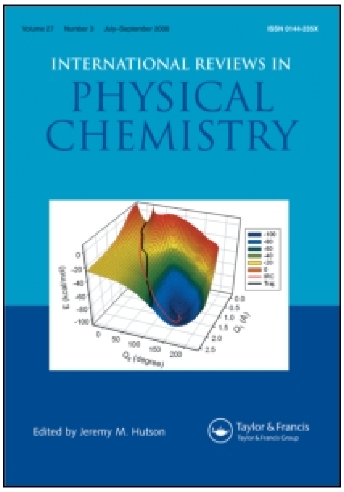

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Early history of the Raman effect

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Early history of the Raman effect

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Introduction

The year 1988 marked the sixtieth anniversary of the discovery of the Raman effect in 1928 and the hundredth anniversary of the birth of C. V. Raman in 1888. To celebrate these anniversaries the Executive Committee of the XIth International Conference on Raman Spectroscopy (ICORS XI), held in London in September 1988, commissioned

Figure 1. This picture of Raman is a copy of a portrait by Homi Bhabha, the famous Indian theoretical physicist who also had a very considerable reputation as a painter. When Bhabha handed it to Raman with the remark 'A scientist painted by a scientist', Raman answered 'No, an artist painted by an artist'.

an exhibition entitled the Early History of the Raman Effect. This historical review article is based on this Exhibition.

The potential of the Raman effect in chemistry and physics was realized very rapidly. By the end of 1928 some 70 papers on the Raman effect had been published; September 1929 saw the first international scientific meeting which included the Raman effect, and by the end of 1929 the number of papers published had grown to over 200.

It is on this exciting and productive early period that this review concentrates. Its features include biographical notes on C. V. Raman; an account of the discovery of the Raman effect; early publications chosen to illustrate the immediate international interest in the new phenomenon, and an account of the Faraday Discussion Meeting on Molecular Spectra and Molecular Structure held at Bristol U.K. in September 1929 at which Raman himself gave a review lecture on the Raman Effect. The accounts of the personalities involved and the equipment used should prove no less interesting than the science. Younger practitioners of Raman spectroscopy may perhaps find encouragement for the future in the wide variety and distinction of the subsequent careers of many of the first Raman spectroscopists.

C. V. Raman

Early career

Chandrasekhara Venkata Raman was born at Trichinopoly in South India on 7 November 1888. His family moved to Vizagapatam on the East Coast of India where he went to the local High School. In 1903 he entered the Presidency College of Madras.

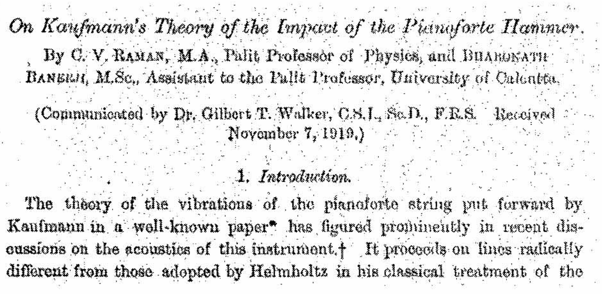
Even as a student at the Presidency College, Raman undertook original investigations in acoustics and optics. His first paper entitled 'Unsymmetrical diffraction bands due to a rectangular aperture' was published in the *Philosophical Magazine* (London) in 1906. This was followed early in 1907 by a note in *Nature* on 'Newton's rings in polarized light'. Both these papers were published in Raman's eighteenth year. It is intriguing to note that Raman's paper in the *Philosophical Magazine* was immediately preceded by a paper by Lord Rayleigh and followed by one by R. W. Wood!

After graduating he spent 10 years in the Indian Finance Department, Calcutta, as Assistant Accountant General, but maintained an active interest in science, carrying out research in his spare time at the Indian Association for the Cultivation of Science, a privately endowed institution in Calcutta, founded in 1876. During this period he contributed some 30 original papers in physics to *Nature*, the *Philosophical Magazine* and *Physical Review*.

In 1917 he joined Calcutta University as the first Palit Professor of Physics but continued his association with the Indian Association for the Cultivation of Science of which he became Honorary Secretary in 1919.

At Calcutta he was active in research in many areas of physics including the theory of musical instruments (including the piano) (figure 2), diffraction (figure 3), colours, interference, colloids, light scattering, X-rays, magnetism and magneto-optics. He rapidly established himself as a physicist of international renown and was elected Fellow of the Royal Society of London in 1924.

Raman travelled widely in the nineteen twenties attending international congresses and lecturing at universities in many countries. His zest for travel led to his becoming



On Kaufmann's Theory of the Impact of the Pianoforte Hammer.

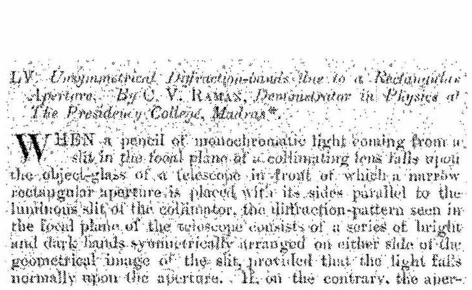
By C. V. Raman, M.A., Palit Professor of Physics, and Bhabonath Banerji, M.Sc., Assistant to the Palit Professor, University of Calcutta.

(Communicated by Dr. Gilbert T. Walker, C.S.I., Sc.D., F.R.S. Received November 7, 1919.)

1. *Introduction.*

The theory of the vibrations of the pianoforte string put forward by Kaufmann in a well-known paper* has figured prominently in recent discussions on the acoustics of this instrument.† It proceeds on lines radically different from those adopted by Helmholtz in his classical treatment of the

Figure 2. From *Proceedings of the Royal Society, Series A*, **97**, 99, 1920.



LV. *Unsymmetrical Diffraction-bands due to a Rectangular Aperture.* By C. V. Raman, *Demonstrator in Physics at The Presidency College, Madras**.

When a pencil of monochromatic light coming from a slit in the focal plane of a collimating lens falls upon the object-glass of a telescope in front of which a narrow rectangular aperture is placed with its sides parallel to the luminous slit of the collimator, the diffraction-pattern seen in the focal plane of the telescope consists of a series of bright and dark bands symmetrically arranged on either side of the geometrical image of the slit, provided that the light falls normally upon the aperture. If, on the contrary, the aper-

Figure 3. From *Philosophical Magazine*, **12**, 494, 1906.

interested in the phenomenon of light scattering and so paved the way for the discovery of the effect which bears his name. In his own words

> 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.

