants Commission

On the cover this quarter

Sir C. V. Raman was a great personality who influenced Indian and world science for six decades. He is the only Indian scientist who achieved global status without leaving India. At the Raman Research Institute a tree was planted on the site of his cremation. This full grown tree which is a splendid sight from the gallery of the Institute, is symbolic of the fact that in the world of Indian science, Raman stands tallest.

Cover design: P. B. Vidyasagar Photograph: Satish Paknikar



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SUBJECT COVERAGE: This journal deals with education and studies in physics-at the level of undergraduate and postgraduate studies in physics in Indian universities.

⁴ The scope of the journal is wide and it would contain articles that may be of interest to not only physics students but also to students from chemistry, mathematics, engineering and other allied disciplines. It is also expected to provide a forum for teachers of physics in

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Editorial

Sir C. V. Raman—scientist and visionary

Sir C. V. Raman will always be remembered not only for his brilliant scientific career and tremendous achievements but also for his true love of science, courage, Indianness and vision for the development of scientific culture in India. His firm belief that science could be the unifying force of mankind crosses the artificial boundaries of nations. He made significant contributions in several fields such as acoustics, optics, diffraction of light, liquid hypersonics, structure of diamonds and theory of vision. The effect named after him has a glorious history with the unique advantage of having a new dimension added with discoveries such as LASER and photoacoustic spectroscopy. Thousands of research publications have appeared based on his discovery and in future many more will be published.

Sir C. V. Raman had a unique multifaceted personality. He was self confident and decisive. His decisions like marrying outside his caste and inviting a scientist such as Max Born to work at the Indian Institute of Science, are enough evidence for this. He experienced ups and downs, hardships, isolation and even negligence from the scientific and political community. But he never gave up and till the end he pursued his search for excellence. He loved colours and had a special fascination for diamonds. A look at the precious collection at the Raman Institute makes one wonder whether a person could do it single handed. But it is then that we realise how Sir C. V. Raman surpassed us all.

On the occasion of his birth centenary, to summarise his life and work would not be a real tribute to him. One wonders whether his ideas about the development of scientific culture in India, achieving excellence in scientific work and using science as a force for uniting mankind would be relevant today. However,-if one carefully examines the present situation in India, it becomes evident that we need his ideas if at all we wish to attain any distinction in the scientific world. Self-reliance and hardwork were his keywords. His dedicated efforts to develop and use self-made instruments for research are badly needed at the present moment. In India we are fast loosing our instrumentation culture. The plans and programmes of research should be followed totally and short cuts should be avoided was one of his demands. Excellence should be nurtured and should not be killed at the cost of mediocrity. Applied research is important but should not be at the cost of academic achievements. Scientists should be given a free hand and in turn scientists should not indulge in political activities. If we could really plan to bring these thoughts into practice that would be a real tribute to him.

This issue is dedicated to Sir C. V. Raman.

The relevance of Raman

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Raman was born almost a hundred years ago and yet he is today perhaps the best known Indian scientist. Naturally his famous discovery that led to the Nobel prize has a lot to do with this. We must, however, be objective enough to concede that brilliant though Raman was, he was but one among the many bright stars in the firmament of science. On the other hand, I personally feel that Raman needs to be remembered even more for many of his personal qualities like his indomitable spirit, his fierce Indianness and his passionate commitment to science--qualities we very much need at present.

To understand Raman's personality, one must first take a quick look at his life. Raman was born on 7 November 1888, the second son of Chandrasekhara Iyer, a college teacher of diverse abilitiesintellectual, athletic and cultural. As a child Raman displayed unusual scholarship, and at the incredibly young age of eleven, passed the Matriculation examination. After two years of Intermediate study he went to Madras to study for his Bachelor's degree in the prestigeous Presidency College. Raman was physically unimpressive, and no one so young had ever attended college. But in the B.A. examination, Raman stood first in the University and won many medals. Already he was beginning to acquire a reputation for his extraordinary command of the English language, and his deep interest in science. His teachers adviced him to go to England for higher studies but the civil surgeon of Madras who examined him advised against such a step as he felt that young Raman would not be able to sustain the rigours of the English climate (sane advice one would say, especially when one recalls the hardship experienced by an equally frail Ramanujam). Year later, Raman remarked, 'I shall ever be grateful to this man.'

Unable to proceed to England, Raman continued in the Presidency College to study for his Master's degree in physics. And now his talents really began to blossom. While other students were going through the routine course work, Raman plunged into original research. Making use of the meagre facilities of the laboratory (intended solely for *student* experiments as prescribed in the curriculam), Raman was able to publish two papers in the prestigeous *Philosophical Magazine*. These were the *first ever* papers to be published from the college, and Raman's effort was entirely his own no assistance from anyone. And he was still a student!

In early 1907 Raman passed the M.A. examination, once again standing first and once again sweeping up all the available prizes. What next? Obviously Raman's heart was in science, but there were no opportunities in science at that time for Indians. True there were many scientific departments in India but the professional staff was entirely European; Indians were hired mainly as assistants and ill-paid staff. Even the professors in the various colleges were Englishmen. The only opening available was government service. Raman therefore appeared for the Financial Civil Service examination, and duly stood first despite having to study various unfamiliar subjects like economics, British history and so on. And in July 1907, he arrived in Calcutta to assume office as the Assistant Account General.

Soon after reaching Calcutta, Raman, while riding a tram to work, spotted a board saying 'Indian Association for the Cultivation of Science.' Curiosity impelled him to investigate and he found that the Association had been established some thirty years earlier on the model of the Royal Institution, London, by one Dr. Mahendralal Sircar, a medical practitioner of repute. Sircar had hoped that the Association would be a premier research centre but during his lifetime it was not to be so, and he died a

disappointed man. When Raman went to the Association for the first time, it wore a deserted look; but as far as he was concerned, it seemed to be an ideal place to pursue his research. He sought for and was instantly granted permission by the Honorary Secretary Amritlal Sircar to use all the available facilities and to come and go as he pleased. Such flexibility was needed since Raman had an office to attend. As he said years later, 'my own work at Calcutta commenced in 1907 and was made possible by the special facilities put at my disposal by the Honorary Secretary Mr. Amritlal Sircar who had the laboratory kept open at very unusual hours in order that I might carry on research in the intervals of my duties as an officer of the Indian Financial Department'.

For ten years, Raman lived at two levels. As Ramaseshan describes, '5.30 A.M. Raman goes to the Association. Returns at 9.45 A.M., bathes, gulps his food in haste and leaves for his office, invariably by taxi so that he may not be late. At 5 P.M. Raman goes directly to the Association on his way back from work. Home at 9.30 or 10 P.M. Sundays, whole day at the Association'.

Prior to Raman there were no publications from the Association but now they flowed in a steady stream to journals like Nature, the Physical Review and the Philosophical Magazine. Raman also started a Bulletin of the Association. At the end of a decade, Raman had published over two dozen papers and picked up two research awards. All this in his spare time! Raman was still a diligent member of the Financial Civil Service, and so efficient that his superior officers (all Englishmen) expected him to fise to the highest possible level and become a member of the Viceroy's Council. But that was not to be. In 1917, Raman responded to the call of Sir Asutosh Mukherji, Vice Chancellor of the Calcutta University, to become Palit Professor of Physics. In accepting the professorship, Raman not only sacrificed an attractive career but settled for far less money.

Raman now began operating on two fronts, namely the Association and the University, and it was a new kind of double life. Students flocked to him, the Association began to throb with vitality and its reputation reached far and wide. At last, a

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centre of excellence truly Indian in origin had emerged. This is exactly what Mahendralal Sircar had dreamt of, but unfortunately he was not around to see the miracle of Raman.

In 1928 the Raman effect was discovered, and honours were poured on the discoverer. It was his hour of glory, but the fairy tale soon came to an end. Unpleasantness erupted, and Raman was voted out of the Honorary Secretaryship of the Association which he had held for over a decade after the death of Amritlal Sircar. Raman was deeply affected by this rejection. While many reasons were attributed at the time the episode occurred, the latter was in fact symptomatic of deficiencies in our scientific ethos.

Around this time, Raman was offered the Directorship of the Indian Institute of Science, Bangalore. This was a most prestigeous job, and he was the first Indian to be appointed to that post. But soon he was the target of critical attacks, and within three years he had to resign from the Directorship. At that time, all the problems were attributed to Raman's (alleged) mismanagement but today when one examines the whole affair, one finds the problems to be deeper in origin.

Two strong rebuffs in quick succession of each other especially after he had reached the summit, left Raman completely shattered; and the damage was far greater than people realized at that time. Raman withdrew, concentrated on research, and once again gathered students around him. While many a star emerged from this new school, the magic of Calcutta could not be recaptured. Raman had slowed down, and he became prone to occasional errors of scientific judgement. However, he stuck steadfastly to science, and there were also great flashes like the Raman-Nath theory and the discovery of the soft mode.

In 1948 Raman retired as the Professor of Physics and moved over to his own research centre, the Raman Research Institute. He refused government support since he disliked the accompanying, irksome constraints. The going was tough especially since he had lost heavily through the collapse of a financial investment he had made. But he pulled through by starting a few industries, the earnings from which he ploughed back into his institute. As far as research was concerned, it was almost a hark back to the very early days—he worked mostly alone and with simple equipment.

For quite a while during this final phase, Raman was a recluse. The odd statements he made were misinterpreted and quoted out of context. But towards the end he came out of his shell and mixed freely with young persons because in them he saw the future of the country. There is a nice photograph in the Institute showing a seventy year old Raman romping in the Institute garden, with twenty or thirty children. One is reminded of a touching short story by Oscar Wilde.

A great admirer of the Buddha and the Mahatma, Raman instituted a Gandhi Memorial Lecture which he himself delivered every year till his death. The end came peacefully in November 1970.

With this background, we are now in a position to make an appraisal of Raman. The first characteristic that is striking is his capacity to plunge into research without waiting for anything. He did that in college and he did so again at the Association. Indeed, short spells at Rangoon and Nagpur where he was posted as a Currency Officer could not keep him away from research; he drew whatever assistance he needed from the local science college. Much later when he moved to his own institute, it was far from complete. There was no electricity and there was no water supply but these handicaps did not deter him. He used sunlight to study the spectral properties of flowers! One of course agrees that modern research is often not that simple but that is not the point. The point is Raman's spirit; he engaged in science with whatever resources he had. It did not matter what the others thought of it. And he did not engage in research just to keep from being idle. He was passionately involved with his work

This is a lesson for those who often complain about lack of facilities and resources. Indeed this is very true in so far as we try to do the latest kind of research conducted in other countries. But is it true that that is the *only* kind of research which can bring pleasure and intellectual satisfaction? Raman repeatedly went back to natural phenomena—colour of mixed plates, colour of heated steel, colour of gems, and so on. One should not jump to the conclusion that such problems are trivial—they certainly are not if one digs deep. Thus, for example, Raman found a connection between the whispering gallery phenomenon in St. Pauls, and iridiscence of pearls! Let us in this context recall the famous Brownian motion phenomenon. It is not merely the wild dancing of a pollen grain, rather it is the quintessence of the random walk phenomena.

There is often a mistaken notion that research of the type I am discussing is not contemporary and that it would not make the *Physical Review*. Both are false notions. Such simple things as dendritic growth (studied, as one American friend told me, with a 5/- apparatus!) can and have become fashionable because sufficient physics has been put into the study. What is there to prevent *us* from doing it? Indeed we enter such subjects *only* when they become fashionable elsewhere!

Before leaving this theme, I would like to pick one more example from Raman's research and that relates to his extensive studies on the violin (probably this would come as a surprise to most readers). Raman's pioneering work has been actively followed up in America, Europe and Japan, and there is today an active school of research in violin physics. Raman started investigating Indian musical instruments like the veena but gave it up as he became absorbed with studies on the scattering of light (culminating, of course, in the discovery of the Raman effect). It is a pity that very little work has been done subsequently on our musical instruments. And there is so much one can do like making holograms, measuring frequency spectra and so on. Indeed there is an almost urgent necessity to completely characterize our instruments for the art of making such instruments which, until now was mainly handed down from father to son, is dying slowly due to rapid changes in our society. More than anything else, such independent enquiry would enable us to become mentally free and not feel we are good only if someone else publishes our papers, pats up on the back, and invites us for conferences.

One of the charges made against Raman when he was the Director of the Indian Institute of Science was that he was against applied research. Many

people think the accusation is valid, for did not Raman criticize the CSIR laboratories and did not Raman extol those in ivory towers? Superficially it would seem so but not if one examines the issue in depth and without bias. Raman was as much interested in science working for the benefit of India as any other patriotic Indian would be. But there is a manner in which science percolates, becomes applied science and finally ends up as technology. There is no point in short circuiting this complex route, and that precisely is what most people (politicians, 'leaders', bureaucrats, indeed even technocrats) constantly try to do. Unfortunately, Raman did not clearly spell out the way this complex process must be organised; he merely condemned the short circuiting. One cannot of course lay the entire blame on him. He was a thorough bred scientist, and he could feel it in his guts that the whole approach was wrong; and he said so bluntly. He had no time for niceties or explanations.

There is another side to this picture which becomes evident when we examine Raman's attitude before coming to broader issue. It is hardly known that even at the very time when Raman's detractors were accusing him of an anti-application bias, Raman was personally a consultant to many industries and bodies. For example, he advised the railways on how to preserve timber, and his advice saved the railways several lakhs of rupees! Indeed, he himself started an industry for the manufacture of gas mantles since the gas lamp was widely used in India. The manufacturing process was evolved by him in association with a chemistry student.

Raman had no quarrels with scientists acting as industrial consultants and believed this was most desirable since thereby they could often bring to bear a penetrative analysis of the problem concerned. But at the same time, he stoutly opposed the idea that laboratories of the *academic* institutions do things which rightly belonged to the industrial domain—like how to extract oil more efficiently from seeds, and so on. Such work when carried on in academic institutions does tend to give the impression that the institution is doing relevant and useful work. But it is not realized at what cost! It greatly dulls the vision of the scientist, narrows his perspective and pretty soon makes him useless for anything creative. More important, the students are not faced with any *intellectual* challenges.

Our society has not learnt that research covers a *wide* spectrum and that there is a delicate alchemy involved in converting basic discoveries into useful products. Instead it expects the scientist in the laboratory—be it of a university, or of the CSIR, to exploit a scientific idea, develop a product, market the knowhow, prepare the documentation and even train the recipient of the knowhow! Nowhere in the world is this done, and this in a nutshell is what Raman was protesting against, though in his own characteristic fashion.

People who accused Raman of an anti-application bias failed to note the tremendous support he gave to instrument development. At the Association, for example, his students devised various apparatuses for accurately measuring the diamagnetic susceptibility of gases, liquids and crystals. Each system required a different approach. The Association workshop assisted in the fabrication. At Bangalore, Raman tried a similar approach, and in fact the Workshop was able to revive an abandoned liquid-air plant and a tilting furnace. He regarded these as exercises in applied science but the management ruled that the Workshop's prime purpose was the training of students! I bring up the question of instrument building for research because today instrumentation development has completely disappeared from the Indian scene. We rely on imported, push-button instruments and are prepared to wait till doomsday for such conveniences! There is no instrumentation culture whatsoever; it has been completely wiped out, even as our import bill has soared to astronomical figures. In the sixties the import mania was not that high, but even so, Raman spoke out harshly against it: 'We are paying for our ignorance', he declared. After he passed away, there was no one left even to protest! One wonders what his comment would be at the present state of affairs!!

It is a little known fact that before being appointed to the Palit Chair, Raman was asked to go to England for training! Raman flatly refused, even though it meant missing an opportunity to go abroad—which he had not yet done at that time.

He bluntly said that he was ready to train Englishmen, and that he did not need any training from them! At the same time, he recognized that there were men of eminence abroad, and that young students often went abroad to learn from such masters. Raman appreciated the motivation of such young aspirants but felt, nevertheless, that the training they received would not be suitable to them when they came back as it was received in an alien environment. So Raman tried to bring to Bangalore many eminent scientists who were then fleeing Hitler's Germany (like Max Born, Schrodinger, Peierls, Ewald and so on). But he failed since there was no support from the Establishment. One cannot but feel that Indian science lost a golden opportunity for rejuvenation, especially when one recalls the gains reaped by America.

Things have changed considerably since Raman's days—there is a lot more money for science and many avenues have been opened. And yet, certain maladies which were present then continue to be virulent.

At the heart of the problems Raman faced in Bangalore was a clash between excellence and mediocrity. The latter was well entrenched in a place it had no right to be in, and Raman resisted the force. This battle for excellence in science in India has been continuing ever since, and one regrets to say that excellence has still to become a way of life in our scientific community. In a complex society like ours this is not easy but at the same time, as Raman firmly declared, 'Nothing is so detrimental to the growth of science in an institution than the existence of dead-wood floating aimlessly which cannot participate in the scientific growth of an institute.' We see plenty of dead-wood everywhere but what are we doing about it? Shouldn't we at least *try* to do something?

Today we find a large number of our young people leaving the country, this despite the fact that things are much better now than before. It is sad to think that the idealism which swayed Raman and people of his generation has practically vanished. When Raman had to resign from the Directorship of the Institute at Bangalore, there was widespread speculation in the press that he would be settling abroad. Nothing could have been easier for him, for he had all the credentials in the world. But he chose to remain and rough it out here. That speaks for his character and tenacity.

After Independence, he could have got any position he wanted in the scientific establishment. Indeed he was even sounded out for the Vice-Presidentship, but he preferred the pursuit of science to power and position. He was quite unique not only in his passionate commitment to science but also for being *active* in research till the very end. In fact, his last paper was published just a few months before his death.

Raman was also unique for his forthrightness. He feared no man, and was one of those rare and courageous persons who did not hesitate to call a spade a spade. On the occasion of his 80th birthday there was a function when speaker after speaker extolled his science. When it came to Raman's turn to reply to the felicitations, he remarked, 'I wish someone had said that I had the heart of a lion!'. How we miss such a person!!

Vision or confidence?

Though Raman effect created quite a sensation in scientific world, the discovery of Raman effect was no accident. It was an outcome of seven years of involved research. However, Sir C. V. Raman told Sir Asutosh Mukherjee in 1925 itself that given the facilities he would bring a Nobel prize within five years. How true was this conviction that he was awarded Nobel prize in 1930.

P. B. VIDYASAGAR

Professor Sir C. V. Raman His life, personality and scientific achievements

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1. Introduction

Major advances in knowledge in any branch of science are always associated with the names of outstanding individuals whose work and contributions are important landmarks in the progress of science. To the student of science, the biographies of such leaders have a fascinating appeal lending a human touch to the study of science which is essentially an expression of the creative urge of the mind and intellect. Very early in the study of science we become familiar with names such as Newton, Kepler, Helmholtz, Faraday, Maxwell, Kelvin, Rayleigh and others. The list goes on lengthening as we go deeper and deeper into the subject. Professor Sir C. V. Raman whose birth centenary falls on 7 November 1988 belongs to this galaxy of scientific immortals. With his towering intellect and scintillating personality he dominated the scientific scene in India for over six decades. His life and achievements are the saga of Indian science and a source of perennial inspiration to young scientists.

Raman had a sweeping vision that embraced several branches of science to many of which he made significant contributions. His name is, of course, associated with the discovery of the 'Raman Effect' for which he was awarded the Nobel prize. Beginning from 1987 the Government of India have decided that the date of Raman's discovery (28 February) should be commemorated as the National Science Day.

The outstanding qualities in Raman that made a deep impression on those who came in contact with him were his courage and self-confidence, his single-minded devotion to the pursuit of knowledge, his unbounded love of nature and the scientific exhuberance that he radiated. As a gifted speaker with eloquence of language and lucidity of exposition his public lectures on scientific topics drew large audiences.

2. The spirit of science

On 22 December 1968 when he was over 80 years old, Raman delivered a lecture at the foundationstone laying ceremony of the Community Science Centre at Ahmedabad. The topic of his lecture was: 'Why the sky is blue'. It was an open air function on a sunny forenoon. Raman was addressing a large gathering of students, teachers and the general public. This was a most inspiring lecture which every student of science should read and reflect upon. Here are some excerpts:

'Why is the sky blue? Oh, the scattering of light by the molecules of the atmosphere. I could have dismissed the whole lecture in one sentence "Then Sir", you would ask me, "Why all this lecture?" Because my young friends. I want you to realise that the spirit of science is not finding short and quick answers. The spirit of science is to delve deeper-and that is what I want to bring home to my audienceand that is what I want to bring home to my audience-and deeper. Don't be satisfied with short, quick answers. You must never be content with that; you must look around and think and ask all sorts of questions; look around the problems and search, and search and go on searching. In the course of time you will find some of the truth, but you never reach the end. The end, as I told you, is the human brain, and that is very far away yet. This is the spirit of science . . .

I think that dreams are the best part of life. It is not realisation but the anticipation I am going to make a discovery tomorrow, that makes a man of science work hard, whether he makes the discovery or not. And that is what I want to emphasise once again. Science essentially and entirely is a matter of the human spirit. What does a poet do? What does a painter do? What does a great sculptor do? He takes a block of marble, chips and goes on chipping and chipping. At the end of it he produces the dream in marble. We admire it. But my young friends, please remember what a tremendous amount of concentrated effort has gone into producing that marble piece. It is the hope of realising something which will last for ever, which we will admire for ever, that made him undertake that work. Essentially, I do not think there is the least difference whatever between the urge that drives a man of science to devote his life to science, to the search for knowledge, and the urge that makes workers in other fields devote their lives to achieving something. The greatest thing in life is not the achievement but it is the desire to achieve. It is the effort that we put in, that ultimately is the greatest satisfaction. Effort to achieve something, in the hope of getting something. Let it come or not come, but it is the effort that makes life worth living. And if you do not feel that urge towards the search for knowledge, you can never hope to be a man of science. You can perhaps get a job in some of the departments, get a nice comfortable salary in which you don't have to do anything except to wait for the monthly cheque; but that is not science. The real business of a scientific man is to try to find something and to look forward to the acquirement of knowledge.

'The subject of my lecture is not the blue of the sky but as you must have understood by this time it is the spirit of science. What is science? And how can we in this country hope to advance science? How can we try to really make ourselves worthy of our ancestors in the past? That is the real topic of my lecture Science never stops. It is going on. The more you find, the more appears that you have to find. It is an endless quest and every new discovery opens new paths for discovery. New questions arise requiring new answers.

The quest, you see, is the more, the deeper you go you keep your eyes open and you see that all around you the whole world bristles with problems to solve. But you must have the will to solve it; and you must have the strength of mind to keep going at it until you get something. That is the lesson which I want to bring home to the younger generation in front of me.

What is the use of all this? Here again, I want to stress the philosophy of my life. Never to ask what is the use of all this. As I told you before, it is the striving that is worthwhile. Because we have certain inherent powers given to us to use—observation and thinking—we must use them. The more we use them the sharper they become, the more powerful they become and ultimately something will come out of it so that humanity is benefited, science is benefited. Ultimately the aim of scientific knowledge is to benefit human life. And that comes automatically because the problems with which we are concerned in science are always those that lie nearest to hand. They are concerned with things around us. So long as we deal with the problems which arise out of our environment, you never can say that any particular piece of work can be useless. The most important, the most fundamental investigations, though at first might seem an abstraction of nature, are precisely those, which in due course, affect human life and human activities most profoundly. This is a very heartening thing because one should not think that scientific work in order to be valuable should be useful. Scientific work is valuable because it will ultimately prove its value for the whole of human life and human activity. That is the history of modern science. Science has altered the complexion of things around us. And precisely those scientists who have laboured, not with the aim of producing this or that, but who have worked with the sole desire to advance knowledge, ultimately prove to be the greatest benefactors of humanity'.

3. The Raman Effect

In 1924 Prof. Raman was elected a Fellow of the Royal Society of London—a very prestigious honour. He was then 36 years old. At a function organised to felicitate him, one of his admirers asked him: 'What next?'. 'The Nobel Prize', was his immediate reply. Perhaps there is no better illustration of his tremendous self-confidence.

The announcement of the discovery of the Raman Effect appeared in the Press on 29 February 1928 before it appeared in the leading scientific journals in India and abroad. Raman was then conducting his researches at the Indian Association for the Cultivation of Science at Calcutta. In a lecture under the title *A New Radiation* delivered on 16 March 1928 at Bangalore under the auspices of the South Indian Science Association, Raman gave a brilliant exposition of the studies leading to the discovery. He concluded his lecture with the following prophetic words:

We are obviously at the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and the wave theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out. Raman was under 40 years of age when he made the discovery. Two years later (in 1930) he was awarded the Nobel prize. Numerous other honours, distinctions and recognitions followed in an endless stream throughout his life.

In September 1978 the Sixth International Conference on Raman Spectroscopy was held at Bangalore 'to commemorate the 50th Anniversary of the Discovery by C. V. Raman of the Effect which bears his name'. Several scientists from India and abroad attended the conference. Rich tributes were paid to Raman who was not alive when the Golden Jubilee of his discovery was being celebrated.

The Raman Effect has had a remarkable history during the decades following its discovery. After an explosive growth with thousands of research publications in the early years, there was a gradual slowing down of the research output. A new revolution in Raman spectroscopy set in around the 1960's with the discovery of the LASER as a powerful beam of monochromatic radiation. Raman spectra of substances which could only be photographed and studied after several hours and even days of exposure in the early years could now be recorded and studied in fractions of a second with very small samples of materials. This was a great technological advance giving rise to many new applications of Raman Effect in industry, biology, atmospheric sciences and so on. Side by side the theoretical aspects of the subject have also expanded vastly.

4. Raman's scientific career and achievements

Raman's scientific career and achievements are phenomenal and legendary. Surveying his life one is left wondering how a single individual could achieve all that he achieved in his life time. He inspired and guided dozens of young persons who went to work in his laboratories, many of whom in later life became teachers and leaders of research in their respective disciplines carrying forward the message of the great master.

Raman's life can be broadly divided into four periods:

- I. Early years (1888–1917)
- II. The Golden Era at Calcutta (1917–1933)
- III. The years at the Indian Institute of Science, Bangalore (1933–1948)
- IV. The years at the Raman Research Institute, Bangalore (1948–1970).

5. Early years (1888-1917)

Raman who was the second child of his parents, was born in a small village near Tiruchirapalli (Trichy) on 7 November 1888. The family for many generations had been engaged in the profession of agriculture. Raman's father broke off from the tradition and became a teacher in the local English High School. From there he migrated to Visakapatnam (Vizag) to take up the position of a lecturer in physics and mathematics in the local college. Raman was then 3 years old. For the next ten years Raman had his education at Vizag. He matriculated at the age of 11 and passed his Intermediate at the age of 13. He won a scholarship and joined the Presidency College at Madras. He passed the B.A. degree in 1904 winning the first place with gold medals for English and physics. He took his M.A. degree at the age of 18 in the first division with record marks and gold medals.

Raman's professors found him to be remarkably intelligent and he received from them certificates such as: 'The best student I have had in 30 years'; 'an unusual appreciation of English literature'; 'a facility for idiomatic expression'; 'possessing great alertness of mind and strong intellectual grasp'; 'a young man of independence and strength of character', etc.

As a student while measuring the angle of a prism with the college spectrometer, Raman noticed some diffraction bands, the study of which formed the subject of his first scientific paper published in the *Philosophical Magazine* (London) in 1906. This was followed by a note in the same journal on a new experimental method of measuring surface tension. These papers were communicated by the author himself and contain no acknowledgements. Raman was then 18 years old.

When he passed the B.A. degree examination with high distinction, his teachers suggested that he should go to England for further studies. However, he was medically disqualified by the civil surgeon of Madras. Referring to this incident Raman is reported to have remarked in later years: 'I shall ever be grateful to this man'.

When Raman graduated, the pursuit of science in India offered little scope for young and talented persons. Following the advice of his professors he appeared for the competitive examination for the Indian Audit and Accounts Service held in 1907 and topped the list. He joined the Indian Finance Department as Assistant Accountant General at Calcutta in June 1907. He had married just before his posting. Lady Raman, as Mrs. Raman came to be known in later years, was a worthy and life-long companion to him.

The next 10 years of Raman's life were spent in Government service mostly at Calcutta with short spells at Rangoon and Nagpur. Even while in Government service with a secure job carrying good emoluments and excellent career prospects, Raman's passion for science continued unabated. Despite his pressing official duties he sought and found opportunities to pursue experimental investigations. One day while travelling by tram at Calcutta shortly after taking up his appointment, he happened to see the sign-board of the 'Indian Association for the Cultivation of Science' at 210 Bow Bazar Street. Raman immediately got down from the tram, entered the building and had a meeting with Dr. Amritlal Sircar, Hon. Secretary of the Association, whose father, the late Dr. Mahendralal Sircar, had established the centre in 1876 for the promotion of scientific research. Raman was full of enthusiasm and asked Dr. Sircar whether he could spend his spare time to conduct scientific research at the Association. Despite the purpose for which it had been founded, no original scientific research had been pursued at the Association over the years and it was in a neglected condition at the time of Raman's visit. Dr. Sircar is reported to have embraced young Raman and told him that they were waiting for a person like him all those years. This was the starting point of Raman's long association with the Indian Association for the Cultivation of Science at Calcutta, which he eventually transformed into a centre of original research of world fame.

From 1907 to 1917 Raman spent all his leisure working at the Association. His routine was to work at the Association from 5.30 to 9.30 A.M. everyday, go home to bathe and eat, rush to the office, and again work in the Association in the evening up to 9.30 P.M. Sundays were devoted to full-time work at the Association. Raman had a faithful assistant in Ashutosh Dey, Assistant Secretary of the Association, who lived on the premises.

Raman's early researches at the Association were concerned with the acoustics of Indian musical instruments—violin, veena and mridangam. He started the Bulletin of the Association and published several monographs incorporating the results of his studies. In course of time the 'Bulletin' became the 'Proceedings' and eventually the Indian Journal of Physics.

Raman made a profound impression on the leading educationists and citizens of Calcutta. His unusual gifts, abilities and talents were spotted by the late Sir Ashutosh Mukherjee who was then engaged in organising post-graduate teaching and research at the Calcutta University. He felt that Raman was the fittest person for the newly created 'Sir Taraknath Palit Professor of Physics' at the University College of Science, and he was able to induce Raman to resign his Government job and accept the Palit Chair. While laying the foundation stone of the University College of Science, Sir Ashutosh made the following announcement:

For the Chair of Physics created by Sir Taraknath Palit, we have been fortunate enough to secure the services of Mr. Chandrasekhara Venkata Raman, who has greatly distinguished himself and acquired a European fame by his brilliant researches in the domain of physical science, assiduously carried on under the most adverse circumstances, amidst the distractions of pressing official duties. I rejoice to think that many of these valuable researches have been carried on in the laboratory of the Indian Association for the Cultivation of Science, founded by our late illustrious colleague, Dr. Mahendralal Sircar who devoted a life time to the foundation of an institution for the cultivation and advancement of science in this country. I should fail in my duty if I were to restrain myself in my expression of the genuine admiration I feel for the

courage and spirit of self sacrifice with which Mr. Raman has decided to exchange a lucrative official appointment with attractive prospects, for a university professorship, which I regret to say, does not carry even liberal emoluments. This one instance encourages me to entertain the hope that there will be no lack of seekers after truth in the temple of knowledge which it is our ambition to erect.

Raman joined the Calcutta University as Palit Professor in 1917. One of the requirements for appointment to the Palit Chair was that the person selected should have been trained abroad. Raman refused to go to England for this purpose and so the provisions of the endowment were suitably ammended by Sir Ashutosh. At the Science Convention held at Calcutta in 1917 Prof. Raman as President of Physio-Mathematical Section gave a survey of the progress of physics in Calcutta since 1907 as follows:

The ten years from July 1907 to June 1917 which preceded my joining the University of Calcutta as Palit Professor of Physics afforded me numerous opportunities for studying, as an impartial and disinterested observer, the efforts made during the period in this University towards fostering higher studies and research in physics. Looking back over those years, one cannot fail to be struck with the genuine progress that has been achieved and with the fact that today, the Calcutta University can claim to possess a real school of physics, the like of which certainly does not exist in any other Indian university and which even now will not compare very unfavourably with those existing in European and American universities. What has impressed me most is the rapidity of the progress, the position now being very different from what it was 10 years ago, and this is obviously a most hopeful sign for the future . . .

My own work at Calcutta commenced in 1907 and was made possible by the special facilities put at my disposal by the present Hon. Secretary, Dr. A. L. Sircar, who had the laboratory kept open at very unusual hours in order that I might carry on research in the intervals of my duties as an officer of the Indian Finance Department. Gradually others were drawn in to take part in the revived activities of the Association . . .

6. The Golden Era at Calcutta (1917–1933)

Prof. Raman commanded great respect, admiration and appreciation from the authorities controlling

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the Association as well as from the University authorities. In 1919 Dr. A. L. Sircar, Hon. Secretary of the Association, passed away and Raman was elected the Hon. Secretary of the Association, a position which he continued to hold with high distinction throughout the period of his stay at Calcutta. Thus, the Physical Laboratories of the Association as well as of the University College came under the control and direction of Professor Raman leading to intense scientific activity. Raman had taken up his residence at Calcutta just behind the Association building. He had provided a backdoor entrance by which he could enter the laboratory at any time of the day or night. He never worked according to the clock. The name and fame of Prof. Raman and of School of Physics that he had established at Calcutta spread throughout the country and many young and brilliant workers came to Calcutta from different parts of the country to pursue research in his laboratories. The years from 1917 to 1933 that Raman spent as Palit Professor of Physics at Calcutta have been referred to as the *golden era* of his scientific career.

Raman's early researches at Calcutta were concerned with the physical theory of musical instruments and problems in wave optics. He visited Europe in 1921 as a delegate to the Congress of Universities held at Oxford. During the voyage he was fascinated by the deep blue opalescence of the waters of the Mediterranean sea. By some simple observations using a nicol prism he convinced himself that the blue colour arose from the molecular scattering of sunlight by the water and not from the reflection of the blue sky by the sea surface as was then believed. Immediately after his return to Calcutta he started work on the scattering of light by liquids, gases and transparent solids. In these studies he was assisted by a number of brilliant young research students some of whom proved to be able collaborators. Among them the outstanding names are those of K. R. Ramanathan and K. S. Krishnan. Other programmes of work which engaged Raman's attention during this period were scattering of X-rays by liquids, viscosity of liquids, mechanical, electric and magnetic birefringence, etc. All these studies resulted in a growing volume of research papers by Raman and his students

published in leading scientific journals. The culmination of the studies in light scattering pursued assiduously over the years was the discovery of the *Raman Effect*.

It is interesting to recall that the presence of the radiation which later came to be recognised as the Raman effect had actually come to notice by workers in Prof. Raman's laboratory several years before the actual discovery. The first to notice it as early as 1923 was K. R. Ramanathan, in his study of the scattering of light by water. In these studies he used a pair of complementary filters each one of them completely obliterating the light transmitted by the other. With sunlight transmitted through one of the filters focussed on the liquid, Ramanathan noticed that the light scattered in the transverse direction was not completely extinguished when viewed through the second filter which should have been the case if the scattered light contained only the incident wavelengths. This residual feeble light was attributed to 'weak fluorescence' due to impurities, and considerable effort was spent for removal of the suspected impurities by repeated distillation. Nevertheless, the weak residual radiation persisted. In later years this phenomenon was noticed by K. S. Krishnan in several organic liquids which he examined at Raman's suggestion. In all these studies the source of illumination employed was sunlight with a condensing lens. Raman had all along an intuition that this persistent 'weak fluorescence' was something fundamental. He decided to change the source of illumination to the monochromatic radiations of the mercury arc lamp and examined the scattered light through a spectroscope. The discovery of the Raman effect was immediate. This was on 28 February 1928. The report of the discovery appeared in the press on the next day.

It is of interest to recall what Raman wrote nearly 40 years later about how he was led to the discovery:

Later, I became aware of the remarkably brilliant monochromatic illumination which could be obtained by the aid of the commercially available mercury arc sealed in quartz tubes. Towards the end of February 1928, I took the decision to make use of such lamps for all further studies in the field of light scattering.

The success which attended this forward step was immediate and highly gratifying. Experience in working with sunlight indicated the technique necessary for the observation of extremely weak phenomena, viz. the rigorous exclusion of stray light and the conditioning of the observer's vision by a prolonged stay in darkness. On setting up the apparatus and making these preparations. I found that the light of the mercury arc diffused by various materials when examined through a direct vision spectroscope showed the presence, besides the lines of mercury, also of other lines the positions of which varied with the substances under study. Amongst the numerous materials thus examined was a large block of clear ice. This showed sharp displaced lines in the spectrum of the scattered light in approximately the same positions as the rather diffuse bands observed with pure water. Within a few days of the discovery, photographic spectra were successfully recorded in which additional lines showed up very clearly.

Following the discovery, studies on the Raman effect in liquids, transparent solids, gases and vapours were vigorously pursued at Calcutta leading to a large output of research papers in the next few years. Among the young workers associated with Professor Raman during this period was S. Bhagavantam who later became professor of physics and leader of an active school of research at the Andhra University, Waltair.

7. Indian Institute of Science, Bangalore (1933–1948)

In April 1933 Raman left Calcutta to take up the Directorship of the Indian Institute of Science at Bangalore. Along with his move to Bangalore a new department of physics was created at the Institute which he guided and directed till his retirement in 1948. The department of physics began functioning from the middle of 1933 with about a dozen young students, myself being one among them.

This was the time when many famous German scientists were seeking asylum in other countries to escape from the tyranny unleashed by Hitler. Raman attempted to get some of them to India. He succeeded in getting Professor Max Born to a Chair created in the Physics Department. Within a couple of years of his taking charge as Director, serious difficulties cropped up between Raman and the management of the Institute leading to his relinquishing the post of Director in 1937 and continuing only as the Professor of Physics thereafter. Raman's association with the Institute was not a happy one, but he buried himself in his scientific work with bands of young workers who always flocked around him.

Under the leadership of Prof. Raman the Physics Department of the Indian Institute of Science soon attained world fame for the quality and originality of its researches. While problems in light scattering and the Raman effect were studied on a continuing basis, several new lines of work were started leading to significant contributions. Among these was the diffraction of light by ultrasonic waves which was pursued experimentally and theoretically. The Raman-Nath theory of the diffraction of light by ultrosonic waves published by Raman in collaboration with one of his young students (Nagendra Nath) was immediately recognised as a major contribution by the scientific community. Among other studies pursued were Doppler shifts in Brillouin scattering by liquids, X-ray study of crystals, thermo-optic, photo-elastic and magneto-optic properties of solids, infrared spectroscopy, second order Raman Effect, colours of stratified media, etc.

One of the significant events shortly after Professor Raman's move to Bangalore was the establishment of the Indian Academy of Sciences in 1934 with distinguished persons from all branches of science as its Foundation Fellows. Professor Raman who played a key role in the creation of the Academy was elected the President, which position he continued to occupy till his death. Bangalore was chosen as the headquarters of the Academy. Along with the establishment of the Academy were started two monthly publications: Proceedings of the Indian Academy of Sciences, Sections A and B, devoted respectively to the publication of the results of original research in the fields of physical and biological sciences, respectively. All the papers by Raman and his students appeared in Section A of the Proceedings. These two journals of the Academy soon gained world recognition. The Academy celebrated its Golden Jubilee four years ago. The

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regularity with which the Proceedings of the Academy have appeared over the years has been a noteworthy feature during Raman's life time and thereafter.

8. Raman Research Institute (1948–1970)

Shortly after the establishment of the Indian Academy of Sciences, the Government of Mysore gifted a piece of land for location of the Academy. Raman collected private donations for the construction of a building which was commenced in 1943 and completed in 1948. About his travels round the country for collecting funds, Raman is reported to have remarked: 'Our greatest men were beggars, the Buddha, Shankara and even Gandhi'.

On his retirement from the Indian Institute of Science, Raman moved to the new building. A centre of research with Raman as Director and a few research assistants began functioning at this place which came to be known as the Raman Research Institute. Here Raman lived and continued to pursue his scientific interests for the rest of his life. A few research students of outstanding ability who joined the Institute made important contributions to areas such as generalised theory of interference, optical activity in crystals, and so on.

It is appropriate to recall here a memorable passage in which Raman has set out his aims and objectives in creating the Research Institute:

... it is my earnest desire to bring into existence a centre of scientific research worthy of our ancient country where the keenest intellects of our land can probe into the mysteries of the universe and by so doing help us to appreciate the transcendent power that guides its activities. This aim can only be achieved if, by his Divine Grace, all lovers of our country see their way to help the cause—C. V. Raman.

At the Institute, Raman assembled an impressive museum consisting of a variety of minerals, crystals, shells, fossils, birds, butterflies, and many other items of scientific interest. He had a great fascination for gem stones, in particular diamonds, and made a fabulous collection of them to study their optical and other properties. When he was in an expansive mood he would spend hours with an interested visitor taking him round the place and telling him all about the latest studies on which he was engaged, completely oblivious of the time. Raman also reared an impressive garden surrounding the Institute with a variety of trees and flowering plants. Towards the later years of his life he devoted much attention to understanding the physical basis of colour perception by the human eye and the physiology of vision. The amazing variety of flowers in his garden provided material for some of these studies.

Raman was highly critical of the scientific trends in India during the years following Independence, particularly the growing dependence of Indian scientists on foreign institutions for equipment, support and ideas. He disapproved of organisations spending large sums of money for equipment. To him creativity of the mind mattered more than external tools in the scientific exploration of nature. He took pride in the fact that his researches never involved costly equipment. He remarked on one occasion: 'The essence of science is independent thinking, hard work and not equipment. When I got my Nobel prize I had hardly spent Rs. 200/- on equipment'. However, the philosophy of post-independent India was not in tune with such a line of thinking and this led to a widening gap between Raman's views on scientific research and the facts of the Indian scientific scene. In the later years of his life Raman is reported to have remarked: 'My life has been an utter failure. I thought I would try to build true science in this country. But all we have is a legion of camp followers of the West'.