Later career

Raman received a knighthood in 1929 and the Nobel Prize for Physics in 1930. Amongst the numerous other honours he received (figure 4), two are particularly interesting. In 1935 the Maharaja of Mysore gave him the title of 'Rajasabhabhushana' which literally translated means 'The Jewel of the King's Court'; and in 1954 the Government of India awarded him the title of 'Bharat Ratna', the only Indian scientist so honoured.

Raman left Calcutta in 1933 to become Director of the Indian Institute of Science at Bangalore. Later he was able to build an Institute of his own in Bangalore, now known as the Raman Research Institute (figure 5). Here he lived and worked actively until his death on 21 November 1970. His mortal remains were cremated in the beautiful gardens of his Institute (figure 6).

There are many comments on record about Raman which illustrate his great talents, his human qualities and his complex personality:

> 'The "Raman effect" must rank among the best three or four discoveries in experimental physics in the last decade'. (Lord Rutherford, 1930)
>
> 'He was richly endowed with a child-like sense of wonder at the unknown and not understood facets of nature...' (S. Bhagavantam)
>
> 'His exuberance was infectious...' (S. Ramaseshan)

> 'I must frankly say I like him [Raman] very much, in spite of his all too human drawbacks, his conceit and his naiveté and therefore his disarming way of bringing himself into the light. I do not take these too seriously as I am finding (on the other hand) a genuine devotion to his work and to the Institute. He is an excellent physicist, full of optimism and activity and besides being interested in everything in the world'. (Max Born in a letter to Lord Rutherford, 1936)

But perhaps Raman himself should have the last word: 'The essence of science is independent thinking, hard work and not equipment. When I got my Nobel Prize I had spent hardly 200 rupees on my equipment'.

Figure 4. Raman in Paris, 1948 when he received the degree of D ès Sc *Honoris Causa*. With him are (from left to right) Prince L. de Broglie, R. S. Mulliken and L. Pauling.

Figure 5. The Raman Institute, Bangalore.

Figure 6. The garden of the Raman Institute with the Memorial Tree marking the place where Raman was cremated.

Discovery

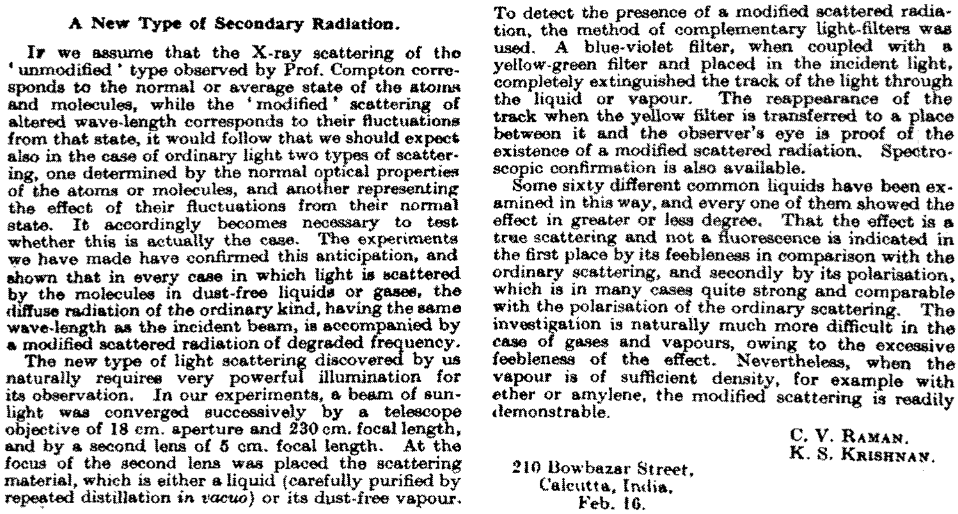
The discovery of the Raman effect

Raman's investigations of light scattering began after his return from Europe towards the end of 1921. During the next six years, Raman, in association with a number of very able students, published over 50 scientific papers on light scattering.

In 1924 at the British Association Meeting in Toronto, Canada, Raman had taken part in a discussion on the recently discovered Compton effect. In 1927 Raman proposed a quantitative theory of the Compton effect. This work undoubtedly convinced him that there must exist an optical analogue of the Compton effect.

The following extracts from the unpublished diary of K. S. Krishnan, one of Raman's collaborators give a vivid account of how, early in 1928, the new phenomenon of modified scattering was discovered. Raman and his students were working at the Indian Association for the Cultivation of Science in Calcutta.

> *Tuesday 7 February 1928*
> Incidentally discovered that all pure liquids show a fairly intense fluorescence also in the visible region, and what is much more interesting, all of them are strongly polarised, the polarisation being the greater for the aliphatics than for the aromatics. When I told Prof. about the results... he remarked: 'you don't mean to suggest, Krishna Iyengar, all that is fluorescence!' After meals at night, Venkateswaran and myself were chatting together in our room when Prof. suddenly came to the house (at about 9 p.m.) and called for me. When we went down, we found he was very much excited and had come to tell me what we had observed this morning must be the Kramers–Heisenberg effect, we had been looking for all these days. We therefore agreed to call the effect modified scattering. We were talking in front of our house for more than a quarter of an hour when he repeatedly emphasised the exciting nature of the discovery.
>
> *Thursday 9 February 1928*
> Set up this morning the long telescope and made preliminary arrangements for observing the effect with vapours. Before the arrangements were completed Prof. left for the college for his lecture. In the afternoon tried Ether vapour and it was surprising that the modified radiation was very conspicuous. Tried a number of others in quick succession without however the same success. When Prof. came from the college at about three, I announced to him the result, and there was still enough sunlight for him to see for himself. He ran about the place shouting all the time, that it was a first rate discovery, that he was feeling miserable during the lecture because he had to leave the experiment, and that however he was fully confident that I '*wouldn't let the grass grow under my feet till I discovered the phenomenon in gases*'. He asked me to '*call in everybody in the place to see the effect*' and immediately arranged in a most dramatic manner, with the mechanics to make arrangements for examining the vapours at high temperatures.
>
> *Thursday 16 February 1928*
> Studied today Pentane vapour at high temperature and it showed a conspicuous polarisation in the modified scattering. We sent a note today to *Nature* on the subject under the title 'A New Type of Secondary Radiation' (figure 7).



A New Type of Secondary Radiation.

If we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. Raman.
K. S. Krishnan.

210 Bowbazar Street,
Calcutta, India,
Feb. 16.

Figure 7. From *Nature*, **121**, 501, 1928.

> *Tuesday 28 February 1928*
> Went to the Association only in the afternoon. Prof. was there and we proceeded to examine the influence of the wavelength of the incident light phenomenon. Used the usual blue violet filter coupled with a uranium glass, the range of wavelengths transmitted by the combination being much narrower than that transmitted by the blue violet filter alone. On examining the track with a direct vision spectroscope we found to our great surprise the modified scattering was separated from the scattering corresponding to the incident light by a dark region. This encouraged us to use monochromatic incident light...

Raman lost no time in giving the newly discovered phenomenon the widest possible publicity both in India and internationally, as the following rapid sequence of events shows.

February 16: Cabled a note to *Nature* 'A new Type of Secondary Radiation' by C. V. Raman and K. S. Krishnan, published 31 March.

February 29: Associated Press of India gives first newspaper report under the heading 'New Theory of Radiation—Prof. Raman's Discovery'.

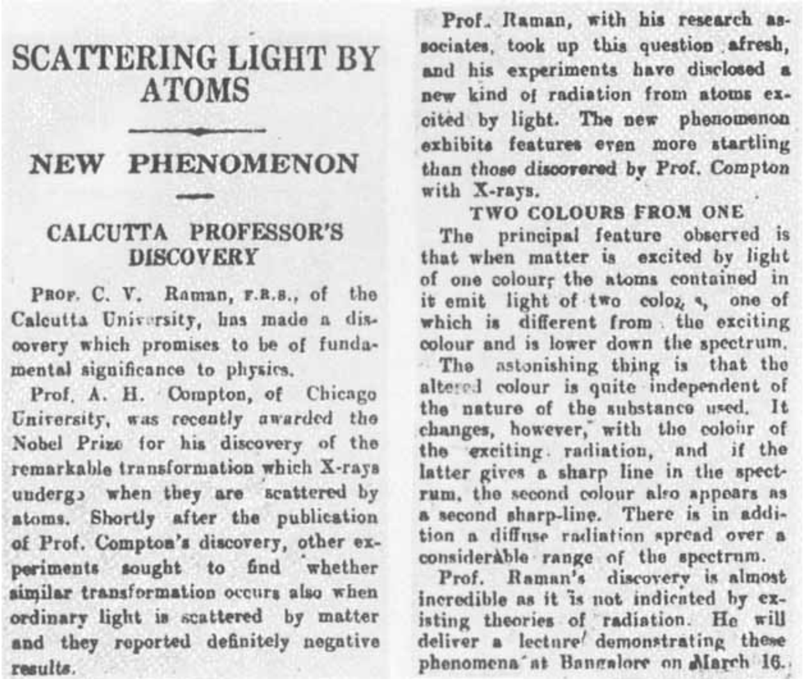
March 1: The Calcutta Newspaper *The Statesman* carries an article entitled 'Scattering light by Atoms—New Phenomenon—Calcutta Professor's Discovery' (figure 8).

March 8: Sent second note to *Nature* 'A Change of Wavelength in Light Scattering' by C. V. Raman published 21 April.

March 16: Lecture given to South Indian Science Association, Bangalore 'A New Radiation' by Prof. C. V. Raman, F.R.S.

March 22: Sent third note to *Nature*, 'The Optical Analogue of the Compton effect' by C. V. Raman and K. S. Krishnan, published 5 May.

March 31: The Bangalore Lecture published in a Special Issue of the *Indian Journal of Physics* which Raman had founded in 1927.



SCATTERING LIGHT BY ATOMS

NEW PHENOMENON

CALCUTTA PROFESSOR'S DISCOVERY

Prof. C. V. Raman, F.R.S., of the Calcutta University, has made a discovery which promises to be of fundamental significance to physics.

Prof. A. H. Compton, of Chicago University, was recently awarded the Nobel Prize for his discovery of the remarkable transformation which X-rays undergo when they are scattered by atoms. Shortly after the publication of Prof. Compton's discovery, other experiments sought to find whether similar transformation occurs also when ordinary light is scattered by matter and they reported definitely negative results.

Prof. Raman, with his research associates, took up this question afresh, and his experiments have disclosed a new kind of radiation from atoms excited by light. The new phenomenon exhibits features even more startling than those discovered by Prof. Compton with X-rays.

TWO COLOURS FROM ONE

The principal feature observed is that when matter is excited by light of one colour, the atoms contained in it emit light of two colours, one of which is different from the exciting colour and is lower down the spectrum.

The astonishing thing is that the altered colour is quite independent of the nature of the substance used. It changes, however, with the colour of the exciting radiation, and if the latter gives a sharp line in the spectrum, the second colour also appears as a second sharp-line. There is in addition a diffuse radiation spread over a considerable range of the spectrum.

Prof. Raman's discovery is almost incredible as it is not indicated by existing theories of radiation. He will deliver a lecture demonstrating these phenomena at Bangalore on March 16.

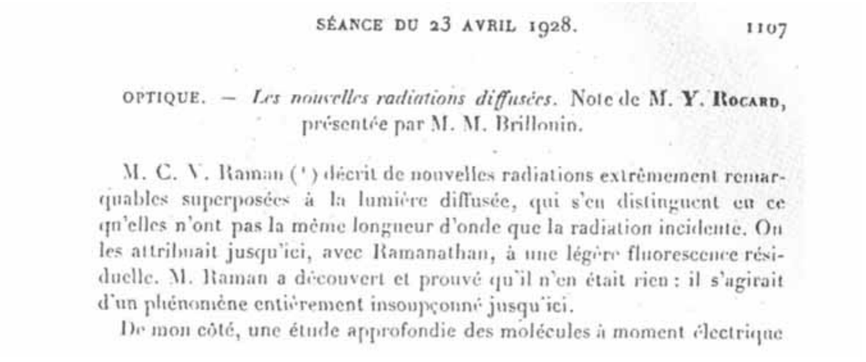
Figure 8. Newspaper report on the discovery of Raman effect appearing in *The Statesman*, an English Language daily of Calcutta on 1 March 1928. The first Raman spectrum was reportedly obtained on 28 February 1928.