Despite his criticism of the official policies in matters of higher education and scientific research, Raman was respected as the Father of Indian science and the Government of India bestowed on him the first National Professorship to enable him to pursue the work that he liked.

For several years Raman had made it a practice to deliver in the auditorium of the Raman Research Institute the *Gandhi Memorial Lecture* on 2 October. He chose an interesting scientific topic on each of these occasions. The lectures were widely attended by students and the elite of Bangalore. The last such lecture on the 'Theory of Hearing' was delivered by him on 2 October 1970. After a short illness Raman died on the morning of 21 November 1970. His mortal remains were cremated on the grounds in front of the Raman Research Institute. The legendary figure of Indian science joined the list of immortal scientists whose names live for ever.

9. Honours, distinctions and awards

Beginning from his school and college days, the prizes, medals, honours, and distinctions that Raman received in his life were numerous. Some among these are:

- Fellow of the Royal Society, London, 1924 Matteucci Medal of the Italian Scientific Society, Rome, 1928 Nobel Prize for Physics, 1930 Hughes Medal of the Royal Society of London,
- 1930 Franklin Medal of the Franklin Institute of Phil-
- adelphia, 1941

International Lenin Prize, 1957

Raman was Honorary Fellow/Member of several foreign academies and learned societies. More than a dozen universities in India had conferred on him honorary Doctorate degrees. He was President of the Indian Academy of Sciences from 1934 till the end of his life.

In 1929 the knighthood was conferred on him by the British Government. Thereafter he came to be popularly known as Professor Sir C. V. Raman. In 1934 the Maharaja of Mysore conferred on him the title of Raja Sabha Bhushana (The jewel of the King's Court). The title of Bharat Ratna was awarded to him by the Government of India in 1954.

10. Some general remarks

To those who had the opportunity to be closely associated with Professor Raman as his students, this was a unique experience. His total dedication to science, penetrating intellect, extraordinary intuition that enabled him to get at the core of a

problem by-passing complicated mathematics, powers of deep concentration, capacity for hard work, child-like simplicity and great generosity of heart left a lasting impression. It was his practice to go round the laboratory every morning spending some time with each one of the research students, discussing progress in the work, suggesting new ideas and expressing joy at any new result that came to his notice. In his public lectures he would mention the names of students whose work he rated high. In this way he inspired and encouraged the young workers who held him in deep veneration, esteem and affection. No one who came in contact with him was the same as he was before. This transformation that he brought about in generations of young students who came under his influence was a 'Raman effect' at the inner level and one of his invaluable contributions to Indian science.

Raman saw the manifestation of God in the marvels of science. In a conversation with Mahatma Gandhi in 1936 he declared: 'If there is a God we must look for him in this universe. If he is not there, he is not worth looking for. I am being looked upon in various quarters as an atheist, but I am not. The growing discoveries in astronomy and physics seem to me further and further revelation of God. Mahatmaji, the religions cannot unite. Science offers the best opportunity for a complete fellowship. All men of science are brothers'.

It was Raman's firm conviction that the real strength of India lay in the fullest development and utilisation of the intellectual potential of the younger generation which constitutes a third of the country's population. In his characteristic way be stated: 'If they are enthused and if they are instilled with a spirit of adventure, the sleeping giant will wake up and we can conquer the world'.

11. Scientific outlook and scientific discovery

It is appropriate to conclude this article on Professor Raman with a quotation from one of his talks relating to scientific outlook and scientific discovery that would be of interest to young scientists as well as to those of the older age group working in universities and other science oriented organisations:

'... If there is one fact more than any other which stands out in the history of science, it is the remarkable extent to which great discoveries and youthful genius stand associated together. Scores of instances can be quoted in support of this proposition. Indeed, if one were to attempt to write a treatise on any branch of science in which all discoveries made by youthful workers were left out, there would be very little to write about. The fact of the matter appears to be that, other things being the same, the principal requisite for success in scientific research is not the maturity of knowledge associated with age and experience, but the freshness of outlook which is the natural attribute of youth. The conservatism which develops with increasing age is thus revealed as a factor which militates against great achievement in science. The great ideas seem to come most easily to vouthful minds. Since, however, much time is required to work out a new idea properly and fully, age and experience are not altogether useless in science. Up to a certain point, conservatism bred by age may even be useful as a brake on the wilder flights of youthful imagination. Further, even the elderly may, if they so choose, retain and cherish a youthful spirit and outlook. So long, therefore, as they do not allow the conservatism of age to function as a suppressor of youthful genius, the elderly may continue to find themselves useful as guides and inspireres of research. On this view, indeed, the principal function of the older generation of scientific men is to discover talent and genius in the younger generation and to provide ample opportunities for its free expression and expansion.

'... I think it will be readily conceded that the pursuit of science derives its motive power from what is essentially a creative urge. The painter, the sculptor, the architect and the poet, each in his own way, derives his inspiration from nature and seeks to represent her through his chosen medium, be it paint or marble, or stone or just well-chosen words strung together like pearls in a necklace. The man of science is just a student of nature and equally derives his inspiration from her. He builds or paints pictures of her in his mind, through the intangible medium of his thoughts. He seeks to resolve her infinite complexities into a few simple principles or elements of action which he calls the laws of nature. In doing this, the man of science, like the exponents of other forms of art, subjects himself to a rigorous discipline, the rules of which he has laid down for himself and which he calls logic. The picture of nature which science paints

for us has to obey these rules, in other words, has to be self-consistent. Intellectual beauty is indeed the highest kind of beauty. Science, in other words, is a fusion of man's aesthetic and intellectual functions devoted to the representation of nature. It is, therefore, the highest form of creative art.'

12. Raman centenary

The birth centenary of Raman falls on 7 November 1988. The Indian scientific community is planning to celebrate in a befitting manner the Raman centenary which also coincides with the Diamond Jubilee of the discovery of the Raman effect. An International Conference on Raman Spectroscopy is being planned to be held in India to commemorate this occasion.

Raman's life was dedicated to the pursuit of science. His remarkable career and achievements

which brought international recognition to Indian science shine as a brilliant beacon beckoning the scientists of the country to strive with determination and self-reliance to create the scientific India of his dreams. This is the fittest tribute that we can pay to cherish his memory.

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Advise to Youth

You, our young men come to the Universities and leave them to face the world ... a world which may seem to be an unsympathetic harsh world. I would like to tell the young men and women before me not to lose hope and courage. Success can only come to you by courageous devotion to the task lying in front of you and there is nothing worth in this world that can come without the sweat of our brow. We have abundant human material in India. Speaking as a teacher of 24 years' experience, I can assert, without fear of contradiction that the quality of the Indian mind is equal to the quality of any Teutonic, Nordic, or Anglo-Saxon mind. What we lack is perhaps courage, what we lack is perhaps driving force which takes one anywhere. We have, I think, developed an inferiority complex. I think what is needed in India today is the destruction of that defeatist spirit. We need a spirit of victory, a spirit that will carry us on to our rightful place under the sun, a spirit which will recognise that, we as inheritors of a proud civilisation, are entitled to a rightful place on this planet. If that indomitable spirit were to arise, nothing can hold us from achieving our rightful destiny.

Sir C. V. Raman

Experimental procedures of laser Raman spectroscopy

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Introduction

We know that light is a form of energy which has both wave and particulate properties. Therefore, either of the two physical models can be used to describe experimental observations. As a wave it is electromagnetic in nature and therefore is characterized by its velocity $c (=3 \times 10^{10} \text{ cm/sec})$ and a wavelength (λ), while its frequency is given by $v = c/\lambda$ (or by $\omega = 1/\lambda$ cm⁻¹, wavenumbers, where λ is in cm, as used in infrared spectroscopy). On the other hand as a particulate nature of light, the amount of energy E per wave-packet (photon) of any frequency is given by the relationship E = hv, where h is Planck's constant ($\sim 6.6 \times 10^{-27}$ erg. sec). If the source radiates light of a single frequency (i.e. single wavelength), it is said to emit monochromatic radiation.

When such a monochromatic radiation of frequency v_0 is incident on systems like dust-free transparent gases and liquids or optically perfect, transparent solids, most of it is transmitted without change but a small fraction of it is scattered in all directions. If the frequency content of the scattered radiation is analysed using a suitable dispersing device, one can observe not only the v_0 associated with the incident radiation but also, in general, pairs of new frequencies $v_R = v_0 \pm v_M$. The scattered radiation with frequency v_R usually has polarization characteristics different from those of the incident radiation and its intensity and polarization vary with the direction of observation. Such a scattering of radiation with change of frequency is called Raman scattering or Raman effect which, as a result of its theoretical prediction by A. Smekal [Naturewiss. 11, 873 (1923)], was experimentally discovered by C. V. Raman and K. S. Krishnan

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[Nature, 121, 501 (8th March 1928)] in India, and a little later but independently by G. Landsberg and L. Mandelstam [Naturewiss. 16, 557 and 772 (1928)] in Russia. Immediately after the discovery of Raman effect, scientists all over the world hurriedly assembled optical instruments available at that time and confirmed the observation of Raman effect in a variety of substances in gaseous, liquid and solid state. The measured values of v_M were found to lie principally in the ranges associated with transitions between rotational, vibrational and electronic energy levels of the molecules of the substance, and were correlated to different modes of molecular vibrations that were found to be characteristic of the molecular structure. A branch of spectroscopy thus emerged and was named Raman spectroscopy.

In the spectrum of scattered radiation the new frequencies (v_R) are termed *Raman lines* or *bands*, and collectively are said to constitute a Raman spectrum. Raman bands at frequencies less than the incident frequency (i.e. $v_R = v_0 - v_M$) are referred to as Stokes bands and those at frequencies greater than the incident frequencies (i.e. $v_R = v_0 + v_M$) as anti-Stokes bands.

The scattering of radiation without change of frequency had been known for some time prior to the discovery of Raman effect and has been attributed to various scattering centres like molecules (small scattering centres) and dust-particles (large scattering centres). Where such scattering arises from scattering centres like molecules, which are much smaller than the wavelength of the incident radiation, it is called *Rayleigh scattering* [*Phil. Mag.* XLI, 274 and 447 (1871)]. Rayleigh scattering always accompanies Raman scattering and so will always be observed with Raman scattering. The natural presence of Rayleigh band at frequency v_0 within Raman spectrum serves as a reference band for determination of v_M from v_R . In practice, however, the scattering at frequency v_0 has an additional component arising from larger scattering centres like dust particles which is generally referred to as *Mie scattering* [Ann. Physik. 25, 377 (1980)].

As an indication of the intensity levels involved, one can say that the intensity of Rayleigh scattering is generally about 10^{-3} of the intensity of incident radiation whereas the intensity of strong Raman bands is generally about 10^{-3} of the intensity of Rayleigh scattering. This justifies the remark of Prof. C. V. Raman in his letter, 'The new type of light scattering discovered by us naturally requires very powerful illumination for its observation'.

In course of his experiments on molecular light scattering, Prof. Raman directed a beam of sunlight, which had been condensed by a telescope, through a liquid like benzene. He observed that when two complimentary light filters, blue-violet and yellow-green, were placed between the telescope and the container of liquid, the track of light was completely extinguished. If, however, the yellow filter was placed between the container and the eye of the observer, the track again became visible indicating that the light had been modified in some way by its passage through the liquid. Little more than a toy game by today's standards, but his experiment was able to spot the incredibly weak, shifted spectral lines emitted by benzene. In a paper submitted to the Royal Society later in 1928, Prof. Raman, however, showed photographically recorded spectra of several liquids for which he substituted a mercury lamp for the capricious sun and a prism spectrograph for the filters and eye. The spectrum of CCl₄ thus recorded using 4350 Å line of mercury lamp having 3000 C.P., 600 ml of sample, required 25 hrs of exposure. Since that time there has been a gradual improvement in instrumentation and light sources. With the advent of lasers and of photoelectronic devices, it is now possible to record photoelectrically even very weak Raman spectra with sample quantities less than 10^{-6} ml and recording time of only a few minutes



Figure 1. Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited by an argon ion laser $\omega_0 = 20487 \text{ cm}^{-1}$ (or $\lambda = 4879.9 \text{ Å}$).

(Fig. 1). The objective of this article is thus to give a broad introduction to the present experimental procedures of Raman spectroscopy using laser as excitation source.

Equipment

The major task in Raman spectroscopy is to isolate the Raman radiation and measure its frequency and intensity. The block diagram of Fig. 2 shows the components of the equipment necessary for the observation of Raman spectra. They are (1) a strong source of monochromatic radiation, (2) an appropriate sample device, (3) fore-optics for collection of Raman radiation, (4) a system for dispersion of the scattered radiation and measurement of its frequency and (5) a detection device to measure the intensity of the dispersed radiation. Some important aspects of these parts shall be described here with concentration on their respective requirements which would allow efficient recording of Raman spectra.



Figure 2. Block diagram of equipment for observation of Raman spectra.

Source

For excitation of Raman spectra the source should be highly monochromatic and capable of producing high irradiance at the sample. In the conventional Raman spectroscopy, the mercury arc lamp had been used as its light source which provides only one strong excitation line in the visible region at 4358.3 Å and another strong resonance line in the ultraviolet region at 2536.6 Å. This restricts Raman spectroscopy to samples which do not absorb in these regions. The power (light intensity) per unit area achievable at the sample was generally of the order of 0.02 watt/mm², and that too at the expense of several kilowatts of electric power. Further due to the spatial spread out of the lamp, it required large quantities of samples and complex fore-optics to collect the Raman light. Thus, due to the several shortcomings with the arc lamps, Raman spectroscopy in the fifties and early sixties was less widely used than infrared spectroscopy. In recent years the situation has dramatically changed as a result of the availability of highly stable gas lasers.

At the focus of the gas laser the power per unit area can be many orders of magnitude (>1 watt/mm²) greater than that of the mercury arc lamp. The output from a laser forms a selfcollimated highly monochromatic and plane polarized beam with extremely high stability at desired intensity. Most gas lasers can provide a number of discrete wavelengths of varying power, while dyelaser can provide an excitation wavelength which is continuously variable over a limited range. The helium-neon, argon-ion and krypton-ion and argon-krypton ion mixed gas lasers are most commonly used. The strong wavelengths at which these lasers can be operated are listed in Table 1. The strongest lines of the argon-ion laser are at 4880 Å and 5145 Å, while they are at 5682 Å and 6471 Å for the Krypton ion laser. In addition to these lines there are always present some spurious lines due to plasma emission. Generally a spike filter or high power grating is used to isolate a particular exciting line and eliminate these spurious lines from the spectrum. Commercial models of gas lasers have a power of the order of 1 watt in one of the lines mentioned above. Other lines with small power can be, however, used for studies of the dependence of

Table 1(a). Wavelengths (and wavenumbers) available from typical gas lasers

		Relati	ve outpu	it powers (mW)
λ_{air}	$\bar{v}_{\rm vac}$				
(Å)	(cm^{-1})	He/Ne	Kr	Ar/Kr	Ar
7993.2	12 507		30		
7931.4	12605		10		
7525.5	13285		100		
6764.4	14779		120	20	
6470.9	15450		500	200	
6328.2	15798	70			
5681.9	17 595		150	80	
5308.7	18832		200	80	
5208.3	19 195	2	70	20	
5145.3	19430			200	800
5017.2	19926			20	140
4965.1	20135			50	300
4879.9	20487			200	700
4825.2	20719		30	10	
4764.9	20981			60	300
4762.4	20992		50		
4726.9	21 1 50				60
4657.9	21 463		e		50
4579.4	21 831			20	150
4545.1	21 996				20
3637.9	27 481 \				20
3511.1	28 473 ∫				20
3564.2	28 049)				
3507.4	28 503 ∫		40		

Notes: The powers for the krypton, argon/krypton and argon lasers relate to typical commercial lasers described as having a nominal output of about 2 W.

Table 1(b). Wavelength (and wavenumber) ranges covered by typical dye lasers

Dye	Wavelength range (Å)	Wavenumber range (cm ⁻¹)
Nile Blue perchlorate Cresyl Violet per-	7100-8000	14 100-12 500
chlorate	6700-7100	14900-14100
Rhodamine B	5900-6900	16900-14500
Rhodamine 6G	5600-6600	17 900-15 200
Rhodamine 110	5300-6200	18 900-16 100
Sodium Fluorescein	5300-5800	18 900-17 200
Coumarin 6	5200-5600	19 200-17 900
Coumarin 102	4600-5200	21 700-19 200
Coumarin 2	4300-4800	23 300-20 800

Notes: (i) Output powers depend on pump laser power but typically range over 100-900 mW.

(ii) The wavelength ranges quoted above are approximate only; they vary somewhat with the solvent and pumping conditions.

Raman intensities on the excitation wavelength. In general 90% of the materials can be studied using the argon-ion laser at 5145 Å wavelength with power densities of the order of 1 watt. Thus, the best currently available and reliable source for excitation of Raman spectra is the argon-ion laser.

Sample illumination and sample device

Using a lens, the laser beam can be focused onto the sample to produce a beam of much smaller diameter and hence of very high power density. The following formula gives the diameter D of the focused beam:

$$D = 4\lambda f/\pi d$$

where d is the diameter of the unfocused beam, f the focal length of the lens used, and λ is the wavelength of the laser line used. It is easy to see that the area of the focused beam can be reduced to 10^{-3} of the unfocused beam and hence the power per unit area at the sample can be increased by about 10^3 . Focused laser beams are therefore normally used for the production of Raman spectra except in special circumstances where the high irradiance may be harmful to the sample. The major advantage of this focusing capability is that extremely small quantity of sample (<0.1 nanolitre) in a capillary of 50 micron diameter can be used for Raman spectrum recording.

Sample compartment and sample cells need to be constructed in a most effective way so that the best possible use is made of the exciting laser light and that the design should allow the collection of the scattered radiation in a most efficient manner for subsequent dispersion. The conventional 90° sampling geometry is used in most spectrometers. The Raman-scattered radiation is viewed at right angles to the direction of excitation. Figure 3 indicates the most simplified and common arrangement for the Raman measurements utilising a laser beam. The lens L_1 focuses the laser beam upto less than a spot of diameter 0.1 mm onto the sample placed in a capillary tube. Thus the irradiance flux density becomes extremely large resulting in intense Rayleigh scattering which causes the glowing of the capillary as a whole. The lens L_2 produces the image of this luminous line like capillary on the piles of the entrance slit of the spectrometer. In a commercial spectrometer the lens L_2 is used in such a way that it collects the maximum possible solid angle of scattered radiation and matches this to the collection solid-angle of the dispersing system. The two additional concave mirrors M1 and M2 increase the observed intensity of scattering ten times. M_1 multipasses the laser beam through the focus in the sample and M₂ virtually doubles the solid angle of scattered radiation fed to the dispersing system.

Filters and other optical devices may be inserted into the incident laser beam or scattered radiation



Figure 3. Simplified arrangement for the Raman measurements utilizing laser beam.

beam. Before focusing the laser beam it may be passed through an interference filter to suppress unwanted laser or plasma frequencies. However, the transmittance of such filters is less than 60% and therefore its insertion can reduce the irradiance at the sample proportionately.

Dispersing system

In general, for investigation of rotational/vibrational Raman spectra the dispersing system is almost invariably based on a diffraction grating rather than a prism. Front surface metal-coated concave mirrors are used to collimate the Raman radiation before dispersion and to refocus it after dispersion on the photoelectric detector. The combination of mirrors and diffraction gratings in the Ebert or Czerny-Turner mount is quite standard in modern photoelectric Raman spectrometers. The optical layout of the Czerny-Turner mount is shown in Fig. 4. The centres of the entrance and exit slit lie in the optical plane of the system at the foci of the concave mirrors, while slits are slightly located off-axis from the mirrors. The cone of light entering the entrance slit is collimated by the mirror M_1 and reflected onto the grating in the form of a parallel beam. The light dispersed by the grating strikes the second mirror which brings the dispersed spectrum to a focus at the exit slit. The spectrum is scanned by rotating the grating about its vertical axis, while mirrors and slits are left stationary. The dispersion is then expressed in angstroms (or wavenumbers, cm^{-1}) per millimetre at the exit slit and it is the wavelength interval



falling within a millimetre width around the exit slit when an entrance slit of infinitesimal width is illuminated with white light. The Czerny-Turner mount shown in Fig. 4 thus forms what is known as single monochromator. If the single monochromator is coupled in tandem with another set of Czerny-Turner mount, i.e. a part of the dispersed spectrum at single monochromator is made to pass once again through another set of Czerny-Turner mount, it is said to constitute a double monochromator (Fig. 5). In a double monochromator, both gratings are driven together in tandem. It is essential therefore that they be reproducibly coupled, so as to avoid tracking errors. Commercially available double monochromators are satisfactory in this respect.

It may be noted that Raman frequencies are the difference of two large numbers, the frequency of the exciting line and the absolute frequency of the shifted Raman band. This means that the grating drive must be very accurate, e.g. consider a Raman frequency shifted 100 cm⁻¹ from an exciting line at 19436 cm⁻¹ (5145 Å). The Raman band will appear at 19336 cm⁻¹. If the grating drive is accurate to ± 1 cm⁻¹, the absolute frequencies are known to be about 2 parts in 20000. The uncertainty in the Raman shifted frequency of 100 cm⁻¹ is, however, about 4 parts in 100. For this reason it is necessary



Figure 4. A Czerny-Turner granting mount in a single monochromator.