The Raman effect and the quantum theory

In 1928 the quantum theory was still in its infancy. In a paper entitled 'On the theory of the Raman effect' published in *Naturwissenschaften*, on the 24 August 1928, Max Born says that Raman's discovery had been predicted by quantum mechanics in all its entirety, and could be thought of as proof for the same. This prediction had been made in two classic papers; one by Smekal, published in 1923 and one by Kramers and Heisenberg published in 1925. (See p. 334.)

France

Raman's discovery was followed up immediately in France. On 23 April a note by Y. Rocard entitled 'Les nouvelles radiations diffusées' (figure 9) was communicated to the French Academy of Sciences by M. Brillouin. This was followed on 30 April by a note by J. Cabannes, communicated by Ch. Fabry (figure 10); and on 4 June by two further notes: 'Analyse spectroscopique de la lumière obtenue par diffusion moléculaire d'une radiation monochromatique an sein d'un fluide'. (Note de M. M. J. Cabannes et P. Daure, présentée par M. Ch. Fabry. *Comptes Rendus*, **186**, 1533, 1928) and 'Remarques à propos de la Note de M. M. Cabannes et Daure sur la diffusion moléculaire' (M. A. Cotton, *Comptes Rendus*, **186**, 1475, 1928.) These were the first four papers on the Raman effect published outside India. Since that time France has continued to make important and substantial contributions to Raman spectroscopy.



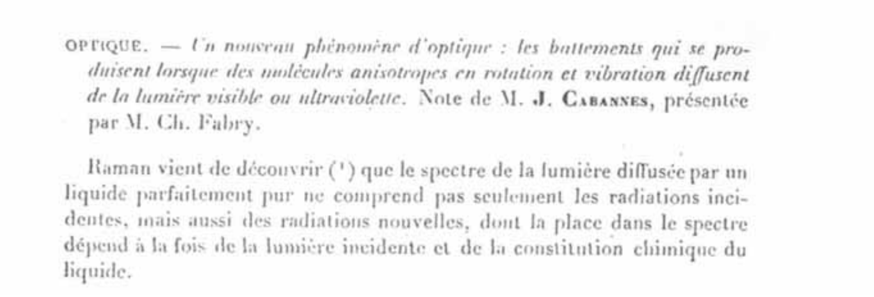
SÉANCE DU 23 AVRIL 1928. 1107

OPTIQUE. — *Les nouvelles radiations diffusées.* Note de M. **Y. ROCARD**, présentée par M. M. Brillouin.

M. C. V. Raman (1) décrit de nouvelles radiations extrêmement remarquables superposées à la lumière diffusée, qui s'en distinguent en ce qu'elles n'ont pas la même longueur d'onde que la radiation incidente. On les attribuait jusqu'ici, avec Ramanathan, à une légère fluorescence résiduelle. M. Raman a découvert et prouvé qu'il n'en était rien : il s'agirait d'un phénomène entièrement insoupçonné jusqu'ici.

De mon côté, une étude approfondie des molécules à moment électrique

Figure 9. From *Comptes Rendus*, **186,** 1107, 1928.



OPTIQUE. — *Un nouveau phénomène d'optique : les battements qui se produisent lorsque des molécules anisotropes en rotation et vibration diffusent de la lumière visible ou ultraviolette.* Note de M. **J. CABANNES**, présentée par M. Ch. Fabry.

Raman vient de découvrir (1) que le spectre de la lumière diffusée par un liquide parfaitement pur ne comprend pas seulement les radiations incidentes, mais aussi des radiations nouvelles, dont la place dans le spectre dépend à la fois de la lumière incidente et de la constitution chimique du liquide.

Figure 10. From *Comptes Rendus*, **186,** 1201, 1928.

Figure 11. Jean Cabannes.

Figure 12. Aimé Cotton.

Figure 13. Yves Rocard.

The many well-known Raman spectroscopists from France include J. Lascombe, now the President of the University of Bordeaux, the University where he began his research in Raman spectroscopy. Lascombe was Chairman of ICORS VIII.

Jean Cabannes (1885–1959) (figure 11) studied at l'Ecole Normale Supérieure and was successively Professor at the University of Montpellier (1919–1939) and the University of Paris (1939–1959). Cabannes made many important contributions to our knowledge of light scattering. As early as 1914 he succeeded in measuring in the laboratory the polarization and intensity of the light scattered by a volume of pure gas of the order of one litre, eliminating all parasitic light. From 1928, with his collaborators, Daure, Rousset and Bouhet, Cabannes undertook extensive and systematic studies of the Raman spectra of liquids, crystals and gases. This work enabled him to establish the relationship between the symmetry of molecular vibrations and the polarization of the Raman scattering.

Aimé Cotton (1869–1951) (figure 12) was educated at l'Ecole Normale Supérieure. He was Professor successively at the University of Toulouse (1895–1900), l'Ecole Normale Supérieure (1900–1920) and the University of Paris (1920–1939). In 1895 he discovered circular dichroism in solutions of compounds with natural optical activity; in 1907 he discovered, in collaboration with Mouton, magnetic birefringence; and in 1935 he discovered circular dichroism in compounds with magneto-rotatory power. His pupils included J. P. Mathieu, author (with H. Poulet) of the well-known book *Spectres de Vibration et Symétrie des Cristaux* and Chairman of ICORS III.

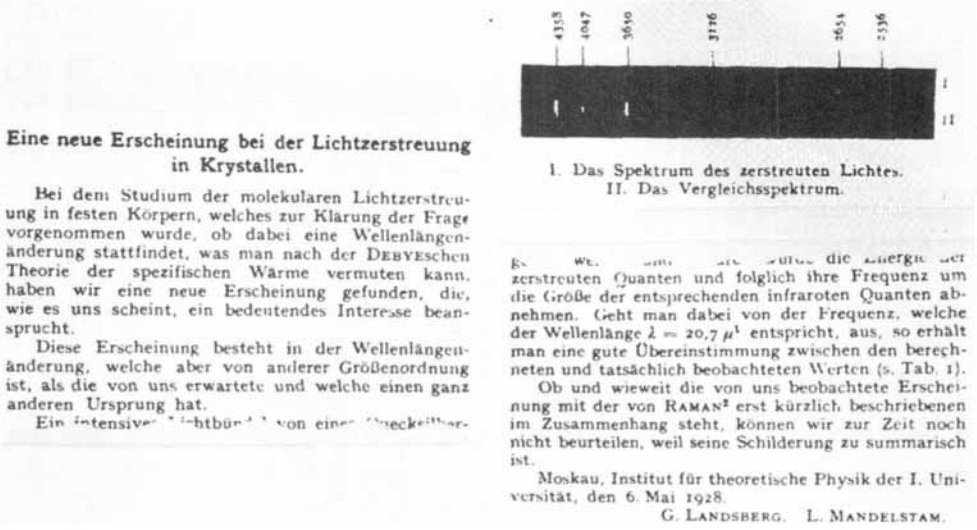
Yves Rocard (b. 1903) (figure 13) studied at the Sorbonne, Paris under Fabry and was successively Professor of Physics at the Sorbonne and Director of the Physics Laboratory of l'Ecole Normale Supérieure. His career was both distinguished and varied. During the second World War he sent valuable scientific information from France to British Scientific Intelligence. He was eventually smuggled out of France by Special Operations Executive and then joined the Free French Navy. In postwar France he played a significant role as a member of the French Atomic Energy Commission. His honours include a CBE for his wartime services, and a submarine volcano near Tahiti, named after him. His son Michel became Prime Minister of France in 1988.

USSR

On 6 May 1928, G. Landsberg and L. Mandelstam in the USSR submitted to *Die Naturwissenschaften* a paper entitled 'Eine neue Erscheinung bei der Lichtzerstreuung in Krystallen' (A new phenomenon in light scattering by crystals) which was published on 13 July 1928. This paper reported the observation of changes in frequency when monochromatic light is scattered by quartz (figure 14).

Raman and Krishnan's first paper published in *Nature* on 31 March 1928 and the succeeding paper published on 21 April are in very general terms without any spectroscopic evidence. It was only in Raman and Krishnan's third paper in *Nature* on 5 May that a spectrum was reproduced, although spectra were included in Raman's Bangalore lecture on 16 March.

Landsberg and Mandelstam's paper was submitted on 6 May, one day after the official publication date of Raman and Krishnan's definitive paper. Landsberg and Mandelstam could not have had any information in Moscow about this paper, but they did refer to Raman's first two publications saying they could not tell whether there was a connection, because Raman's description was too vague. However, they themselves



Eine neue Erscheinung bei der Lichtzerstreuung in Krystallen.

Bei dem Studium der molekularen Lichtzerstreuung in festen Körpern, welches zur Klärung der Frage vorgenommen wurde, ob dabei eine Wellenlängenänderung stattfindet, was man nach der DEBYEschen Theorie der spezifischen Wärme vermuten kann, haben wir eine neue Erscheinung gefunden, die, wie es uns scheint, ein bedeutendes Interesse beansprucht.

Diese Erscheinung besteht in der Wellenlängenänderung, welche aber von anderer Größenordnung ist, als die von uns erwartete und welche einen ganz anderen Ursprung hat.

Ein intensives Lichtbündel von einer Quecksilber-

I. Das Spektrum des zerstreuten Lichtes.
II. Das Vergleichsspektrum.

[illegible] die Energie der zerstreuten Quanten und folglich ihre Frequenz um die Größe der entsprechenden infraroten Quanten abnehmen. Geht man dabei von der Frequenz, welche der Wellenlänge $\lambda = 20{,}7\,\mu^1$ entspricht, aus, so erhält man eine gute Übereinstimmung zwischen den berechneten und tatsächlich beobachteten Werten (s. Tab. 1).

Ob und wieweit die von uns beobachtete Erscheinung mit der von RAMAN[2] erst kürzlich beschriebenen im Zusammenhang steht, können wir zur Zeit noch nicht beurteilen, weil seine Schilderung zu summarisch ist.

Moskau, Institut für theoretische Physik der I. Universität, den 6. Mai 1928.

G. LANDSBERG. L. MANDELSTAM.

Figure 14. From *Die Naturwissenschaften*, **16,** 557, 1928.

Figure 15. L. I. Mandelstam.

Figure 16. G. D. Landsberg.

had clearly brought out the connection between the frequency shifts and the infrared frequencies of quartz, a recognition which came only in Raman's third paper published one day before the date of submission of their paper.

The two discoveries were thus independent, but of course Raman had the priority. It is perhaps not too surprising that until recently the term 'combination scattering' was used in the USSR rather than 'Raman effect'.

L. I. Mandelstam (1879–1944) (figure 15) was educated at Strasbourg University. In 1911 he became a professor at Strasbourg, and stayed there until 1925 when he was elected a professor at Moscow University. He became a member of the Academy of Sciences in 1929. In addition to his extensive research on light scattering he made important contributions in a number of other branches of physics.

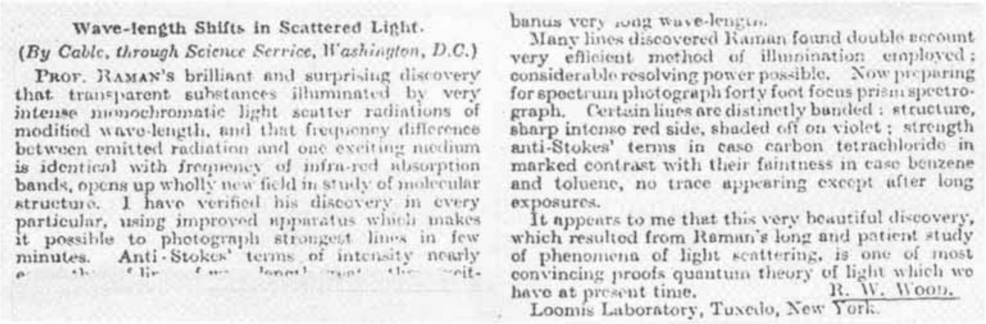
G. D. Landsberg (1890–1957) (figure 16) was educated at Moscow University and became a professor there in 1924. He was elected a member of the Academy of Sciences in 1946.

USA

Robert W. Wood (1868–1955) (figure 17) was the first American to publish results on Raman spectroscopy. He had discovered resonance fluorescence in 1906, and thereafter had devoted much effort to spectroscopic studies of scattered light. He was spending the summer of 1928 in the private laboratory of Alfred L. Loomis in Tuxedo Park, N.Y. when he read Raman and Krishnan's first note in *Nature*. He quickly improvised experiments to repeat the work and sent a cable to *Nature* (figure 18). The wording is awkward because prepositions and articles were omitted to save money!

This was quickly followed by a lengthy paper in the *Philosophical Magazine* for October 1928 showing the spectra of ten substances (figure 19). It contains many

Figure 17. Robert W. Wood. This photograph, taken about 1938, shows him holding a large mosaic replica diffraction grating. (Courtesy of AIP Niels Bohr Library).