Figure 5. Typical double monochromator grating dispersing system for the study of Raman spectra under medium resolution.

to put a calibration spectrum on the Raman spectrum for very accurate work. Neon lamps are useful for this purpose.

The resolving power of a double monochromator is given by the formula,

$$R = \frac{\omega}{\Delta \omega} = \frac{2t}{\lambda} \sin\left(\frac{\alpha + \beta}{2}\right) \cos\left(\frac{\alpha + \beta}{2}\right) = mN$$

where ω is the wavenumber of the exciting radiation, t the width of the grating ruling, α the angle of incidence, β the angle of diffraction, $\Delta \omega$ the dispersion, N the number of grooves/mm, and m the order of the spectrum. For a commercial double (monochromator) spectrometer, which has two 1800 grooves/mm of the grating, then for $\omega = 19435$ cm⁻¹, the reciprocal linear dispersion is ~10 cm⁻¹/mm. This means a 50 micron output slit opening will give a band pass of 0.5 cm⁻¹. In practice, however, there are many factors which affect the resolution.

It is already mentioned that strong Rayleigh scattering and Mie scattering always accompany the Raman scattered light, and therefore these radiations also enter the dispersion system along with the Raman radiation. This light with v_0 mostly gets dispersed away, but appreciably large part of it also gets scattered in all directions inside the spectrometer from even a carefully designed and fabricated dispersing optics, e.g. gratings and mirrors of the first part of the double monochromator. This undesired scattered light with frequency v_0 , referred to as stray excitation radiation, escapes through the exit slit along with the desired Raman radiation irrespective of the nominal frequency setting of the monochromator. The stray radiation thus masquerades the Raman scattered radiation and can sometimes be greater than the Raman radiation whose true frequency is under measurement. In the second part of the double monochromator, the radiation is redispersed so that the unwanted stray radiation is rejected. There is no universally accepted figure of merit for stray light rejection of the monochromators. Typically what is done is to set the slits at some narrow width, say 10 micron, and shine a laser, not directly but through some neutral density filters to reduce the intensity, into the entrance slit. The intensity of the radiation transmitted through the spectrometer is measured at the laser (excitation) frequency, and then at a nominal monochromator setting at 20 cm⁻¹ away from the laser excitation frequency. For a good double monochromator the ratio of the two measurements should be less than 10^{-14} . For most systems, a double monochromator serves better, although a third monochromator becomes a must when one deals with solid state materials.

The number of monochromators decrease the transmittance of the spectrometer. That is, if light of intensity I_{ν}^{0} , and frequency ν enters the spectrometer through the entrance slit, and if I_{ν}^{t} is the transmitted intensity at the exit slit, then $I_{\nu}^{t}/I_{\nu}^{0} < 1$. This ratio is called *throughput* of the monochromator. A good double monochromator has its value near 0.25 in the range 4000–8000 Å.

Matching of fore-optics

For the best collection of Raman radiation, one needs to match the fore-optics with the spectrometer. The fore-optics in simple arrangement is like that of lens L_2 in Fig. 3, while more specifically it is, as shown in Fig. 6, a combination of lenses with short and long focal lengths (which is almost similar to a camera (compound) lens). The lens A is of much shorter focal length than lens B and it has the sample (source of Raman radiation) at its focus, whereas the position of lens B is adjusted such that the spectrometer entrance slit lies at its focus. Thus the image of the sample (radiating Raman light) is formed at the entrance slit of the spectrometer, and the light enters the spectrometer in the form of cone of light with its vertex at the entrance slit. The



Figure 6. Matching of fore-optics to a spectrometer using lenses A and B.

matching of the fore-optics now needs to be done in such a way that the cone of light just fills up the first collimating concave mirror in the spectrometer. Hence the primary goal of fore-optics matching is to get the maximum flux into the spectrometer. This involves having the sample quite close to the optics and having the input lens A subtend a large solid angle at the sample. Ordinarily, for back reflection geometry a camera lens serves extremely well. Commercial manufacturers of such spectrometers also have developed their own sample illuminator device along with the matching of the fore-optics.

The scattered Raman radiation collected by the fore-optics may be allowed to pass through a combination of a polarization analyzer and polarization scrambler. The analyzer allows depolarization studies whereas the scrambler ensures that the same kind (natural light) is incident on the entrance slit of the spectrometer irrespective of whether the analyzer has its axis parallel or perpendicular to the incident light polarization electric vector. In this way possible errors in polarization measurements due to differential transmission by the spectrometer of light of different polarization are avoided.

Detector system

A photographic plate was the best known detector and spectrum recording system available in the early days of Raman spectroscopy. The advantage with a photographic plate is that it records the whole spectrum at a time while its longer exposure time automatically permits the integration of weak signals. In fact, if background (stray) radiation is very low the photographic plates serve as an extremely good detector for high resolution spectroscopy. However, there are several drawbacks with the photographic detectors. Their response is non-uniform in the visible region and they need special attention for their developments. Finally they involve very long exposure times.

In modern instruments, the detector is a special kind of photo-cell, called a *photomultiplier tube* (PMT). When a photon of light falls on the photo-

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sensitive cathode of a PMT, the photoelectron that is released in accelerated to a first dynode which is maintained at about 100 volts above the cathode. The accelerated electron releases several electrons from the first dynode, and these electrons are then accelerated to the next dynode where further electrons are released. Since ten or more dynode stages are usually involved, there can emerge from the last stage of PMT a pulse of about 10⁶ electrons associated with the arrival of one photon at the photocathode. This electron multiplication process makes the PMT very suitable for the detection of low level light signals such as Raman radiation. However, there can be random emission of electrons from cathode even in the absence of any photons. These can be even from thermionic or field emission processes inside the PMT, and it can show some signal. These pulses are low in height and cause what is known as noise. Thermal noise can be reduced by cooling the PMT to low temperature (below -30° C).

The individual photoelectron pulses, which are proportional to the intensity of Raman radiation, are further processed on the basis of pulse counting. The most direct method of pulse count is achieved by the use of a digital-to-analog converter. This device produces an output voltage proportional to the number of pulses counted in a preset fixed time interval. The output voltages are displayed on a chart recorder or the cathode-ray-tube (CRT) screen of a micro-processor. Thus all the statistical fluctuations in the signal will be displayed in the recorded spectrum. The fluctuation about a true signal can be reduced by integrating the output of pulse counting electronics built in the microprocessor. This is done with the help of a programmed stepping motor drive for the grating. This motor sits at a given frequency for a preset time interval and then turns the grating to the next preset frequency. The stepping motor and drive device can enable to scan the grating with stepping speed as high as $90 \text{ cm}^{-1}/\text{sec}$ and as small as $0.0025 \text{ cm}^{-1}/\text{sec.}$ With a computer aided spectrometer, the count rate as a function of the wavenumber difference between the exciting laser line and momentary setting of the scanning monochromator is stored digitally as the Raman

spectrum. A useful relationship between slit width, scan speed and time constant is given by

$$W = Snt/60$$

where W is the slit width in cm^{-1} , t the time constant in seconds, S the speed in $\text{cm}^{-1}/\text{min}$, and n an integer.

This equation relates the number of time constants required for a given scan speed to scan over a given spectral slit width. The spectral slit width is normally chosen so that it is less than the half-band width of a given band. For routine runs *n* is usually set equal to 2 cm^{-1} . The instrument is set-up by adjusting the gain control to maximize a specific band or to set the strongest band at approximately 100 scale divisions at a given spectral slit width. The time constant is then adjusted to give the desired signal-to-noise ratio, and the scan speed computed from above equation. The intensity of Raman scattered radiation is proportional to the fourth power of the frequency of the excitation line. Hence it is, in general, more advantageous to use a higher frequency excitation line such as 4880 Å (20487 cm⁻¹) or 5145 Å (19430 cm⁻¹) lines of argon-ion laser than the 6358 Å (15728 cm⁻¹) line of helium-neon laser. The scattering efficiency increase is thus (20487/15728)⁴ = 2.8. However, the higher frequency excitation lines tend more to excite fluoresence than do the lower frequency lines. Hence one is often forced to compromise.

The observed Raman intensity is dependent on the monochromator throughput, phototube sensitivity, spectral slit width, and laser power as well as scattering efficiency. There is a variety of PMT detectors with different sensitivity in different wavelength regions. RCA C 31034/76 is one of such good PMT which has uniform sensitivity over vis-



Figure 7. Modern computer driven laser Raman spectrometer installed at National Chemical Laboratory, Pune. CL—Cylindrical lens, FO—Camera lens as fore-optics. The solid line shows the path of excitation laser beam whereas broken bold lines show the Raman signal processing electrical circuit diagram. Thin broken lines near FO indicate collection and focussing of Rayleigh and Raman radiation on to the entrance slit of the double-spectrometer.

ible range and when cooled down to -30° C, shows dark counts less than 10 counts per second (Fig. 7).

Depolarization ratios

As mentioned earlier, in addition to being monochromatic and coherent, laser radiation is also plane polarized. When a polarization analyzer is placed between the sample and the entrance slit of the monochromator the intensity of Raman scattered radiation changes as the analyzer is rotated. When the analyzer is set to pass radiation that is polarized in the same direction as the source, the Raman scattered radiation will be more intense than when the analyzer is set to pass radiation polarized perpendicular to the direction of polarization of the source. The intensities of Raman band observed in these two analyzer settings are referred to as I_{\parallel} and I_{\perp} , respectively. The depolarization ratio ρ is defined as,

$$\rho = I_{\perp}/I_{\parallel}$$

The maximum value of ρ for a plane polarized source is 0.75, and a band with this depolarization ratio is said to be depolarized. The value of ρ depends on the nature of the vibration, particularly from molecular symmetry point of view. Non-totally symmetric vibrations give Raman bands for which $\rho = 0.75$. Whenever $\rho < 0.75$, the band is said to be polarized. Totally symmetric vibrations give bands for which $\rho < 0.75$. The symmetry of a molecular vibration can be quickly determined from depolarization measurements, and these data are particularly useful in molecular structure determination.

"'Big Science' not my cup of tea"

Raman had a strong conviction that science should be a passionate way to understand nature. One should persue it with one's own abilities without worrying about relevance and practical utility. However, because of this he had to keep himself away from the activities of big National Laboratories. He staunchly believed that just by imitating western scientists and accumulating a vast array of scientific equipments would not bring excellence. The reason for this strong belief had roots in the type of equipment he used to carry out the experiment which fetched him Nobel prize. The total cost of the equipment was just Rs. 200/-. This only prompted him to suggest to one of his students to put ten kilowatt brain on one kilowatt X-ray tube, so he could get equally good results as the scientist who was working on the same problem with 10 kilowatt X-ray tube.

P. B. VIDYASAGAR

Basic interactions in X-ray scattering

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Introduction

The study of the interactions between radiation and matter has led to a considerable extent to the understanding of a large number of physical phenomena in particular, and to the progress of physics in general. While studying X-ray scattering. we are actually dealing with an interaction between the radiation (whose nature is not known; after all X stands for the unknown) and the scattering material, which is like a black box. When the intensities and the wavelengths of the radiation scattered from this black box are measured at different angles, it becomes possible to obtain valuable information about the nature of the incident radiation itself and about the particles in the material responsible for the scattering interaction.¹ Many stalwarts in physics, like C. G. Barkla, J. J. Thomson, A. H. Compton, E. Schrödinger, C. V. Raman and a host of other scientists have thought it fit to make investigations in this field. These studies have resulted in a very large number of beautiful experiments and many very interesting theories. From the work which has been so far carried out, it appears that the basic processes which are involved in X-ray scattering are:

- i) The Thomson scattering process,
- ii) The Compton scattering process, and
- iii) The Raman scattering process.

The above processes, which occur simultaneously, depend upon the different aspects of radiation and matter. We shall discuss them in brief in the following sections.

THOMSON SCATTERING PROCESS

1. The basic process

The first theory of X-ray scattering based on classical ideas of radiation was put forth by J. J. Thomson² in the year 1912. Thompson made the following assumptions in formulating his theory:

- 1) X-rays are electromagnetic waves and that they put into forced vibration the electrons which they encounter while traversing through matter.
- 2) The electrons by virtue of the acceleration thus obtained themselves radiate energy in the form of secondary X-rays.
- The electrons in the scattering material are not subject to any appreciable forces of constraint. All the electrons in a material are supposed to participate in the scattering process.
- 4) The primary X-ray beam is unpolarised.

With these assumptions J. J. Thomson calculated the intensity of the scattered beam making an angle ϕ with respect to the incident X-ray beam. It is well known from classical theory that an accelerated charge emits an electromagnetic wave whose electric field of intensity E and magnetic field of intensity H are always at right angles to each other. The magnitudes of these electric and magnetic intensities at a point **r** from the charge e are given by

where a is the acceleration of the charge and θ is the

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angle between ${\bf r}$ and the direction of the acceleration.

Let us now suppose that a beam of X-rays of electric intensity E traverses an electron of charge e and mass m. Then because of the interaction between the beam and the electron, it will get an acceleration

$$a = eE/m. \tag{2}$$

This accelerated electron will radiate a secondary wave whose electric intensity at a distance r is

$$E_{\theta} = \frac{e \sin \theta}{rc^{2}} \cdot \frac{eE}{m}$$
$$= \frac{E e^{2} \sin \theta}{rmc^{2}},$$
(3)

where θ is the angle between the electron's acceleration and the secondary scattered wave.

Since the square of the electric field intensity of an electromagnetic wave is proportional to its intensity, we can write,

$$\frac{I_{\theta}}{I} = \frac{E_{\theta}^{2}}{E^{2}} = \frac{e^{4} \sin^{2} \theta}{r^{2} m^{2} c^{4}}.$$
(4)

We have shown in Fig. 1 the basic Thomson process of X-ray scattering in which OX is the direction of the primary beam and OP is the direction of the scattered beam.



Figure 1. The basic Thomson scattering process.

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Because the primary beam is assumed to be unpolarized, the acceleration of the scattering electron will be in a random direction in the plane perpendicular to the primary beam OX. We take two rectangular axes OY and OZ in this plane, such that OY lies in the plane POX in which also lies the scattered wave. We can resolve the electric vector in the primary wave into two components E_y and E_z , so that

$$E_{y}^{2} + E_{z}^{2} = E^{2}.$$
 (5)

Since the direction of E in the YOZ plane is assumed to be random, $E_y = E_z$ on the average. Hence,

$$E_{y}^{2} = E_{z}^{2} = \frac{1}{2}E^{2}.$$
 (6)

Thus,

$$I_y = I_z = \frac{1}{2}I. \tag{7}$$

The intensity of the scattered wave at the point P due to the Y component of the incident wave is

$$I_{\theta y} = I_y \frac{e^4 \sin^2 \theta_y}{r^2 m^2 c^4} \tag{8}$$

or
$$I_{\phi y} = \frac{1}{2} I \frac{e^4}{r^2 m^2 c^4} \cos^2 \phi,$$
 (9)

where ϕ is the angle between the primary and the scattered waves. Similarly, the intensity due to the Z component of the incident wave is

$$I_{\theta z} = I_{z} \frac{e^{4} \sin^{2} \theta_{z}}{r^{2} m^{2} c^{4}}$$

$$I_{\phi z} \equiv \frac{1}{2} I \frac{e^{4}}{r^{2} m^{2} c^{4}}.$$
(10)

Thus the intensity of the beam scattered by a single electron is

$$I_e = I_{\phi y} + I_{\phi z}$$

= $I \frac{e^4}{2r^2 m^2 c^4} (1 + \cos^2 \phi).$ (11)

If we suppose that the scattering material contains n electrons per unit volume and assume that all the electrons are independently effective in scattering,

$$I_s = \frac{Ine^4}{2r^2m^2c^4}(1 + \cos^2\phi).$$
 (12)

Integrating the above equation over the surface of a sphere of radius r, one obtains the total power P_s in the scattered beam. Thus,

$$P_{s} = \int_{0}^{\pi} I_{s} 2\pi r \sin \phi \, r d\phi$$

= $\frac{\pi I n e^{4}}{m^{2} c^{4}} \int_{0}^{\pi} (1 + \cos^{2} \phi) \sin \phi \, d\phi$
= $\frac{8}{3} \frac{\pi n e^{4}}{m^{2} c^{4}} I.$ (13)

Since I, the intensity of the primary beam, represents the energy in the beam per square centimeter per second, the fraction of the primary energy which is scattered per centimeter of path is

$$\sigma = \frac{P_s}{I} = \frac{8}{3} \frac{\pi n e^4}{m^2 c^4},$$
 (14)

where σ is called the scattering coefficient and represents the fraction of the incident X-rays scattered per unit volume of the irradiated material. The mass scattering coefficient σ/ρ represents the fraction of the incident intensity scattered per unit mass of matter.

2. Experimental confirmation of Thomson's theory

Thomson's theory of X-ray scattering can be *tested* experimentally in a number of ways. We shall describe briefly the experiments which support Thomson's theory.

(a) The polarization of scattered X-rays

Thomson's theory predicts that the scattered beam should be linearly polarized at the scattering angle of 90°, since the intensity component I_y vanishes at $\phi = \pi/2$, as can be seen from Eq. (9). Barkla³ found, by measuring the intensity of the scattered beam by a carbon scatterer at 90°, that the secondary rays were about 70% polarized. Later experiments^{4,5} showed that the polarization of the scattered X- rays is complete within about 1 or 2%. The polarization experiments are in very good accord with Thomson's theory.

(b) The intensity of scattered X-rays

On plotting the scattering coefficients calculated using Eq. (14) and those obtained experimentally against X-ray wavelengths, it was found that for wavelengths between 0.1 Å and 1.0 Å, the scattering coefficient is nearly independent of the wavelength and proportional to the atomic number for the light elements. For the heavier elements the scattering coefficient is greater than that predicted by Thomson's theory.

If the distances between the electrons in an atom are small as compared to the wavelength of the Xrays, all the electrons in the atom will act as a unit, participating in the scattering process. Under this circumstance if Z is the number of electrons in the atom, the electric charge scattering the radiation is Ze and the intensity of the scattered X-rays by a single atom is therefore,

$$I_{sa} = I \frac{(Z e)^4}{2r^2 (Zm)^2 c^4} (1 + \cos^2 \phi)$$

= $\frac{I Z^2 e^4}{2r^2 m^2 c^4} (1 + \cos^2 \phi)$
= $I_e Z^2$, (15)

where I_e is defined in Eq. (11).

On the other hand if the electrons in an atom scatter individually, the intensity of the scattered beam will be,

$$I_{sa} = I \frac{Ze^4}{2r^2m^2c^4}(1 + \cos^2\phi)$$

= $I_e Z.$ (16)

The experiments on the measurement of the intensity of the scattered X-rays confirm that Thomson's theory is strictly speaking valid only for light elements. For heavier elements Thomson's scattering does occur but the intensity of scattering from such elements is not directly proportional to the atomic number Z as in the case of the light elements. In the heavy atoms the scattered waves from different

parts of the atom may interfere with, or reinforce, each other. The intensity of the scattered ray depends on the distribution of electrons in the atom, the incident wavelength and the scattering angle. The scattering power of an atom is denoted by the parameter f_a , called the atomic structure factor, which is defined as the ratio of the amplitude of the wave scattered coherently by the atom as a whole to the amplitude scattered by a single electron. The values of the atomic structure factor can be calculated theoretically. Their knowledge is extremely useful in X-ray crystallographic studies.

One can make use of Thomson's scattering for determining the number of electrons in light atoms. Historically, an X-ray scattering experiment performed by Barkla⁶ on graphite gave the first accurate estimate of the number of electrons in the carbon atom.

Hewlett⁷ measured the intensity of scattered Xrays from carbon over an angular range $\phi = 0$ to $\phi = \pi$ and obtained the value of the mass scattering coefficient $\sigma/\rho = 0.20$. Assuming the integration as given in the steps of Eq. (14), one can write

$$\frac{n}{\rho} - \frac{\sigma}{\rho} \frac{3m^2 c^4}{8\pi e^4}.$$
 (17)

Putting the values of σ/ρ , e, m, and c in this equation, we get

$$\frac{n}{\rho} = 3.0 \times 10^{23}$$
 electrons per gram.

The number of carbon atoms per gram is

$$\frac{N}{M} = \frac{6.06 \times 10^{23}}{12}$$

= 5.05 × 10²² atoms per gram,

where N is the number of molecules per grammolecule (Avogadro's number) and M is the atomic weight of carbon. Thus the number of electrons per atom which scatter X-rays is

$$\frac{n}{\rho} \left| \frac{N}{M} = \frac{3.0 \times 10^{23}}{5.05 \times 10^{22}} \right| = 6.0$$

which is the atomic number of carbon. Hence, we

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see that the number of electrons effective in scattering is equal to the atomic number of the scattering element. It was fortunate that Barkla and later Hewlett performed their experiments on a carbon scatterer. Had the experiments been performed on a scatterer of higher atomic number, such a good result would not have been obtained.