Wave-length Shifts in Scattered Light.

(By Cable, through Science Service, Washington, D.C.)

PROF. RAMAN'S brilliant and surprising discovery that transparent substances illuminated by very intense monochromatic light scatter radiations of modified wave-length, and that frequency difference between emitted radiation and one exciting medium is identical with frequency of infra-red absorption bands, opens up wholly new field in study of molecular structure. I have verified his discovery in every particular, using improved apparatus which makes it possible to photograph strongest lines in few minutes. Anti-Stokes' terms of intensity nearly [illegible]

bands very long wave-length.

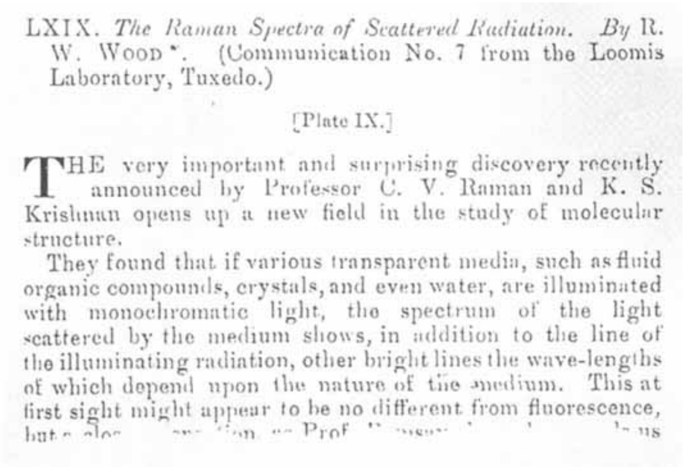
Many lines discovered Raman found double account very efficient method of illumination employed: considerable resolving power possible. Now preparing for spectrum photograph forty foot focus prism spectrograph. Certain lines are distinctly banded: structure, sharp intense red side, shaded off on violet; strength anti-Stokes' terms in case carbon tetrachloride in marked contrast with their faintness in case benzene and toluene, no trace appearing except after long exposures.

It appears to me that this very beautiful discovery, which resulted from Raman's long and patient study of phenomena of light scattering, is one of most convincing proofs quantum theory of light which we have at present time.

R. W. WOOD.

Loomis Laboratory, Tuxedo, New York.

Figure 18. From *Nature*, **122**, 349, 1928.



LXIX. *The Raman Spectra of Scattered Radiation.* *By* R. W. Wood*. (Communication No. 7 from the Loomis Laboratory, Tuxedo.)

[Plate IX.]

THE very important and surprising discovery recently announced by Professor C. V. Raman and K. S. Krishnan opens up a new field in the study of molecular structure.

They found that if various transparent media, such as fluid organic compounds, crystals, and even water, are illuminated with monochromatic light, the spectrum of the light scattered by the medium shows, in addition to the line of the illuminating radiation, other bright lines the wave-lengths of which depend upon the nature of the medium. This at first sight might appear to be no different from fluorescence, but [illegible]

Fig. 1.

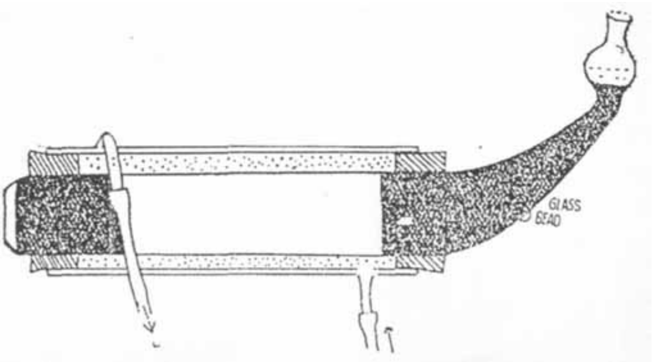
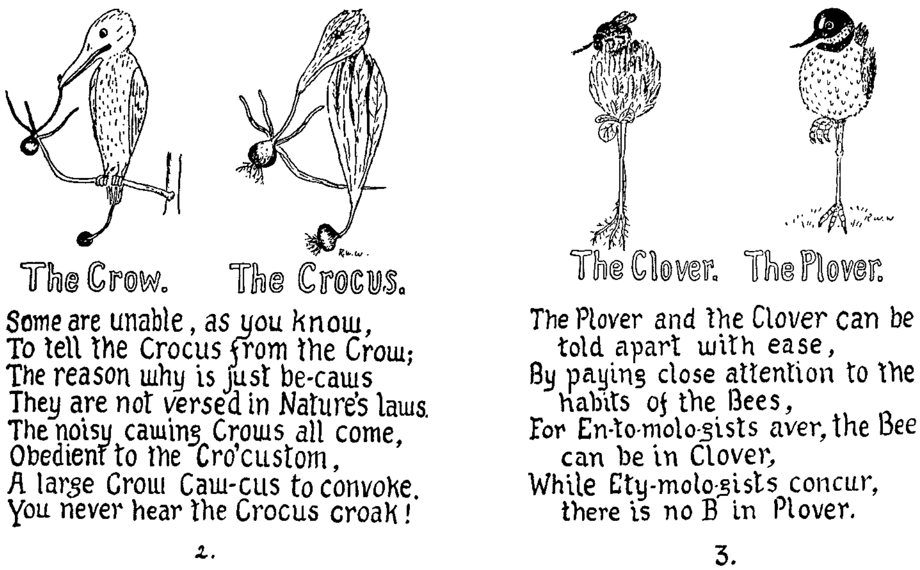


Figure 19. From *Philosophical Magazine*, **6**, 729, 1928.

fascinating experimental details, including an extended discussion of the use of a light horn. The techniques which he introduced, carried over from his work on fluorescence, were standard practice in Raman spectroscopy for about 30 years. Wood was also the first to use a diffraction grating in Raman spectroscopy, and he and Rasetti independently were the first ones to obtain clear-cut Raman spectra of gases. From 1928 to 1938 he published about 30 papers on Raman spectroscopy, all but three by himself.

R. W. Wood spent most of his career as Professor of Experimental Physics at Johns Hopkins University (1901–1938). He was a renowned experimenter in physical optics and spectroscopy. He invented the echellete grating, and provided high-quality diffraction gratings for workers throughout the world.