(c) Variation of intensity with scattering angle

Equation (12) indicates that the intensity of the scattered X-rays depends upon the scattering angle. It was observed experimentally by Hewlett⁸ that for moderate X-ray wavelengths Thomson's theory is valid to a close approximation, except for small angles ϕ .

The above experiments confirm that Thomson's theory is very well valid in the case of light elements, for medium and long wavelengths and when the scattering angle is not very small. It does not say anything directly about the wavelengths of the scattered radiation. It was observed later that there occurs a change in the wavelength of the scattered radiation which cannot be accounted for by Thomson's theory.

COMPTON SCATTERING PROCESS

1. The basic process

A. H. Compton⁹, while carrying out experiments on X-ray scattering, observed in the year 1921 that the spectrum of the scattered beam contains in addition to the primary wavelength another wavelength slightly shifted towards the long wavelength side. This shift in wavelength between the primary and modified radiations is called the *Compton shift*. Compton explained this effect taking recourse to the quantum nature of radiation. He made, in particular, the following assumptions to explain the new observations obtained by him:

- 1) The X-ray beam consists of quanta whose energy is hv and momentum hv/c.
- 2) An X-ray photon in the scattering process collides with an individual electron in the scatterer, assumed to be free and at rest.

3) Due to the impact of the photon the electron recoils. The energy of the recoil is taken from the energy of the incident photon, so that the scattered photon has a somewhat smaller energy.

These assumptions led Compton to visualise the scattering process as shown in Fig. 2. By the principle of conservation of momentum, the electron which scatters the primary ray must recoil at an angle θ with a momentum equal to the vector difference between that of the primary and that of the scattered photon. Assuming v to be the frequency of the incident ray corresponding to the wavelength λ , and v' that of the ray scattered by the electron corresponding to the wavelength λ' , we get from the principle of conservation of energy,

$$hv = hv' + mc^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1\right),$$
 (18)

where $mc^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right)$ is the relativistic kinetic

energy of the recoiling electron. Similarly, the principle of conservation of momentum gives us two equations

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\phi + \frac{m\beta c}{\sqrt{1-\beta^2}}\cos\theta$$
(for the X component) (19)



Figure 2. The basic Compton scattering process.

and

$$0 = \frac{hv'}{c} \sin \phi - \frac{m\beta c}{\sqrt{1 - \beta^2}} \sin \theta$$
 (for the Y component). (20)

Solving these equations simultaneously, we get

$$\lambda' = \lambda + \frac{h}{mc}(1 - \cos\phi) \tag{21}$$

or
$$\delta \lambda = \lambda' - \lambda = \frac{h}{mc} (1 - \cos \phi).$$
 (22)

Similarly, the kinetic energy of the recoiling electron in terms of the recoiling angle θ and $\alpha = h\nu/mc^2$ can be shown to be

$$E_{\rm kin} = hv \frac{2\alpha \cos^2 \theta}{(1+\alpha)^2 - \alpha^2 \cos^2 \theta}.$$
 (23)

The scattering angle ϕ and the electron recoil angle θ are related to each other by

$$\cot (\phi/2) = -(1+\alpha) \tan \theta. \tag{24}$$

We see from Eq. (22) that the scattered ray is of greater wavelength than the primary ray and that the increase in wavelength depends upon the scattering angle only. Equation (24) shows that for each X-ray photon scattered in a definite direction ϕ , we must get an electron recoiled at an angle θ whose energy can be calculated by Eq. (23).

2. Experimental confirmation of Compton's theory

Compton's theory of X-ray scattering can be experimentally confirmed in the following ways.

(a) Measurement of the change in wavelength

Compton, in his classic experiments, used X-rays from a molybdenum target to fall on a carbon scatterer. The X-ray beam scattered at different angles ϕ was analysed with the help of a Bragg spectrometer. It was found by Compton that at every angle there appears in the scattered spectrum one line of exactly the same wavelength as that of the primary beam and that there also occurs a second line of greater wavelength. The shift in each



case is very well accounted for by Eq. (22). The measurements revealed that the difference between the wavelengths of the scattered and primary rays increases rapidly as the angle of scattering increases. Later experiments showed that the theory is satisfactory not only for elements of low atomic number but also for heavy elements. Figures 3 and 4 show the scattered spectrum observed at different angles of scattering and for different scatterers,

SILVER K_c LINE $\phi = 90^{\circ}$



Figure 3. Compton scattering with graphite scatterer observed at different angles.

Figure 4. Compton scattering observed with different scatterers at a fixed angle.

respectively. One notes that the Compton shift changes with the scattering angle, but does not depend upon the scatterer. However, it is interesting to note that the intensity ratio between the unmodified and modified lines diminishes progressively with the increase in atomic number of the scatterer.

It may be mentioned here that the unmodified line in the scattered spectrum can be attributed to the Thomson scattering process, while the modified line is attributed to the Compton scattering process. In the former, most of the electrons in the atom participate in the scattering process and the radiation manifests itself as a wave, whereas in the latter process only the free electrons in the atom participate in scattering and the radiant energy exhibits corpuscular character.

(b) Detection of recoil electrons

While working with a Wilson cloud chamber, C. T. R. Wilson¹⁰ in 1923 brought direct evidence for the existence of Compton recoil electrons which produce tracks. These can be distinguished from those obtained from the photoelectrons by their length and appearance. A number of experiments by several workers also confirmed the existence of recoil electrons in the scattering process.

Measurements of energies of recoil electrons were carried out by C. T. R. Wilson¹⁰ and Compton and Hubbard.¹¹ It was observed that the experimentally determined values of the recoil electrons are in good agreement with those calculated using Eq. (23).

(c) Simultaneity of the scattered photon and recoil electron

The simultaneity of the emission of a scattered photon and the corresponding recoil electron was first established by Cross and Ramsey¹² in 1950, who used a collimated beam of γ -ray photons from a Ra-Th source and a beryllium foil scatterer. The scattered photons were detected by a fast counting scintillation counter and the recoil electrons by another scintillation counter. The pulses from these

two counters were fed into a coincidence circuit which registers only the particles ejected simultaneously. Their observations confirmed that the scattered photon and the recoil electron are emitted simultaneously in the scattering process within the experimental limits of time resolution.

ALTERNATE THEORIES OF THE COMPTON EFFECT

When Compton first announced his experimental results showing the modification in the wavelength of scattered X-rays and gave the theoretical interpretation of the wavelength shift using the photon concept of radiation, his work was not readily acceptable to the scientific world. Actually, there were many experimentalists who were rather skeptical of Compton's experimental work and prominent amongst them was Duane who did not believe in Compton's results. Duane had already attained considerable reputation in the scientific world at that time because of his important work on the short wavelength limit of the continuous X-rays. The Duane-Compton controversy* finally ended when more precise experiments were carried out in different parts of the world. In due course the existence of the Compton effect was established as a fact of nature. There were still many scientists who did not like the idea of invoking the photon aspect of radiation in the X-ray region. Till then, the photon aspect of light had been used only by Einstein to explain the photoelectric effect. And now here was Compton to use the photon concept in the X-ray region! Several attempts were made to explain the Compton shift using the classical ideas of radiation. Amongst them, mention may be made of the theories proposed by Schrödinger and Raman, which are briefly described in the following sub-sections.

^{*} An interesting description of the controversies which arose after the announcement of Compton's work can be found in the book "The Compton Effect: Turning point in physics" by R. H. Stuewer (Science History Publications, New York, 1975).

1. Schrödinger's theory

Schrödinger¹³ in 1927 attempted to account for the change in wavelength of scattered X-rays by using de Broglie's concept of matter waves for the scattering electrons. He assumed that the incident radiation consists of electromagnetic waves which interact with the standing wave pattern of the scattering electron, as shown below.

In the case of the Compton process shown earlier in Fig. 2 if the coordinates are changed in such a way that the conditions before and after the impact of photon and electron are symmetrical, the Compton process can be depicted as shown in Fig. 5(a). Assuming that the velocity of electron's recoil in the fixed coordinates is such that $v \ll c$, the velocity in the moving coordinates is $\frac{1}{2}v$. At impact, the momentum of the electron changes from -mv/2 to +mv/2 as expressed in the moving system, while the component of the photon's momentum changes from $+(h/\lambda)\sin\phi/2$ to $-(h/\lambda)\sin\phi/2$. From the principle of conservation of momentum, we get

$$-\frac{mv}{2} + \frac{h}{\lambda}\sin\phi/2 = \frac{mv}{2} - \frac{h}{\lambda}\sin\phi/2, \qquad (25)$$

or $2\frac{h}{\lambda}\sin\phi/2 = mv. \qquad (26)$

According to Schrödinger, the incident electron can be represented by a continuous train of ψ waves of wavelength h/(mv/2) moving along -Y, and the recoil electron by a similar train of same wavelength moving along +Y, the two trains together forming standing waves. The de Broglie waves representing the electron thus form a Bragg grating of grating spacing d = h/mv. This grating will diffract the incident X-ray waves as shown in Fig. 5(b) according to the Bragg equation

or
$$\lambda = 2d\sin\phi/2$$

 $\lambda = 2\frac{h}{mv}\sin\phi/2$, for $n = 1$. (27)

Transforming back to the fixed coordinates we find that the grating of stationary de Broglie waves is receding from O with a velocity v/2. Treating the

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Figure 5 (a) Compton scattering process according to Schrödinger. (b) Diffraction of incident waves from the standing wave pattern due to incident and recoil electrons.

grating as a mirror, this is equivalent to receiving the light from a virtual image of the source S" which is moving away from S with velocity v. According to Doppler's principle, a wavelength λ emitted from S" would reach P with a value

$$\lambda' = \lambda \left(1 + \frac{v}{c} \sin \phi / 2 \right), \tag{28}$$

giving rise to an increase in the wavelength of

$$\delta \lambda = \frac{v}{c} \sin \phi / 2. \tag{29}$$

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Substituting the value of v from Eq. (26) we get

$$\delta \lambda = \frac{2h}{mc} \sin^2 \phi/2$$
$$= \frac{h}{mc} (1 - \cos \phi), \qquad (30)$$

which is exactly that same expression as obtained from the photon theory given by Compton.

Although Schrödinger's theory can explain very well the change in wavelength of the scattered Xrays, it fails to account for the other observed experimental facts. It visualises the electron to be localised in the scattering material and hence cannot explain the existence of recoil electrons which are ejected out of the scattering material and are actually observed experimentally.

2. Raman's classical theory

With the aid of an atomic model in which the electrons are regarded as a gas distributed in a spherical enclosure surrounding a nucleus, C. V. Raman¹⁴ in 1928 put forth a theory in an attempt to show that the Compton effect could be accounted for with the help of the classical ideas of radiation. The assumptions made by Raman in his theory are as follows:

- 1) The X-ray beam is scattered by a group of electrons in the atom, moving independently of each other.
- 2) Each electron in the atom has the same probability of *occurring* at a given position as every other electron.
- The electron distribution has spherical symmetry.

Let us consider a beam of X-rays of wavelength λ moving in the direction OX and traversing an electron cloud in the atom. Assuming O to be the centre of the electron cloud, let OP be the direction of the scattered beam as shown in Fig. 6. The amplitude of the scattered waves by different electrons in the atom is the same, say A_e . The waves differ only in their phases. Let $\delta_1, \delta_2, \ldots, \delta_z$ be the



Figure 6. Scattering by an electron cloud in an atom according to Raman's classical theory.

phase of the waves scattered by the Z electrons. The total electric field of the scattered wave due to the Z electrons will be

$$E = A_e[\cos(pt + \delta_1) + \cos(pt + \delta_2) + \dots + \cos(pt + \delta_2)].$$
(31)

Considering δ to be the phase of the resultant vibration, it can be shown by vector algebra that the electric field of the scattered beam is

$$E = A_e \{ [\cos\delta_1 + \dots + \cos\delta_Z]^2 + [\sin\delta_1 + \dots + \sin\delta_Z]^2 \}^{1/2} \cos(pt + \delta).$$
(32)

The intensity of the scattered beam therefore can be written as

$$I = \frac{c\overline{E}^2}{8\pi} = \frac{c}{8\pi} A_e^2 [\{\cos\delta_1 + \ldots + \cos\delta_Z\}^2 + \{\sin\delta_1 + \ldots + \sin\delta_Z\}^2].$$
(33)

The above expression can be alternatively written as

$$I = I_e \left[Z + \sum_{m=n}^{Z} \sum_{(m \neq n)}^{Z} \cos(\delta_m - \delta_n) \right], \qquad (34)$$

where δ_m and δ_n are the phases due to the m^{th} and n^{th} electrons.

Let us describe a plane passing through an electron e_1 perpendicular to OQ, a line which bisects the angle X'OP. This plane intersects OQ at the point B. It will be seen from Huyghen's principle that wherever in this plane the electron e_1 lies, the

phase of the wave scattered to the plane P will be the same. Thus the phase is the same as if the electron e_1 were at B. The path difference between the rays scattered by the electrons at O and e_1 is given by $2z\sin\phi/2$, where ϕ is the scattering angle and z the distance between O and B. Since the phase difference for λ is 2π , the phase difference for the path difference $2z\sin\phi/2$ will be $4\pi z/\lambda \sin\phi/2$. In the general case, the phase of the m^{th} electron will be

$$\delta_m = \frac{4\pi z_m}{\lambda} \sin \phi/2 = k\mu_m a_m, \tag{35}$$

where
$$k = \frac{4\pi}{\lambda} \sin \phi/2$$
 (36)

and $\mu_m = z_m/a_m$ is the direction cosine of a_m with respect to the line OQ.

If u(a)da is the probability for any particular electron to be situated between a and a + da, the chance that the phase of the m^{th} electron will be within the range $d\delta_m$ is

$$dP_m = u(a_m) da_m d\mu_m. \tag{37}$$

The statistical average of $\cos(\delta_m - \delta_n)$ will be therefore,

$$\int_{0}^{\infty} \int_{0}^{\infty} \int_{-1}^{+1} \int_{-1}^{+1} \cos k(\mu_{m}a_{m} - \mu_{n}a_{n})u(a_{m})da_{m} d\mu_{m} \times u(a_{m})da_{m} d\mu_{m}$$
(38)

Since the variables are all independent, this expression can be integrated with respect to μ_m and μ_n giving

$$\left[\int_{0}^{\infty} u(a) \frac{\sin ka}{ka} da\right]^{2} = f_{e}^{2}.$$
 (39)

The quantity f_e is called the electronic structure factor.

The double summation of Eq. (34) contains $Z^2 - Z$ terms, each of which taken as a statistical average is the same and equal to f_e^2 .

Therefore, we can modify Eq. (34) and write

$$I = I_e [Z + (Z^2 - Z)f_e^2]$$

= $I_e [Z^2 f_e^2 + Z(1 - f_e^2)].$ (40)

While discussing Thomson's theory it was shown that if the atom is considered as a unit to scatter the X-rays, meaning thereby that there are no phase relations between the waves scattered by the different electrons, then the intensity of the scattered beam is proportional to Z^2 (see Eq. (15)). On the other hand, it was shown that if the electrons scatter independently (such a situation will exist mostly in the case of light elements) so that one can imagine that there exist phase relations between the scattered waves, we would get the intensity of the scattered beam to be proportional to Z (see Eq. (16)). We may therefore attribute the first term in Eq. (40), i.e. $I_{e}Z^{2}f_{e}^{2}$ in the scattered intensity to coherent scattering, i.e. Thomson's scattering, and the second term, i.e. $I_e Z(1-f_e^2)$ to the incoherent scattering. Raman attributed this incoherent part to Compton scattering. He explained the change in wavelength upon scattering invoking the Doppler's principle in the following way.

If it is assumed that the electron moves with a velocity v in the direction of propagation of the primary waves, the wavelength of the spherical secondary waves scattered by it will show a change in wavelength. The apparent wavelength observed at the angle ϕ , the angle of scattering would be, by Doppler's principle,

$$\lambda' = \lambda + \frac{\lambda v}{c} (1 - \cos \phi). \tag{41}$$

Assuming further that the incident radiation acts on the electron by way of radiation pressure, the scattering electron gets a momentum in the forward direction which is equal to the momentum hv/c of the photon. Thus, mv = hv/c and therefore $\lambda v = h/m$. Substituting this value of λv in Eq. (41), we get

$$\lambda' = \lambda + \frac{h}{mc} (1 - \cos \phi), \qquad (42)$$

This expression is exactly the same as obtained by Compton using the photon concept of radiation.

The above theory proposed by Raman was modified by Woo¹⁵ and by Wentzel¹⁶. Woo considered that each electron in the atom has its own probability $U_n(a_n)da$ of lying between distances a and a + da from the centre of the atom, thus giving a somewhat more general basis to the theory. Wentzel considered the modern picture of electron distribution in different shells using quantum mechanics and gave a better shape to Raman's classical theory.

It may be remarked that both the above theories proposed by Schrödinger and Raman are based upon rather crude assumptions which are not very satisfying and moreover they do not explain the existence of the observed recoil electrons corresponding to each scattered photon. Compton's theory, which gives a much better understanding of the scattering phenomenon, has come to be therefore universally accepted for interpreting incoherent scattering.

RAMAN SCATTERING PROCESS

The foregoing discussion shows that in the X-ray scattering phenomenon both the wave and photon aspects of radiation are brought into play. While Thomson's theory, which invokes the wave aspect, accounts for the coherent scattering, Compton's theory, based upon the photon concept of radiation, accounts for the incoherent scattering. There is yet another basic process of X-ray scattering, the *Raman scattering process*, which is generally not so well recognised. It gives rise to a totally different kind of incoherent scattering. We shall first describe the Raman effect in brief in the optical region and then show how this basic process is manifested in the X-ray region.

1. The basic process

In 1928, C. V. Raman¹⁷, while studying the scattering of light by liquids with the intention of understanding the natural phenomena of the blue of the sea and that of the sky, observed that when a beam of monochromatic light was passed through organic liquids, such as benzene, toulene, etc., the scattered light contained other frequencies in addition to that of the incident light. Raman observed in the spectrum of the scattered light a number of new lines on both sides of the main line. Those on the low frequency side were more numerous and more intense than those on the high frequency side.

Most of the new lines were strongly polarized and their spacing was symmetrical about the main line. They are now generally referred to as *Raman lines*, and the effect is called the *Raman effect*. It may be mentioned here that although this effect was theoretically predicted by Smekel¹⁸ as early as 1923, Raman was the first to observe it experimentally. Immediately after the Raman effect was discovered, it was shown by several workers¹⁹ that many liquids, vapours, gases and transparent solids exhibited the effect, proving it to be a more general phenomenon.

The Raman effect can be explained on the basis of the classical ideas of radiation as follows. When a light wave represented by $E_0 \cos(2\pi v_0 t)$ falls on a molecule, it induces in the molecule an oscillating electric dipole moment, $aE_0\cos(2\pi v_0 t)$, where *a* is called the *deformability* or *polarizability* of the molecule. The deformed molecule behaves like a Hertzian oscillator and radiates energy in the form of electromagnetic waves of frequency v_0 . If we now suppose that some kind of mechanism intrinsic in the molecule itself, such as its rotation or vibration, alters the amplitude of the emitted wave periodically with a frequency v, then the electric moment of the oscillator at any instant is given by

$$aE_0\cos(2\pi v_0 t)\cos(2\pi v t + \delta), \tag{43}$$

which may be written as

$$\frac{1}{2}aE_0[\cos\{2\pi(\nu_0+\nu)t+\delta\}+\cos\{2\pi(\nu_0-\nu)t-\delta\}].$$
(44)

This expression shows that the emitted light will consist of frequencies $v_0 + v$ and $v_0 - v$ around the main frequency v_0 . The set of frequencies $v_0 + v$ observed in the spectrum due to the various rotational and vibrational states of the molecule is known as anti-Stokes' lines and that of frequencies $v_0 - v$ is known as Stokes' lines.

Although the classical explanation of the Raman effect predicts the existence of frequencies on both sides of the main frequency, the number of lines in the scattered spectrum and their relative intensities could not be accounted for by it.