He had an unusually colourful personality. Legions of stories are told about him, of which one example will be given. During an exceptionally cold winter in Baltimore a water pipe in his home froze. He took a portable motor-generator set, attached electrical leads to each side of the frozen section, and passed a heavy current through the pipe. The resistance heating quickly melted the ice. It was so easy that he decided to sell his services to other homeowners. One customer, upon seeing how quickly his problem was solved, objected to the amount of the charge. 'All right', said Wood, 'if you



The Crow. The Crocus.

Some are unable, as you know,
To tell the Crocus from the Crow;
The reason why is just be-caws
They are not versed in Nature's laws.
The noisy cawing Crows all come,
Obedient to the Cro'custom,
A large Crow Caw-cus to convoke.
You never hear the Crocus croak!

2.

The Clover. The Plover.

The Plover and the Clover can be
told apart with ease,
By paying close attention to the
habits of the Bees,
For En-to-molo-gists aver, the Bee
can be in Clover,
While Ety-molo-gists concur,
there is no B in Plover.

3.

Figure 20. From *How to Tell the Birds from the Flowers.*

don't want to pay me, I'll just reverse the current and re-freeze it'. The homeowner hastily paid.

He had a reputation for improvisation. For example he used barrels ranged along the wall for filing, each barrel being labelled 'R. W. Wood 19..'; and his domestic cat was employed to walk inside a subterranean spectrograph to brush aside cobwebs.

Wood was much more than a scientist. He was a superb lecturer and showman, and a talented artist, musician, and writer. He is well known for a book of verse entitled *How To Tell The Birds From The Flowers*, delightfully illustrated with his own *Wood*-cuts. A sample page is shown here (figure 20). A copy was sent to President Theodore Roosevelt, who liked it so much that he requested more of the author's writing. Wood responded with his book *Physical Optics!*

The USA has provided three Chairmen for ICORS: E. R. Lippincott (ICORS IV); J. R. Durig (ICORS VI); and W. L. Peticolas (ICORS X).

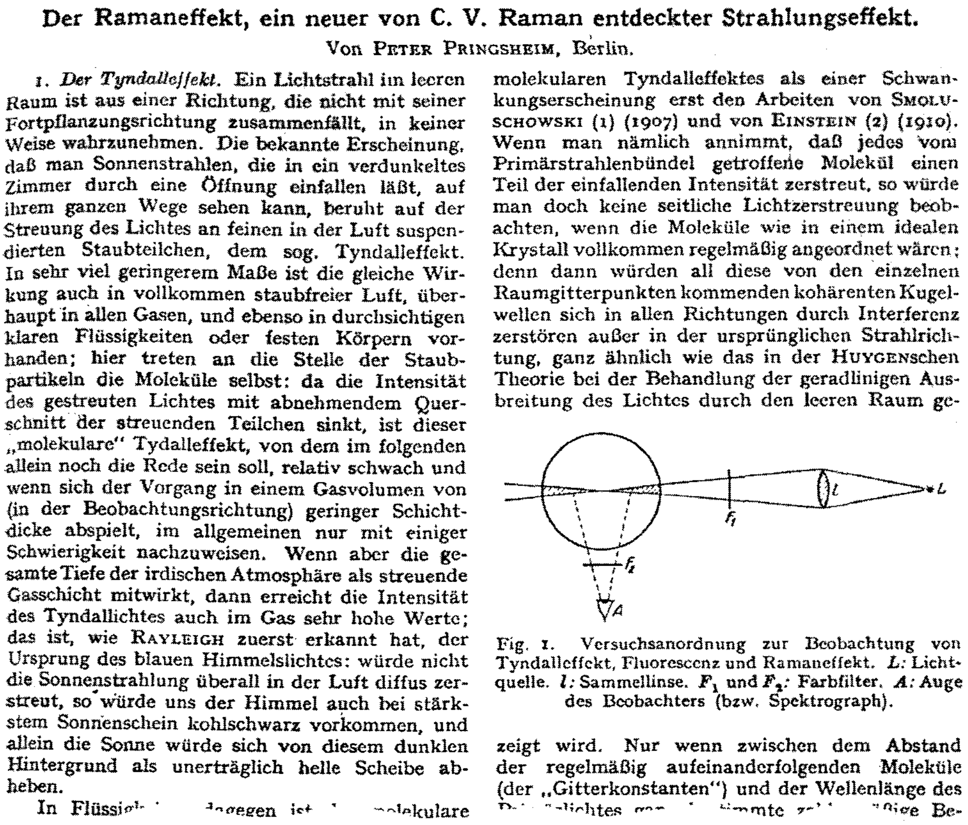
Germany

Die Naturwissenschaften for 3 August 1928, contained the first review article on the new phenomenon (figure 21). The author was P. Pringsheim, brother-in-law of Thomas Mann, who proposed that the new effect should be called the Raman effect.

> So kann man kaum mehr daran zweifeln, dass hier wirklich ein neuer effekt aufgefunden worden ist, den man konsequenterweise als *Ramaneffekt* zu bezeichnen haben wird.

In *Die Naturwissenschaften* for 24 August, M. Born clarified some problems relating to the quantum theory of the Raman effect which Pringsheim had raised in his review.

On 6 August 1928 Pringsheim lectured on the Raman effect at the VIth Congress of Russian Physicists in Moscow. This was subsequently published with A. Carelli and B. Rosen as co-authors in the October issue of *Zeitschrift für Physik* (**51**, 511, 1928).



Der Ramaneffekt, ein neuer von C. V. Raman entdeckter Strahlungseffekt.

Von Peter Pringsheim, Berlin.

1. *Der Tyndalleffekt.* Ein Lichtstrahl im leeren Raum ist aus einer Richtung, die nicht mit seiner Fortpflanzungsrichtung zusammenfällt, in keiner Weise wahrzunehmen. Die bekannte Erscheinung, daß man Sonnenstrahlen, die in ein verdunkeltes Zimmer durch eine Öffnung einfallen läßt, auf ihrem ganzen Wege sehen kann, beruht auf der Streuung des Lichtes an feinen in der Luft suspendierten Staubteilchen, dem sog. Tyndalleffekt. In sehr viel geringerem Maße ist die gleiche Wirkung auch in vollkommen staubfreier Luft, überhaupt in allen Gasen, und ebenso in durchsichtigen klaren Flüssigkeiten oder festen Körpern vorhanden; hier treten an die Stelle der Staubpartikeln die Moleküle selbst: da die Intensität des gestreuten Lichtes mit abnehmendem Querschnitt der streuenden Teilchen sinkt, ist dieser „molekulare" Tydalleffekt, von dem im folgenden allein noch die Rede sein soll, relativ schwach und wenn sich der Vorgang in einem Gasvolumen von (in der Beobachtungsrichtung) geringer Schichtdicke abspielt, im allgemeinen nur mit einiger Schwierigkeit nachzuweisen. Wenn aber die gesamte Tiefe der irdischen Atmosphäre als streuende Gasschicht mitwirkt, dann erreicht die Intensität des Tyndallichtes auch im Gas sehr hohe Werte; das ist, wie Rayleigh zuerst erkannt hat, der Ursprung des blauen Himmelslichtes: würde nicht die Sonnenstrahlung überall in der Luft diffus zerstreut, so würde uns der Himmel auch bei stärkstem Sonnenschein kohlschwarz vorkommen, und allein die Sonne würde sich von diesem dunklen Hintergrund als unerträglich helle Scheibe abheben.