A simple but more satisfactory explanation based on the quantum theory of radiation solved the problem of intensities as well. When a light

photon of energy hv_0 hits a molecule of the scatterer, three things might happen. The molecule might merely deviate the photon without absorbing its energy which would result in the appearance of the unmodified line in the scattered beam. The molecule might, on the other hand, absorb a part of the energy of the incident photon, giving rise to the modified Stokes' line, whose frequency would be less than that of the incident radiation. It may also happen that the molecule, if it is in an excited state, may impart some of its intrinsic energy to the incident photon, producing the anti-Stokes' line of frequency greater than that of the incident radiation. The mechanism of Raman scattering can be analytically expressed as follows:

Consider a collision between a photon and a molecule. Let E_p be the intrinsic energy of the molecule and v its velocity before collision. Let the frequency of the incident photon be v_0 . After the collision between the photon and the molecule takes place, the intrinsic energy of the molecule changes to E_q and is velocity to v'. The frequency of the photon changes to v' after collision. Applying the principle of conservation of energy, we can write

$$E_{p} + \frac{1}{2}mv^{2} + hv_{0} = E_{q} + \frac{1}{2}mv'^{2} + hv'.$$
(45)

As the collison does not cause any appreciable change of temperature, we may assume that the kinetic energy of the molecule remains practically unaltered in the process and hence the above equation becomes

$$E_p + hv_0 = E_q + hv'. \tag{46}$$

Therefore,

$$h(v' - v_0) = E_p - E_q \tag{47}$$

or
$$v' = v_0 + \frac{E_p - E_q}{h}$$
. (48)

In this expression, if $E_p = E_q$, $v' = v_0$, which represents the unmodified line; if $E_p < E_q$, $v' < v_0$ and one obtains a Stokes' line; and if $E_p > E_q$, $v' > v_0$ one obtains an anti-Stokes' line. It is well known from quantum principles that

$$E_p - E_q = nhv_m, \tag{49}$$

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where, n = 1, 2, 3, ... etc., and v_m is the characteristic frequency of the molecule. We can write therefore, by substituting for $E_p - E_q$ in Eq. (48) for n = 1

$$v' = v_0 \pm v_m. \tag{50}$$

This expression indicates that the difference in frequency $(v_0 - v')$ between the incident and scattered lines in the Raman effect corresponds to the frequency v_m , characteristic of the molecule. It thus accounts for the experimentally observed fact that the Raman lines are symmetrically situated on either side of the parent line at intervals corresponding to the characteristic frequency of the molecule.

The intensities of the lines in the Raman spectrum can be explained as follows. It is well known that the molecules of a material medium are distributed amongst a series of quantum states of energies E_1, E_2, \ldots . The statistical distribution of the molecules in these different quantum states is governed by Boltzmann's law and hence the number of molecules N_p in a particular state E_p is given by

$$N_p = C N g_p e^{-E_p/kT}, (51)$$

where C is a constant, N the total number of molecules, g_p the statistical weight of the state and k the Boltzmann's constant.

It can be seen from the above equation that since the Stokes' lines in the scattered spectrum of the molecule are caused by molecules of low energy value, they should be more intense and more in number than the corresponding anti-Stokes' lines.

2. Raman effect in the X-ray region

Raman¹⁷ in 1928 envisaged the possibility of the occurrence of the X-ray analogue of the Raman effect originally observed in the optical region. Krishnan²⁰ actually was the first to observe such an effect in the X-ray spectrum. His experiments involved the scattering of the MoK_{α} radiation from graphite. He observed new narrow lines shifted on the low frequency side of the Thomson peak by about the atomic ionisation energies of the K and L electrons. The positions of these lines were found to be independent of the scattering angle ϕ , thus

distinguishing them from the Compton band. Krishnan's experiments were repeated by Mitchell and Davies²¹ on graphite, Davies and Mitchell²² on aluminium, beryllium and graphite, Coster *et al.*²³ on beryllium and graphite, and DuMqnd²⁴ on beryllium with essentially similar results. However, many workers failed to observe the Raman scattering in the X-ray region. This conflicting evidence led Compton and Allison¹ to write the following remark in their famous book: 'The existence of such (Raman) radiation as a part of scattered Xrays, though frequently suspected, has never been established. It is probably too weak to be detected.'

The controversy regarding X-ray Raman scattering remained dormant until Dasgupta^{25, 26, 27} revived it in the 1950's. He carried out very careful experiments using high resolving power instruments on the scattering of the MoK_a and CuK_a radiations by the light elements beryllium, boron and graphite, and observed discrete lines on the long wavelength side of the Thomson peak. He^{28, 29} could resolve the Compton and the Raman lines very well as can be seen in Fig. 7. The positions of the Raman lines were found to be independent of the scattering angles as expected for the Raman process. Many workers³⁰⁻³⁴ later con-



Figure 7. Dasgupta's curve showing the basic scattering processes obtained in one spectrum: Thomson (P_1, P_2) , Compton (C) and Raman (R_1, R_2) .

firmed Dasgupta's work using high intensity sources and high resolution spectrographs. Thus the existence of the Raman scattering process in the Xray region was conclusively established.

The X-ray Raman process is shown schematically in Fig. 8. A part of the energy hv_i of the incident photon is used in raising an inner electron to the available unoccupied level in the atom, bringing the atom to an excited state. This system excitation energy is given by

$$\Delta E = h v_i - h v_s, \tag{52}$$

where hv_s is the energy of the scattered photon. This situation is somewhat similar to the X-ray absorption process in which an inner electron is raised to an outer available unoccupied level. Since the discrete atomic states are not characterized by momentum, there is no momentum conservation equation. In free atoms the atomic levels are discrete and one would therefore expect to get sharp Raman lines. However, in solids one must consider bands of unoccupied levels to which the Raman transitions take place. The Raman lines become Raman bands in solids and they are also sometimes referred to as Raman edges similar to the X-ray absorption edges. It may be mentioned that in the X-ray region only the Stokes' lines are observed. The probability of having the system already in the excited state so that the anti-Stokes' lines will be observed in the X-ray Raman process is very low.



Figure 8. The basic X-ray Raman scattering process.

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X-ray Raman scattering is essentially an incoherent scattering process. The change in energy when an electron is excited in this process can be calculated using the following equation

$$\Delta E = \frac{hc}{\lambda_i} - \frac{hc}{\lambda_s} = hc \left(\frac{1}{\lambda_i} - \frac{1}{\lambda_s}\right),\tag{53}$$

where λ_i and λ_s are the measured wavelengths of the incident and scattered lines in the spectrum. Thus, in principle one can determine the excitation energies or energy states of atoms by X-ray Raman scattering. One should also be able to study the effect of bonding on the inner levels, if the scattered spectra are studied in compounds and solids. One can observe Raman scattering experimentally by using a modern set-up shown in Fig. 9. Fortunately the experimental techniques have developed very rapidly in recent years and one can make use of them in studying the scattering phenomena.

Concluding remarks

Before concluding this article, it is necessary to emphasise once again that all the three basic processes of X-ray scattering described in the above sections occur simultaneously. The scattering cross-section in any experiment depends upon the angle of scattering and the scattering material, as well as the wavelength of the incident radiation. For a particular experimental situation (CrK_β radiation for beryllium scatterer at 40°) the scattering cross-sections calculated by Pimpale and Mande³⁵ are given in Table 1. In this table are summarised the various aspects of matter and radiation which are manifested in the scattering process.

Out of the three processes the Thomson process is the most dominant one in the medium X-ray region. It is this process which is responsible for Xray diffraction which is very widely used in crystal structure analysis; as a matter of fact, X-ray diffraction is a special case of Thomson scattering. Luckily no change in wavelength is involved in this process, making the diffraction studies comparatively simpler. In most X-ray diffraction studies the Compton scattering is not taken into account explicitly because it mainly contributes to the

Figure 9. A modern experimental set-up for studying X-ray scattering.

background intensity and cannot be readily distinguished from that caused by Thomson scattering.

X-ray diffraction has made it possible to study the structures of a variety of materials like metals and alloys, inorganic and organic compounds, glassy and amorphous materials. It has also made it possible to study the structure of very complicated biological molecules such as proteins, nucleic acids, etc. Similarly, the investigations of Thomson scattering by liquids give valuable information about the arrangement of molecules in them. Besides these, from the scattering by gases we learn about the distribution of electrons in atoms themselves, bringing a direct confirmation of the shell structure of electronic orbitals in atoms. We thus have in Thomson's scattering an invaluable tool for investigating the most intimate aspects of matter.

While discussing Compton scattering, it was assumed that the scattering interaction takes place with a single free electron at rest. Jauncey³⁶ and DuMond³⁷ modified Compton's theory by taking into account the motion of the free electrons in



Interaction details			Processes	
		Thomson	Compton	Raman
1.	Nature of the incident radiation	electromagnetic wave	photon	photon
2.	Interaction with	all electrons in the scatterer	free electrons at rest in the scatterer	a bound single electron
3.	Wavelength of the scattered radiation	no change in wavelength observed	change in wavelength and a recoil electron observed	change in wavelength but no recoil electron observed
4.	Wavelength dependence on scattering angle	wavelength independent of the scattering angle	wavelength depends on the scattering angle	wavelength independent of the scattering angle
5.	Dominance in different regions	medium X-ray region	mainly in the hard X-ray region	observed with intense sources in the medium X-ray region
6.	Scattering cross section (for CrK_{β} radiation for $\phi = 40^{\circ}$ for beryllium scatterer)	$4.65 \times 10^{-26} \text{ cm}^2$	$3.95 \times 10^{-27} \text{ cm}^2$	$4.00 \times 10^{-28} \text{ cm}^2$
7.	Applications	basic processes of X- ray diffraction	study of momentum states in solids	study of electron states in materials

Table 1. Comparison of basic X-ray scattering processes

solids. They showed that this modification results in widening of the Compton line, giving rise to a band. It has been shown that the Compton profile studies can help in determining momentum distribution of electrons in solids. In many materials, the free electrons oscillate collectively giving rise to what is called a *plasmon*. When scattering takes place involving a plasmon, one gets a plasmon band in the scattered spectrum. The plasmon band helps in obtaining information about the collective motion of free electrons in a material.^{38, 39}

Raman scattering in the X-ray region, as described earlier, can help in determining the energies of atomic states. However, since the process is comparatively weaker, not many such studies have been carried out. With the advent of new powerful X-ray sources like the synchrotron storage rings and the development of new spectroscopic techniques,⁴⁰ it may now be possible to carry out more meaningful experiments on X-ray scattering. The study of Raman lines or bands in the X-ray region will, it is hoped, provide fruitful information regarding the electron states of atoms, molecules and solids, complementary to that presently available from X-ray absorption and photoelectron spectroscopic work.

To conclude this article we might mention that the intimate overlapping of classical and quantum features of X-ray scattering have made it a very valuable field of study for clarifying our fundamental notions in physics. The field is by no means a closed one. It can be hoped that in the near future many more interesting studies in this field would be forthcoming, helping us to better appreciate the beauties of modern physics.

Acknowledgements

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Mind of a scientist

While Raman was an officer in finance department a person brought to him a bundle of currency notes which were badly burnt. Any other officer would have easily rejected the claim and would have said good bye to the person. Raman had a scientific mind, so he took it as a problem and found out the numbers and other markings from the charred bits of the notes. He analysed the whole data and was satisfied that the case was a genuine one. The applicant could get whole of his burnt lot replaced by a fresh one. P. B. VIDYASAGAR

Life and work of Sir C. V. Raman A photo feature

Presentation: P. B. Vidyasagar

Photographs: Satish Paknikar

Special thanks are due to Prof. S. Ramaseshan, RRI, Bangalore. Reprinted with permission from Raman Research Institute, Bangalore.



Raman as a student of Presidency College, Madras, second row from top, fourth from right.



Sir C. V. Raman and Loksundari Devi-A revolutionary marriage.

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Mahindralal Sirkar: A man of vision and founder of the institution where Raman did his Nobel prize-winning research.



The laboratory where Raman carried out his all time great work.



Raman with spectrograph-the two inseparables



Raman with Max Born at the Indian Institute of Science, Bangalore—an extraordinary appointment.



An excellent lecturer.



Raman the wonderful showman and classic demonstrator.



Raman with S. Radhakrishnan, then President of India.



Raman with Yukawa.



Raman with Heisenberg.



Raman with children, whom he considered as resources for the future India.



A stamp released by the Government of India to honour his contribution to science.



Raman in different moods. He was a very simple man, quite childlike but with a lion's heart.

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NOBEL PRIZE FOR PHYSICS

Stockholm, 11 December 1930

Presentation speech*

H. PLEIJEL

Chairman, Nobel Committee for Physics of the Royal Swedish Academy of Sciences

Your Majesty, Your Royal Highnesses,

Ladies and Gentlemen,

The Academy of Sciences has resolved to award the Nobel Prize in Physics for 1930 to Sir Venkata Raman for his work on the scattering of light and for the discovery of the effect named after him.

The diffusion of light is an optical phenomenon, which has been known for a long time. A ray of light is not perceptible unless it strikes the eye directly. If, however, a bundle of rays of light traverses a medium in which extremely fine dust is present, the ray of light will scatter to the sides and the path of the ray through the medium will be discernible from the side. We can represent the course of events in this way; the small particles of dust begin to oscillate owing to electric influence from the ray of light, and they form centres from which light is disseminated in all directions. The wavelength, or the number of oscillations per second, in the light, thus diffused is here the same as in the original ray of light. But this effect has different degrees of strength for light with different wavelengths. It is stronger for the short wavelengths than for the long ones, and consequently it is stronger for the blue part of the spectrum than for the red part. Hence if a ray of light containing all the colours of the spectrum passes through a medium, the yellow and the red rays will pass medium without appreciable through the scattering, whereas the blue rays will be scattered to

* Reproduced with permission from The Nobel Foundation, Stockholm, Sweden.

the sides. This effect has received the name of the Tyndall effect.

Lord Rayleigh, who has made a study of this effect, has put forward the hypothesis that the blue colours of the sky and the reddish colouring that is observed at sunrise and sunset are caused by the diffusion of light owing to the fine dust or the particles of water in the atmosphere. The blue light from the sky would thus be light scattered to the sides, while the reddish light would be light that passes through the lower layers of the atmosphere and which has become impoverished in blue rays owing to scattering. Later, in 1899, Rayleigh threw out the suggestion that the phenomenon in question might be due to the fact that the molecules of air themselves exercised a scattering effect on the rays of light.

In 1914 Cabannes succeeded in showing experimentally that pure and dustless gases also have the capacity of scattering rays of light.

But a closer examination of scattering in different substances in solid, liquid, or gaseous form showed that the scattered light did not in certain respects exactly follow the laws which, according to calculation, should hold good for the Tyndall effect. The hypothesis which formed the basis of the effect would seem to involve amongst other things, that the rays scattered to the sides were polarized. This, however, did not prove to be exactly the case.

This divergence from what was to be expected was made the starting-point of a searching study of the nature of scattered light, in which study Raman was one of those who took an active part. Raman sought to find the explanation of the anomalies in symmetry observed in the molecules. During these studies of his in the phenomenon of scattering, Raman made, in 1928, the unexpected and highly surprising discovery that the scattered light showed not only the radiation that derived from the primary light but also a radiation that contained other wavelengths, which were foreign to the primary light.

In order to study more closely the properties of the new rays, the primary light that was emitted from a powerful mercury lamp was filtered in such a way as to yield a primary light of one single wavelength. The light scattered from that ray in a medium was watched in a spectrograph, in which every wavelength or frequency produced a line. Here he found that, in addition to the mercury line chosen, there was obtained a spectrum of new sharp lines, which appeared in the spectrograph on either side of the original line. When another mercury line was employed, the same extra spectrum showed itself round it. Thus, when the primary light was moved, the new spectrum followed in such a way that the frequency distance between the primary line and the new lines always remained the same.

Raman investigated the universal character of the phenomenon by using a large number of substances as a scattering medium, and everywhere found the same effect.

The explanation of this phenomenon, which has received the name of the Raman effect, after its discoverer, has been found by Raman himself, with the help of the modern conception of the nature of light. According to that conception, light cannot be emitted from or absorbed by material otherwise than in the form of definite amounts of energy or what are known as light quanta. Thus the energy of light would possess a kind of atomic character. A quantum of light is proportionate to the frequency of rays of light, so that in the case of a frequency twice as great, the quanta of the rays of light will also be twice as great.

In order to illustrate the conditions when an atom emits or absorbs light energy, we can, according to Bohr, picture to ourselves the atom as consisting of a nucleus, charged with positive electricity round which negative electrons rotate in circular paths at various distances from the centre. The path of every such electron possesses a certain energy, which is different for different distances from the central body.

Only certain paths are stable. When the electron moves in such a path, no energy is emitted. When, on the other hand, an electron falls from a path with higher energy to one with lower energy—that is to say, from an outer path to an inner path light is emitted with a frequency that is characteristic of these two paths and the energy of radiation consists of a quantum of light. Thus the atom can give rise to as many frequencies as the number of different transitions between the stable paths. There is a line in the spectrum corresponding to each frequency.

An incoming radiation cannot be absorbed by the atom unless its light quantum is identical with one of the light quanta that the atom can emit.

Now the Raman effect seems to conflict with this law. The positions of the Raman lines in the spectrum do not correspond, in point of fact, with the frequencies of the atom itself, and they move with the activating ray. Raman has explained this apparent contradiction and the coming into existence of the lines by the effect of combination between the quantum of light coming from without and the quanta of light that are released or bound in the atom. If the atom, at the same time as it receives from without a quantum of light, emits a quantum of light of a different magnitude, and if the difference between these two quanta is identical with the quantum of light which is bound or released when an electron passes from one path to another, the quantum of light coming from without is absorbed. In that case, the atom will emit an extra frequency, which either will be the sum of or the difference between the activating ray and a frequency in the atom itself. In this case, these new lines group themselves round the incoming primary frequency on either side of it, and the distance between the activating frequency and the nearest Raman lines will be identical with the lowest oscillation frequencies of the atom or with its ultrared spectrum. What has been said as to the atom and its oscillations also holds good for the molecule.

In this way, we get the ultrared spectrum moved up to the spectral line of the activating light. The

discovery of the Raman lines has proved to be of extraordinarily great importance for our knowledge of the structure of molecules.

So far, indeed, there have been all but insuperable difficulties in the way of studying these ultrared oscillations, because that part of the spectrum lies so far away from the region where the photographic plate is sensitive. Raman's discovery has now overcome these difficulties, and the way has been opened for the investigation of the oscillations of the nucleus of the molecules. We choose the primary ray within that range of frequency where the photographic plate is sensitive. The ultrared spectrum, in the form of the Raman lines, is moved up to that region and, in consequence of that, exact measurements of its lines can be effected.

In the same way, the ultraviolet spectrum can be investigated with the help of the Raman effect. Thus we have obtained a simple and exact method for the investigation of the entire sphere of oscillation of the molecules.

Raman himself and his fellow-workers have, during the years that have elapsed since the discovery was made, investigated the frequencies in a large number of substances in the solid, liquid, and gaseous state. Investigations have been made as to whether different conditions of aggregation affect atoms and molecules, and the molecular conditions in electrolytic dissociation and the ultrared absorption spectrum of crystals have been studied.

Thus the Raman effect has already yielded important results concerning the chemical constitution of substances; and it is to foresee that the extremely valuable tool that the Raman effect has placed in our hands will in the immediate future bring with it a deepening of our knowledge of the structure of matter.

Sir Venkata Raman, the Royal Academy of Sciences has awarded you the Nobel Prize in Physics for your eminent researches on the diffusion of gases and for your discovery of the effect that bears your name. The Raman effect has opened new routes to our knowledge of the structure of matter and has already given most important results.

I now ask you to receive the prize from the hands of His Majesty.

'You are blind or mad or both'

One witnesses Raman's outspokenness when he was transferred to Rangoon as Assistant Accountant General in the Indian Finance Department. The A.G. was an Englishman accustomed to accepting and expecting a meek behaviour from his juniors. The very independent nature of Sir Raman did not fit in those circumstances.

Once Sir Raman criticised some order of the A.G. This made the A.G. very angry and he came storming in Sir Raman's room, waving his note at his face. The Englishman, then pointed to a red ink bottle on the table and said, 'Mr. Raman, if I point to this red ink bottle and say "I am sure this is black ink" your duty is to say, "Yes, sir, it is black"'. Raman could not put up with this show of authority and replied coolly, 'If you did that my duty would be to say, "Sir, you are either blind or mad or both"'.

NEELA RANADE

NOBEL LECTURE The molecular scattering of light

C. V. RAMAN (at Stockholm on December 11, 1930)

The colour of the sea

In the history of science, we often find that the study of some natural phenomenon has been the starting point in the development of a new branch of knowledge. We have an instance of this in the colour of skylight, which has inspired numerous optical investigations, and the explanation of which, proposed by the late Lord Rayleigh, and subsequently verified by observation, forms the beginning of our knowledge of the subject of this lecture. Even more striking, though not so familiar to all, is the colour exhibited by oceanic waters. A voyage to Europe in the summer of 1921 gave me the first opportunity of observing the wonderful blue opalescence of the Mediterranean Sea. It seemed not unlikely that the phenomenon owed its origin to the scattering of sunlight by the molecules of the water. To test this explanation, it appeared desirable to ascertain the laws governing the diffusion of light in liquids, and experiments with this object were started immediately on my return to Calcutta in September, 1921. It soon became evident, however, that the subject possessed a significance extending far beyond the special purpose for which the work was undertaken, and that it offered unlimited scope for research. It seemed indeed that the study of light-scattering might carry one into the deepest problems of physics and chemistry, and it was this belief which led to the subject becoming the main theme of our activities at Calcutta from that time onwards.

The theory of fluctuations

From the work of the first few months, it became clear that the molecular scattering of light was a

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very general phenomenon which could be studied not only in gases and vapours but also in liquids and in crystalline and amorphous solids, and that it was primarily an effect arising from molecular disarray in the medium and consequent local fluctuations in its optical density. Except in amorphous solids, such molecular disarray could presumably be ascribed to thermal agitation, and the experimental results appeared to support this view. The fact that molecules are optically anisotropic and can orientate freely in liquids was found to give rise to an additional type of scattering. This could be distinguished from the scattering due to fluctuations in density by reason of its being practically unpolarized, whereas the latter was completely polarized in the transverse direction. The whole subject was critically reviewed and the results till then obtained were set out in an essay published by the Calcutta University Press in February 1922.

The various problems requiring solution indicated in this essay were investigated with the aid of a succession of able collaborators. It is possible to mention briefly only a few of the numerous investigations which were carried out at Calcutta during the six years from 1922 to 1927. The scattering of light in fluids was studied by Ramanathan over a wide range of pressures and temperatures with results which appeared to support the fluctuation theory of its origin. His work also disclosed the remarkable changes in the state of polarization which accompany the variations of intensity with temperature in vapours and in liquids. Liquid mixtures were investigated by Kameswara Rao, and furnished optical proof of the existence in such systems of simultaneous fluctuations of density, composition, and molecular orientation. Srivastava studied the scattering of light in crystals in relation to the thermal fluctuations of density and their increase with temperature. Ramdas investigated the scattering of light by liquid surfaces due to thermal agitation, and established a relation between surface-tension and surface-opalescence. He also traced the transition from surface-opalescence to volume-opalescence which occurs at the critical temperature. Sogani investigated X-ray diffraction in liquids, in order to connect it with their optical behaviour, and test the application of the fluctuation theory to X-ray scattering.

The anisotropy of molecules

As stated above, the state of polarization of the light scattered in fluids is connected with the optical anisotropy of the molecules. Much of the work done at Calcutta during the years from 1922 to 1927 was intended to obtain data concerning this property and to establish its relations with various optical phenomena. Krishnan examined a great many liquids, and by his work showed very clearly the dependence of the optical anisotropy of the molecule on its chemical constitution. Ramakrishna Rao studied the depolarization of scattered light in a very large number of gases and vapours and obtained information of high importance for the progress of the subject. Venkateswaran studied the scattering of light in aqueous solutions to find the influence on it of electrolytic dissociation. Ramachandra Rao investigated liquids having highly elongated molecules and also highly polar substances over a wide range of temperatures, and discovered the influence of molecular shape and molecular association on the depolarization of scattered light in liquids.

The interpretation of the observations with liquids involved the development of a molecular theory of light-scattering in dense media which was undertaken by Ramanathan, I myself, and Krishnan. A revised opalescence formula was derived which differed from that of Einstein and yielded results in better agreement with observation. Krishnan and I also published a series of investigations showing how the optical anisotropy of the molecules deduced from light-scattering could be utilized to interpret the optical and dielectric behaviour of fluids, and also the electric, magnetic, and mechanical birefringence exhibited by them. The conclusions derived from these studies enabled a connection to be established between the molecular anisotropy observed in fluids and the optical, electric, and magnetic aeolotropy exhibited by solids in the crystalline state.

A new phenomenon

The investigations referred to above were in the main guided by the classical electromagnetic theory of light, the application of which to the problems of light-scattering is chiefly associated with the names of Rayleigh and Einstein. Nevertheless, the possibility that the corpuscular nature of light might come into evidence in scattering was not overlooked and was in fact elaborately discussed in the essay of February 1922 which was published at least a year before the well-known discoveries of Compton on X-ray scattering. While our experiments in the main appeared to support the electromagnetic theory of light, evidence came to hand at a very early stage of the investigations of the existence of a phenomenon which seemed to stand outside the classical scheme of thought. The scattering of light in transparent fluids is extremely feeble, much weaker in fact than the Tyndall effect usually observed in turbid media. It was experimentally discovered that associated with the Rayleigh-Einstein type of molecular scattering was another and still feebler type of secondary radiation, the intensity of which was of the order of the magnitude of a few hundredths of the classical scattering and differed from it in not having the same wavelength as the primary or incident radiation. The first observation of this phenomenon was made at Calcutta in April 1923 by Ramanathan who was led to it in attempting to explain why in certain liquids (water, ether, methyl and ethyl alcohols), the depolarization of scattered light varied with the wavelength of the incident radiation. Ramanathan found that after exhaustive chemical purification and repeated slow distillation of the liquid in vacuum, the new radiation persisted undiminished in intensity, showing that it was a

characteristic property of the substance studied and not due to any fluorescent impurity. Krishnan observed a similar effect in many other liquids in 1924, and a somewhat more conspicuous phenomenon was observed by me in ice and in optical glasses.

The optical analogue of the Compton effect

The origin of this puzzling phenomenon naturally interested us, and in the summer of 1925, Venkateswaran attempted to investigate it by photographing the spectrum of the scattered light from liquids, using sunlight filtered through colour screens, but was unable to report any decisive results. Ramakrishna Rao in his studies on the depolarization of scattering during 1926 and 1927 looked carefully for a similar phenomenon in gases and vapours, but without success. This problem was taken up again by Krishnan towards the end of 1927. While his work was in progress, the first indication of the true nature of the phenomenon came to hand from a different quarter. One of the problems interesting us at this time was the behaviour in light-scattering of highly viscous organic liquids which were capable of passing over into the glassy state. Venkateswaran undertook to study this question, and reported the highly interesting result that the colour of sunlight scattered in a highly purified sample of glycerine was a brilliant green instead of the usual blue. The phenomenon appeared to be similar to that discovered by Ramanathan in water and the alcohols, but of much greater intensity, and, therefore, more easily studied. No time was lost in following up the matter. Tests were made with a series of filters transmitting narrow regions of the solar spectrum and 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 it towards the red. The radiations were also strongly polarized. These facts indicated a clear analogy between the empirical characters of the phenomenon and the Compton effect. The work of Compton had made familiar the idea that the wavelength of radiation could be degraded in the process of scattering and the observations with

glycerine suggested to me that the phenomenon which had puzzled us ever since 1923 was in fact the optical analogue of the Compton effect. This idea naturally stimulated further investigation with other substances.

The chief difficulty which had hitherto oppressed us in the study of the new phenomenon was its extreme feebleness in general. This was overcome by using a 7-inch refracting telescope in combination with a short-focus lens to condense sunlight into a pencil of very great intensity. With these arrangements and using complementary light-filters in the path of the incident and scattered beams, as was done by Ramanathan in 1923 to isolate the modified radiations, it was found that they could be readily observed in a great many liquids, and that in many cases they were strongly polarized. 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. Compressed gases such as CO_2 and N₂O, crystalline ice, and optical glasses also were found to exhibit the modified radiations. These observations left little doubt that the phenomenon was really a species of light-scattering analogous to the Compton effect.

The spectroscopic character of the new effect

Thanks to the vastly more powerful illumination made available by the 7-inch refractor, the spectroscopic examination of the effect, which had been abandoned in 1925 as indecisive, now came within the reach of direct visual study. With a Zeiss cobaltglass filter placed in the path of the incident beam and one or other of a series of organic liquids as the scattering substance, a band in the blue-green region was observed by me in the spectrum of the scattered light, separated by a dark interval from the indigo-violet region transmitted by the filter. Both of these regions in the spectrum became sharper when the region of transmission was narrowed by insertion of an additional filter in the incident beam. This suggested the employment, instead of sunlight, of the highly monochromatic radiations given out by a mercury arc in combination with a condenser of large aperture and a cobalt-glass filter. With these arrangements, the spectrum of the scattered light from a variety of liquids and solids was visually examined, and the startling observation was made that the spectrum generally included a number of sharp lines or bands on a diffuse background which were not present in the light of the mercury arc.

The quartz mercury lamp was so powerful and convenient a source of monochromatic illumination that, at least in the case of liquids and solids, photographing the spectrum of scattered light was found to present no extraordinary difficulties. The earliest pictures of the phenomenon were in fact taken with a portable quartz spectrograph of the smallest size made by the firm of Hilger. With a somewhat larger instrument of the same type, Krishnan obtained very satisfactory spectrograms with liquids and with crystals on which measurements of the desired precision could be made, and on which the presence of lines displaced towards the violet was first definitely established. The experimental difficulties were naturally greater in the case of gases or vapours, though they could be lessened by working with the substance under pressure. With an improvised instrument of a large aperture (F/1.8), Ramdas obtained the first spectrograms with a gaseous substance (ether vapour) at atmospheric pressure.

In interpreting the observed phenomena, the analogy with the Compton effect was adopted as the guiding principle. The work of Compton had gained general acceptance for the idea that the scattering of radiation is a unitary process in which the conservation principles hold good. Accepting this idea, it follows at once that, if the scattering particle gains any energy during the encounter with the quantum, the latter is deprived of energy to the same extent, and accordingly appears after scattering as a radiation of diminished frequency. From thermodynamic principles, it follows that the reverse process should also be possible. Adopting these ideas, the actual observations could be interpreted, and the agreement of the observed displacements with the infrared frequencies of the molecules

made it clear that the new method opened up an illimitable field of experimental research in the study of the structure of matter.

Interpretation of the effect

It appears desirable to emphasize that the conservation principle of Compton is useful in interpreting the effects disclosed by experiment; it is by itself insufficient to explain the observed phenomena. As is well known from studies on molecular spectra, a gaseous molecule has four different species of energy of increasing orders of magnitude, namely, those corresponding to translatory motion, rotation, vibration, and electronic excitation. Each of these, except the first, is quantized and may be represented by an integer in an extended sequence of quantum numbers. The aggregate energy of a molecule may, therefore, assume any one out of a very large number of possible values. If we assume that an exchange of energy occurs in the collision between the molecule and the quantum, and limit ourselves to cases in which the final energy of the molecule is less than that of the incident quantum, we arrive at the result that the spectrum of the scattered light should contain an immense number of new lines and should in fact rival in its complexity the band spectrum of the molecule observed in the emission or absorption of light. Nothing more different from what is actually observed can be imagined than the foregoing picture. The most conspicuous feature revealed by experiment is the beautiful simplicity of the spectra of even complicated poly-atomic molecules obtained in lightscattering, a simplicity that is in striking contrast to the extreme complexity of their emission or absorption spectra. It is this simplicity that gives to the study of light-scattering its special significance and value. It is clear that the effect actually observed was not and could not have been foreseen from an application of the conservation principles.

The general principle of correspondence between the quantum and classical theories enunciated by Niels Bohr enables us, on the other hand, to obtain a real insight into the actual phenomena. The classical theory of light-scattering tells us that if a molecule scatters light while it is moving, rotating or vibrating, the scattered radiations may include certain frequencies, different from those of the incident waves. This classical picture, in many respects, is surprisingly like what we actually observe in the experiments. It explains why the frequency shifts observed fall into three classes, translational, rotational and vibrational, of different orders of magnitude. It explains the observed selection rules, as, for instance, why the frequencies of vibration deduced from scattered light include only the fundamentals and not the overtones and combinations which are so conspicuous in emission and absorption spectra. The classical theory can even go further and give us a rough indication of the intensity and polarization of the radiations of altered frequency. Nevertheless, the classical picture has to be modified in essential respects to give even a qualitative description of the phenomena, and we have, therefore, to invoke the aid of quantum principles. The work of Kramers and Heisenberg and the newer developments in quantum mechanics which have their root in Bohr's correspondence principle seem to offer a promising way of approach towards an understanding of the experimental results. But until we know much more than we do at present regarding the structure of molecules, and have sufficient quantitative experimental knowledge of the effect, it would be rash to suggest that they afford a complete explanation of it.

The significance of the effect

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 determined 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 physicochemical 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.

Some concluding remarks

From a physical point of view, the quantitative study of the effect with the simplest molecules holds out the largest hope of fundamental advances. The beautiful work of McLennan with liquefied gases, and that of R. W. Wood and Rasetti are pioneer investigations in this field which command the highest admiration. The quantitative study of the effect with crystals of the simplest possible chemical constitution is naturally of great importance. The case of the diamond, which has been investigated by Ramaswamy, Robertson, and Fox and with especial completeness by Bhagavantam, is of special interest. Very surprising results have been obtained with this substance, which may be the pathway to a fuller understanding of the nature of the crystalline state. I should also like to draw attention to the work of Krishnamurti, who has traced a remarkable dependence of the intensity of the spectral lines observed in scattering on the nature of the chemical bond, and followed the transition from the homopolar to the heteropolar type of chemical combination. Krishnamurti's observation that the paramagnetism of crystals apparently influences the observed intensity of the displaced lines is one of the most remarkable ever made in this new field of research.

Why the sky is blue*

C. V. RAMAN

Prof. C. V. Raman's lecture on "WHY THE SKY IS BLUE"* delivered on December 22, 1968, at the foundation stone laying ceremony of the Community Science Centre, Ahmedabad

When I was asked to choose a scientific subject for my lecture I had no difficulty at all in choosing the subject of "Why the sky is blue." Fortunately, nature has been kind today; as I look up and see, the sky is blue; not everywhere, as there are many clouds. I chose this subject for the simple reason that this is an example of something you do not have to go to the laboratory to see. Just look up, look at the sky. And I think it is also an example of the spirit of science. You learn science by keeping

"And the great problem today, which Dr. Sarabhai has addressed himself to, is how to rouse the younger generation of our country to meet this great challenge before us, once again to build up India into a great centre of knowledge and learning and endeavour."

your eyes and ears open and looking around at this world. The real inspiration of science, at least to me, has been essentially the love of nature. Really, in this world, wherever we see, we see all kinds of miracles happening in nature. To me, everything I see is something incredible, something absolutely incredible. We take it all for granted. But I think the essence of the scientific spirit is to look behind and beyond and to realise what a wonderful world it is that we live in. And everything that we see presents to us not a subject for curiosity, but a challenge, a challenge to the spirit of man to try to understand something of this vast mystery that surrounds us. Science continually attempts to meet this challenge to the spirit of man. And the great problem today, which Dr. Sarabhai has addressed himself to, is how to rouse the younger generation of our country to meet this great challenge before us, once again to build up India into a great centre of knowledge and learning and endeavour. Well, I wish you all success. Now let me turn back to my problem, "Why the sky is blue".?

I raised this question because it is an easy subject. I only have to look up and see that the sky is blue. But why is it blue? The interesting point is that it is easy to answer that question in a casual way. If you ask a botanist, why are leaves green? He murmurs, 'Chlorophyll'. Finished. You see, all scientific questions can be disposed of in that summary fashion, in one or two words. You can surely pass your examinations with that kind of answer, but that is not the real answer. As I said before, the scientific challenge of nature is to think, not only to discover but to think, to think continually and to try to penetrate this mystery: "Why is it blue?" That is a very interesting problem, because two things are there. The sky is there and I am here. I see it is blue. It is the human brain and the human mind as well that are involved in this problem. Now suppose we put this problem before the young people. Don't read any book about it, don't ask your teacher. Let us sit down and try to think out this problem; why is the sky blue? Look at it as if it is a completely new scientific problem about which nobody has troubled himself before. You sit down and think it out and you will find it a most exciting thing to ask yourself that question and see if you can discover the answer for yourelf. Now I will put it to you in this way. The best way to answer a question is to ask another. At night, we all see the stars. On a

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fairly clear night you see the stars twinkling in the sky. Why are the stars not visible in day time? Please ask yourself this question. Well, the reason obviously is that the earth, as a modest lady, has hidden herself under a veil. The sky is a veil which she has thrown around us. We cannot see the stars during the day, because the veil hides the stars. And what is this veil? The veil obviously is the atmosphere of the earth. The same veil which at night is

"As I said before, the scientific challenge of nature is to think, not only to discover but to think, to think continually and to try to penetrate this mystery."

so transparent that we can see the faintest star and the milky way is covered up in day-time. Obviously, it is the atmosphere which is the veil. And we see the sky as blue only because we have not got other thicker veils like these clouds. You see, for example, those clouds high in the blue sky. Obviously, therefore, for the sky to be really blue, there must be nothing else, no clouds and perhaps no dust. The clearer the sky is, the bluer it is. So the sky is not always blue; it is sometimes blue and sometimes not blue at all. So that the mere looking at the sky enables us to understand the condition of the atmosphere.

"Why is it that the sky which appears blue in sunlight, does not appear blue in moonlight?"

Let me say one thing more. Obviously, the sky and the atmosphere are lit up by the sunlight. Sunlight is passing through this great column of air and obviously it is the atmosphere, something that is transparent and invisible at night, that is seen to us by the light—sunlight—passing through the atmosphere. Now I want you to ask yourself another question. I don't know if any of you have had the curiosity to look at the clear sky on a fullmoon night. You know that moonlight is only the sunlight incident on the moon and is diffused or reflected. I don't know if any of you have really watched the sky on a clear full-moon night. You will be astonished to find that the sky is not blue. It

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appears pale, you just see some light and you see some of the stars even under the full-moon sky, but the sky is not blue. Why is it that the sky which appears blue in sun-light, does not appear blue in moonlight? The answer obviously is: the illumination is far less powerful. You don't require to be much of a mathematician to calculate the ratio of the intensities of full-moon light and sunlight. I present it to some young mathematician to sit down and work out. How big is the moon? What should be the brightness of moonlight? It is a little astronomical problem. Rough arithmetic would tell you that moonlight is something like half a millionth part as bright as sunlight; you would think, it is terribly small. But moonlight, when it is there seems very bright though it is only half a millionth part of the brightness of sunlight. Why does it look so bright? Well, the eyes have got accustomed to much lower levels of illumination. So moonlight appears very bright, but not so bright, as to veil all the stars. But the sky, it does not appear blue. So, this comparison of sunlight and moonlight brings to our notice a very remarkable fact. It is an absolutely fundamental aspect of human vision that to perceive colour, you must have a high level of illumination. The sky is blue, merely because sunlight is brilliant; moonlight is much less brilliant and so you don't perceive colour. This is a principle which perhaps is not so widely appreciated as it ought to be. Colour is only perceived at high levels of illumination. The higher the illumination the brighter are the colours. You go down to low levels of illumination, say, a millionth part, half a millionth or a hundred thousandth part of sunlight, the sense of colour disappears. Now this is a very fundamental fact of human vision, which simply comes out of nothing else but just observation and thinking, that's all. I can go on giving any number of illustrations. Perhaps the most striking illustration emerges when you look at the stars or such objects as the Orion nebula through small telescopes. Let me say here and now, my belief that there is no science so grand, so elevating, so intensely interesting as astronomy. It is amazing to see how many people high up have never seen the sky through the telescope. I want to tell them something which is absolutely incredible: Nothing more than a pair of binoculars, a good pair of binoculars is needed to educate oneself in the facts of astronomy. I think a man who does not look at the sky even through that modest equipment—a pair of bionculars—cannot be called an educated person, because he has missed the most wonderful thing and that is the universe in which he lives. You must have a look at it. You don't see much of it, but you see a little and even this little is enough to elevate the human soul and make us realise what a wonderful thing this world is.

I come back now to the problem of the blue sky. I want to pose to you a very difficult question. Why is it that we perceive the blue colour only under intense illumination in sunlight, and not in moonlight? I will by pass that and come back to the question: Why is the sky blue? Well, we all know that white light is composed of all the colours in the spectrum. You divide white light into various colours; you start with deep red at one end, light red,

"Let me say here and now, my belief that there is no science so grand, so elevating, so intensely interesting as astronomy."

orange, yellow, green, blue and violet, so on, the whole range of colours. When I look at the sky, I see only the blue; what has happened to the rest of the spectrum? This is the basic question. The question becomes a very pressing one when I remark that when we actually spread out sunlight into a spectrum, the blue part of it is the least intense part. Less than 1/40th of the whole energy of the brightness of the sunlight appears in the blue of the spectrum and we see only that 1/40th part. You don't see the rest of the spectrum. It has simply vanished. It is not there at all. You can look very very hard and try to see if you can see any red or yellow or green in blue sky. We don't see it. The blue has just masked the rest of the spectrum. This is a very remarkable fact. If you watch the sky on some occasions, you get great masses of white clouds, what they call, the cumulus clouds not huge things, just little bunches. It is a beautiful sight to see the blue sky and these little masses soaring above. I have derived great satisfaction in just

doing nothing at all and looking at these masses of clouds and the blue sky. The interesting point is precisely when you have the clouds moving about that the sky is bluest. What it means is that these cumulus clouds in the course of their formation just cleaned up the rest of the atmosphere. They take up the dust particles and concentrate them on the white clouds. The rest is left nice and clean. You see the beautiful blue view against the brilliant white, it is a very lovely sight. A sight for the Gods; only you don't bother to look at it because it is so common. You may ask me, how is the cleaning process accomplished? Now here is a wonderful story. When I ask the young people, "What is the cloud?" "Oh! Sir, it is steam". The usual answer you get is that the cloud is steam, but it is nothing of the sort. The cloud consists of particles and what looks to us as great masses of white clouds are just droplets of water. Water is heavy but why does it not fall down? We find it floating in the air! You see that is another problem. Already I am going from one problem to another. We ask ourselves, what is a cloud? Why is it floating in the air? The moment you ask the question, "Why the sky is blue?" you go deeper and deeper into some of the deepest problems of physics. Now the interesting point is this you cannot have a cloud unless you have dust particles about which it can form.

"The question becomes a very pressing one when I remark that when we actually spread out sunlight into a spectrum, the blue part of it is the least intense part. Less than 1/40th of the whole energy of the brightness of the sunlight appears in the blue of the spectrum and we see only that 1/40th part."

There must be particles of some sort, may be very small, may be very large. They call it in learned language 'Nuclei'. If there is no dust in the air, there will be no cloud and no rain. You see, how from the blue sky, we have got on to the origin of rain, rainfall and so on. One thing leads to another. That is the essence of science. You must go deeper where it leads you. You cannnot go thus far and no further. The moment you raise a question, another question arises, then another question, so on and so forth. Ultimately, you find that you have to travel

the whole field of science before you get the answer to the question: Why the sky is blue? So I told you this fact about the clouds. Well, I should say the cloud cleans up the atmosphere. Cloud forms and then leaves the atmosphere clean, comparatively free from dust particles and other nuclei and that is why the sky is blue. So we come down at last to getting some kind of answer to the problem. The sky is blue because the atmosphere is clean and free from dust and all nuclei. The clearer it is, the bluer it looks, provided there is enough light. So you come somewhere near the answer to the question. What is it you are able to see? The fact is that when we see a blue sky, we see the atmosphere of the earth, the gases of the atmosphere, they diffuse the light and we see the blue light of the sky. But still we are far from the answer.

I told you that blue is only 1/40th part of the sunlight. What happens to the rest of the light, the sunlight? That is the question. Now this question can be answered in the following fashion. You look at the white cloud and look at the blue sky. You can compare them with the help of a pocket spectroscope and you find strangely enough that you have to look very very carefully before you find any difference in the spectrum of the blue sky and the spectrum of the white cloud. White cloud is certainly very much brighter. But so far as spectrum is concerned, you see in the blue sky and in the cloud the same spectrum. It also starts with the red end and goes on till the blue. But in one case you see the blue, in the other case you see the white. And with great trouble, you look very carefully. You see that there is some difference in the relative brightness.

"The light is blue simply because the yellow is absorbed and the blue comes into vision."

You can see the yellow and the red, not so bright relatively. Mind you, it is a mental calculation. You see the relation of brightness between the blue part of the sky, the blue part of the spectrum and the violet part and the rest of the spectrum. Relatively to the red, the yellow and the green, the blue and violet are stronger in the scattered light, in the diffused light of the blue sky. Still you are very far

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from the answer. It does not explain why don't we see the rest of the spectrum. Actually in the blue sky the green and the yellow and the red are still there, they are still far brighter, perhaps not so, perhaps not 40 times but perhaps ten times brighter than the blue. Then why do we see the blue and why don't we see the rest? Here again you come across an extremely difficult question to answer, The actual brightness of the blue part of the spectrum in skylight is still much smaller than the brightness of the rest of the spectrum but we don't perceive that part of the spectrum. Now this is very simple and very surprising. But there is a nice little experiment which, perhaps one day, will be shown at the Science Centre which will enable you to see at least that it is not an exceptional phenomenon. It is one of the most fundamental facts of human vision that the blue part of the the spectrum inspite of its weakness dominates the spectrum in certain conditions and plays a role tremendously far more important than its actual brightness warrants. Now the experiment is the following. It is a very easy experiment. You take water and put a little copper sulphate in it and then put excess ammonia in it. You will get a solution called cuprammonium. If it is very strong it will transmit only deep violet light. Put it in a cell. You go on adding water in the cell and look at the colour of the bright lamp and see that the following thing happens. The deep violet changes into blue. The blue changes to a lighter blue and so on. But till the very last, it remains blue. In the spectrum of the light the solution is transmitting red light, green light, not of course yellow. Lot of light comes through the spectrum and the blue is still only a minor part of the whole. Whatever light comes through the spectrum you cannot see and you cannot even imagine any other colour coming through. And the reason for it is as follows. If you examine the transmitted light through a spectroscope you will find that the yellow part of the spectrum is diminished by the influence of cuprammonium. It absorbs and cuts out the small part of the width of the spectrum, but a very important part and that very important part is the yellow of the spectrum. Never mind how it absorbs the yellow part and controls the colour. The light is blue simply because the yellow is absorbed and the blue

comes into vision. If you take the whole spectrum and if you reduce the strength of the yellow part of the spectrum, at once you find the blue part of the spectrum and the blue colour dominates. This is again a fact of physiology. If you want any colour whatsoever to be shown, you must take out the yellow. Take for example that red carpet, which has been spread in my honour, I suppose. You look at it through a spectroscope. I can tell you beforehand, there will be no yellow in it at all. To get any colour, red, green or blue, you must take out the yellow. Yellow is the deadly enemy of colour. All other colours. I mean. Look at the green leaf. All the leaves are green not because of the presence of chlorophyll-the chlorophyll has a strong absorption of red, no doubt. But the real factor which makes the colour green is the fact that the yellow is taken off. Chlorophyll has enough absorption of the yellow to reduce the strength of yellow. Well, I examined silks for this. Bangalore is a great place for silk manufacture. I managed to purchase about 25-30 blouse pieces. I got them to verify the proposition that all brilliant colours require the suppression of the yellow region of the spectrum. Look at the rice field. It is wonderful. Look at the rice field with a spectroscope.

"All brilliant colours require the suppression of the yellow region of the spectrum."

It looks very much like the spectrum of the blue sky. But the only visible difference you can actually see at a glance between the blue sky and the green rice field is that the blue part of the spectrum has been cut off and that is produced by the so-called carotenoid pigments that are present here, which cut off the blue; the rest of the spectrum looks almost alike. But if you look very carefully you will see that in the colour of the rice field, you do not get the yellow. The removal of yellow is essential, before you can perceive the leaves as green. You see always this predominance of the yellow. On the contrary, if the yellow is taken off, the blue dominates. If you don't take off the yellow, the yellow dominates. The two are contradictory and they are enemies to each other. The fact is that you can divide-the physical explanation is deeper stillyou can divide the whole spectrum into two parts. The division is just where the blue ends; that part of the spectrum extending to green, yellow, orange and red amounts only to yellow. The other parts of the spectrum summed up amounts to blue. Now if vou take off this or reduce this you get the other. This is the real explanation of the blue colour of the sky and is very significant. You reduce-not that you abolish-the intensity of the yellow in the spectrum and of course of the green and the red. It is the reduction of the yellow of the spectrum that is to say the predominance of the blue which is responsible for the blue light of the sky. Well, one can carry further and say that it is the reduction of yellow that is basic. And why is it reduced? So here comes the second part of it. I could have started with that and said "Why is the sky blue?" "Oh, the scattering of light by the molecules of the atmosphere." I could have dismissed the whole lecture in

"Because, my young friends, I want you to realise that the spirit of science is not finding short and quick answers. The spirit of science is to delve deeper—and that is what I want to bring home to my audience and deeper. Don't be satisfied with the short and ready quick answers. You must never be content with that; you must look around and think and ask all sorts of questions; look round the problem, and search and go on searching."

one sentence. I could have said just as the botanist says "Why is it green?" "Just chlorophyll." I could have said "Why is the sky blue?" "Scattering of light by the molecules of the atmosphere." One sentence. "Then sir", you would ask me, "Why all this lecture?" Because, my young friends, I want you to realise that the spirit of science is not finding short and quick answers. The spirit of science is to delve deeper—and that is what I want to bring home to my audience—and deeper. Don't be satisfied with the short and ready quick answers. You must never be content with that; you must look around and think and ask all sorts of questions; look round the problem and search, and search and

go on searching. In the course of time you will find some of the truths, but you never reach the end. The end, as I told you is the human brain, but that is very far away yet. This is the spirit of science. I should give you an illustration of how by pursuing a simple question, I can go on talking to you as if I have just begun, the real subject of my lecture: "Why the sky is blue?"

Criteria for Success

Ambition, Courage and Endeavour have been my watchwords.

SIR C. V. RAMAN

Advice to Research Scientists

Develop self-confidence, self-reliance and a little desire to work. Young friends, do this and research will come afterwards. SIR C. V. RAMAN

On Importing Equipment for Research

There will be no science in India if we continue to rely on imported equipment for *research* work. I call it paying for our ignorance—nay, paying for our incompetence. Science can and shall advance in very simple ways. We often pay Rs. 50,000 for

something we can make for Rs. 5,000. The difference we pay for our ignorance. SIR C. V. RAMAN

Memorial for Gandhiji

The best way for perpetuating the memory of Mahatmaji is to inculcate into the minds of the coming generation the best teachings of Gandhiji. Each boy and girl from the primary standard to post-graduate course must be made to read the best sayings of Gandhiji—these sayings being selected suitably, according to the intellectual standards of the pupils. This would be the best and potent way of doing homage to the memory of the world's greatest man and Father of Indian Nation and is better than building memorials and erecting statues. SIR C. V. RAMAN

On the Education of Women

No one who is a patriot, no one who looks to the future of India can fail to be impressed by the importance of women receiving the best and the highest kind of education. No nation of which one half was sunk in superstition and ignorance could even hope to rise. SIR C. V. RAMAN

Jatkar episodes

Prof. S. K. K. Jatkar, a retired scientist and close associate of Prof. Raman, narrates some episodes from the life of the great scientist. Prof. Jatkar, now approaching 90 (Born 23.9.1897), started his career as a student in the IISc, Bangalore (1920), from where he retired in 1950 as head of the Physical Chemistry department. The same year he joined Poona University and in 1962 retired as the head of Chemistry department. These episodes are based on his narration and are compiled by Neela Ranade.

EPISODE 1

They are here to exploit students

Prof. Jatkar first met Sir C. V. Raman in 1922 when he (Sir Raman) had visited IISc as a member of the enquiry committee. The other two members were Sir Ashutosh Mukherjee and Sir William Pope. They had come to enquire about the student's complaints. The complaint was, 'The Professors were exploiting the students for their private practice and earning money while paying nothing to the institution'. This caused a lot of frustration amongst the students. To this complaint Sir C. V. Raman said, 'Why do you complain against them? They are here to rule over you and so they would exploit'.

This was indeed a very bold statement in those days. Who would have known then that after some time he was himself to head the institution and face a similar predicament?

EPISODE 2

'He is looking for complementary filters'

Prof. Jatkar had met Prof. Raman when the latter had visited the Indian Institute of Science, Bangalore, where he was a student. Some time afterwards he and his friend Dr. Damle had gone to Lucknow to attend Science Congress in 1924. From there they had gone to Calcutta to meet Prof. Raman, but their meeting could be attributed more to accident than planning. Let us see how it came about.

In Calcutta Prof. Jatkar and his friend boarded a tram to go to Bow Bazar Street (Prof. Raman's Laboratory). They found that the tram was empty, but for them. On enquiring they learnt that there was a strike and hence the trams were returning to the depot and would not stop enroute. This was a very peculiar situation and so with some difficulty the driver agreed to slowdown the tram (not to stop it) near Shyambazar Street where the two visitors were supposed to jump out. When the tram slowed down Dr. Damle jumped but before Prof. Jatkar could follow him, the tram gained speed and when Prof. Jatkar jumped, he really had a nasty fall and became unconscious for a few seconds.

As providence could have it, who else but Prof. Raman himself came running to enquire after the unconscious young man. In the meanwhile young Jatkar recovered and had to narrate the episode of jumping to Prof. Raman. All this was so sudden and unexpected that he could not reveal his identity or tell Prof. Raman the purpose of his visit.

Prof. Raman then returned to the junk shop where he was busy selecting strain free complementary filters from a pile of coloured glass pieces. This he would do by inspecting each piece with a Nicholas prism in sunlight.

In the meanwhile the two young scientists had recovered enough and were approaching Prof. Raman. On looking at him Prof. Jatkar commented to his friend, 'He is looking for complementary filters'. This remark really aroused Prof. Raman's interest in the young man. They got an invitation to visit his laboratory, to witness the wonderful experiment with the simple apparatus.

EPISODE 3

It was something different

Prof. Raman's experimental apparatus was very simple and improvised. He would always demonstrate his experiments to visitors with great enthusiasm. He was a wonderful showman.

His apparatus was made up of an old battered telescope which was used as a condenser. The source of illumination was the sun. The rays were reflected from a mirror placed on *Tulsi vrindavan* and entered the dark room through a hole in the door. So this was the set up.

Prof. Raman invited the two visitors inside and said, 'I will show you something'.

He took two complementary filters (these together would not allow any light to pass through) and placed them in the path of beam coming out of the telescope. The track of light became dark. He then took his liquid sample and placed it between the two filters and asked the visitors, 'Can you see?'

Well the visitors could not, so Prof. Raman said, 'You will, when your eyes get used to the darkness'. After sometime they did see some light. This indicated that the light was now modified in some way by the liquid.

Prof. Raman then told them that it was the resolution of light. There was some discussion on the point when Prof. Jatkar pointed out that the illumination could be due to fluoroscence or due to some impurities. But Prof. Raman was convinced that it was something different.

Moral: Good ideas and not fancy equipments get the result.

EPISODE 4

The shock that cleaned

As the first Indian Director of IISc his visit to the Institute was a great shock to him. The Institute

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had European directors and professors so far, hence the students had got used to liberal ways of life. The sight of girls in billiards room with attached bar was too much for the orthodox man and he proclaimed 'Stop! Stop this'.

Looking at the overall picture Sir Raman was not satisfied and wanted to cleanse the whole institution. In this process no one was spared. Once a professor with fourteen children was asked to leave. Prof. Raman was requested to reconsider the matter. 'Well where will the fourteen children go?' was the question asked. Prof. Raman was quick to reply, 'That is no qualification'.

EPISODE 5

'You could befool a Nobel laureate'

What is the test of wisdom? When we take an action we do not know whether it is right or wrong. Sometimes a right action may not give good results. And thus during the course of life one goes through many ups and downs. The higher up the person these are likely to be higher or lower. Prof. Raman who started his life with the financial service (!) decided to put his (Nobel prize) money with a private money-lender at 36% per annum interest. He was told that if he (Raman) would invest the interest also the rate of interest would be 60%. Unfortunately the money lender turned insolvent. When Sir Raman learnt this, he said, 'Gopalrao [the money lender]! you deserve this prize more as you could befool a Nobel laureate.'

EPISODE 6

'Mister Prime Minister, all that glitters is not gold'

Ever since Prof. Raman built his own Institute, his wide interests in science became more apparent than ever. His collections of natural objects ranged from colourful minerals to diamonds, rubies and sapphires; every type of musical instrument from the mridangam to the violin; from birds, beetles and butterflies to the finest collection of roses, bouganvilleas and jacarandas; stately trees from the common eucalyptus to the rare mahogany—indeed, he was literally surrounded by a fantastic array of biological materials. Prof. Jatkar vividly remembers the way he laid two similarly dressed ores of copper and gold in the palms of the late Prime Minister Pandit Jawaharlal Nehru when he visited his Institute and switched on the ultraviolet light and asked the Prime Minister as to which was copper and which gold. The brighter piece under the ultraviolet light was promptly named gold by the Prime Minister and Professor Raman in his inimitable way burst out: 'Mister Prime Minister, all that glitters is not gold'.

EPISODE 7

A pink riddle

Why and when does an event occur? Well it occurs when the time for it is ripe. Now, 'Prof. Raman happened to be there and discovered Raman effect' should be a sufficient answer. But is it? Prof. Jatkar wonders.

Prof. Jatkar, then a student, used to arrange the demonstrations accompanying Prof. Raman's lectures. Prof. Raman's lectures were always spectacular and accompanied by slides (carbon arcs were used as a source). His popular lectures were popular in the true sense.

Once during such a demonstration, looking at

the scattered light coming from the liquid (toluene), Prof. Jatkar mused, 'why did Prof. Raman choose this particular liquid for his experiment?' Benzene and toluene are known to give large scattering, a fact which made the effect visible to the naked eye. Interestingly enough he himself found the explanation in a poetic episode.

The episode relates to a renowned marathi poet and dramatist Shri. Ram Ganesh Gadkari. In his famous marathi poem 'Gulabi Kode' (the pink riddle) he narrates the incident of the sunset being watched by two lovers. A conversation proceeds with the sweetheart querrying, 'Dear! how is it that the setting sun makes not only the west pink but the east also'.

His answer is the demonstration that the blush on the cheek is shared by the other.

This is the gist of the poem.

Brooding over this incident in the poem, Prof. Jatkar went to a hill top to find out and confirmed it. Later he asked Shri. Gadkari, 'Have you ever witnessed that the east also becomes red at sunset?' This scientific investigation was neatly snubbed by Shri. Gadkari, 'Ha! I do not know. It is just poetic imagination.'

The answer did not satisfy Prof. Jatkar then and returning to reality he reflects 'what faculty makes one think in a particular direction? Why do some persons write science fiction which is not fiction today. Why do some poets precisely write truth without knowing it? Why does one person choose one particular liquid, and etc etc'. Well we do not know.

A real hardworker

Sir C. V. Raman firmly believed that there is no substitute for hard work. Almost till the end of his life he followed a rigorous routine from 5.30 a.m. till 10.00 p.m. During his early years in Calcutta he worked in Finance Department and in the Institute with the same vigour. He worked from 5.30 a.m. till 9.45 a.m. in the Institute. After attending the office he worked in the laboratory from 5 p.m. till 10.00 p.m. Because of this he would always advice youth in no uncertain terms. He used to say, 'Young men, you must work hard. You must aim high and work hard towards your goal'.

THE HINDU, Nov. 26, 1970

Honours Bestowed on Raman

- 1924 Elected Fellow of the Royal Society, London.
- 1928 Matteucci Medal—Societa Instaliana Della Scienza, Rome.
- 1929 Knighted by the British Government in India.
- 1930 Hughes Medal-Royal Society, London
- 1930 Nobel Price-Stockholm, Sweden.
- 1935 Rajasabhabhushana—Decoration by the Maharaja of Mysore.
- 1941 Franklin Medal, USA
- 1954 Bharata Ratna—Decoration by the President of India.
- 1957 Lenin Prize, USSR

Honorary Doctorates from the Universities of:

Allahabad, Benaras, Bombay, Calcutta, Dacca, Delhi, Freiburg, Glasgow, Kanpur, Lucknow, Madras, Mysore, Osmania, Paris, Patna, Sri Venkateswara

Honorary Member:

Deutsche Academy of Munich Hungarian Academy of Sciences Indian Science Congress Association and several other Indian Science Organisations. Royal Irish Academy Royal Philosophical Society, Glasgow Zurich Physical Society.

Honorary Fellow:

Optical Society of America Minerological Society of America

- Foreign Associate: Academy of Sciences, Paris
- Foreign Member:

Academy of Sciences, USSR

Honorary Member:

Academy of the Socialist Republic of Romania Catgut Acoustical Society.

General President:

Indian Science Congress, 1929

President:

Indian Academy of Science, 1934-1970

A Titan Passes

Rich tributes were paid and several editorials were written after Prof. Raman's passing away on 21 November 1970. We are reproducing one of the most striking editorials from The Times of India, dated 23rd Nov. 1970.

Editor

An era has ended with the passing of one of our most gifted and distinguished scientists, C. V. Raman. He was a dedicated investigator in a world of much shoddiness; in the midst of increasing pretence and superficiality he was a true polymath. His range of interests and activities was colossal: in the 65 years of his adult life he did research and made several remarkable discoveries in acoustics. optics, theory of musical instruments, crystallography, magnetism, diffraction of light, liquid hypersonics, structure of diamonds, theory of vision. The corpus of his work was so large and varied that it would be grossly inadequate to remember him exclusively by his first major discovery, in 1928, of what came to be known as the Raman Effect (for which he was awarded the Nobel prize in 1930). This flung open a wide window on the unseen minuscule universe: with this began a whole new line of research into the structure of molecules and atoms, leading to hundreds of new theories and applications. In subsequent years the field receded into the background, but with the recent discovery of the laser principle the Raman Effect made a come-back with a vengeance, so much so as there is now a new tool of investigation known as Raman laser spectroscopy. A Titan in science, he waswithal a full man; essentially an "aesthete", as he was fond of saying about himself. In his later years, as the ever-active but ever-recluse National Professor of Physics, his interests centred on flowers and trees, their colours and the vast panorama of their beauty. He was the first scientist to look at a flower spectroscopically and disprove some of the established chemical theories of floral pigmentation. As a debunker of the pompous and the unoriginal, he had few parallels in the country. He was fiercely independent and self-reliant, and had many unflattering but true things to say about officially sponsored research. "Many Indian scientists," he once said, "are in a deep freeze; they are carpet baggers." The relevance of this thought is all too evident in these confused times.

Fascination for diamonds

Sir C. V. Raman had a great fascination for gem-stones. He carried out investigations on opals, feldspars, moonstones, agates, rubies and diamonds. He was mainly interested in the structure and physical properties of these stones. Raman effect was studied on the diamond which was obtained from the wedding ring of his brother. He bought as many as 100 diamonds with his own money. Amusingly he used to say that he could earn enough money just by making a few diamonds in the laboratory. He was very proud of his collection and used to take visitors to show his treasure. He used to call the room where he had his collections as Ali Baba's cave. This beautiful collection had been preserved at Raman Research Institute, Bangalore.

P. B. VIDYASAGAR

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