In Flüssi dagegen ist molekulare

molekularen Tyndalleffektes als einer Schwankungserscheinung erst den Arbeiten von Smoluchowski (1) (1907) und von Einstein (2) (1910). Wenn man nämlich annimmt, daß jedes vom Primärstrahlenbündel getroffene Molekül einen Teil der einfallenden Intensität zerstreut, so würde man doch keine seitliche Lichtzerstreuung beobachten, wenn die Moleküle wie in einem idealen Krystall vollkommen regelmäßig angeordnet wären; denn dann würden all diese von den einzelnen Raumgitterpunkten kommenden kohärenten Kugelwellen sich in allen Richtungen durch Interferenz zerstören außer in der ursprünglichen Strahlrichtung, ganz ähnlich wie das in der Huygenschen Theorie bei der Behandlung der geradlinigen Ausbreitung des Lichtes durch den leeren Raum ge-

Fig. 1. Versuchsanordnung zur Beobachtung von Tyndalleffekt, Fluorescenz und Rameneffekt. *L:* Lichtquelle. *l:* Sammellinse. F_1 und F_2: Farbfilter. *A:* Auge des Beobachters (bzw. Spektrograph).

zeigt wird. Nur wenn zwischen dem Abstand der regelmäßig aufeinanderfolgenden Moleküle (der „Gitterkonstanten") und der Wellenlänge des lichtes mmte ßige Be-

Figure 21. From *Die Naturwissenschaften*, **16**, 44, 1928.

An earlier paper in the September issue of the same Journal by Pringsheim and Rosen reported Raman spectra of a number of organic compounds and also of quartz (**50**, 741, 1928).

The study of the Raman effect quickly spread to a number of other universities in Germany: Gerlach in Tubingen and later Munich; Grassmann and Weiler in Munich; Schaefer, Matossi and Aderhold in Breslau; Goubeau in Göttingen; and Mecke in Freiburg i. Br. One of Mecke's pupils E. D. Schmid was chairman of ICORS V.

United Kingdom

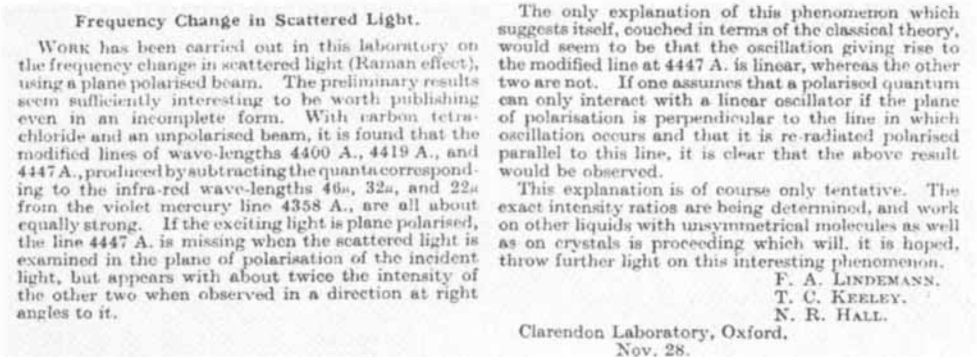
The first Raman paper from the UK came from the Clarendon Laboratory, Oxford, in November 1928 (figure 22). The senior author was the head of the laboratory, Professor F. A. Lindemann, who achieved distinction in a number of fields. As a young physicist he worked out how to bring an aircraft out of a spin and received the DFC for his courage in testing his theory in person. At a Faraday Discussion Meeting in the twenties he formulated the mechanism underlying first-order chemical reactions. Under his leadership the Clarendon which had previously languished became a laboratory of international renown in physics. He was scientific adviser to Sir Winston Churchill during the Second World War and later a member of Churchill's post-war cabinet. For these services he was created a peer and took the title Lord Cherwell (figure 23).

In Oxford he maintained a unique style. Having been prepared by his valet, he arrived at the laboratory in a chauffeur-driven Rolls Royce and on entering, placed his bowler hat on a special peg labelled 'This peg reserved for Lord Cherwell'.

In the period just after the discovery of the Raman effect, a young Oxford chemist L. A. Woodward (figure 24) also began to work with the Raman effect—but in Leipzig in the laboratory of P. Debye (figure 25). His colleagues at Leipzig included, E. Teller, G. Placzek and S. Mizushima. Later Woodward established a strong school of Raman Spectroscopy in Chemistry at Oxford. His many pupils included D. A. Long, the Chairman of ICORS II.

Another early contribution came from A. C. Menzies (figure 26), at the then University College of Leicester, who published the first Raman spectrum from a powdered solid. Later Menzies became professor of physics at Southampton and then Research Director of Hilger and Watts, London (figure 27).

Other early practitioners of Raman spectroscopy in the United Kingdom included G. B. B. M. Sutherland at Cambridge and C. K. Ingold at University College London, where R. J. H. Clark, the Chairman of ICORS XI now actively applies Raman spectroscopy to chemical problems.



Frequency Change in Scattered Light.

WORK has been carried out in this laboratory on the frequency change in scattered light (Raman effect), using a plane polarised beam. The preliminary results seem sufficiently interesting to be worth publishing even in an incomplete form. With carbon tetrachloride and an unpolarised beam, it is found that the modified lines of wave-lengths 4400 A., 4419 A., and 4447 A., produced by subtracting the quanta corresponding to the infra-red wave-lengths 46μ, 32μ, and 22μ from the violet mercury line 4358 A., are all about equally strong. If the exciting light is plane polarised, the line 4447 A. is missing when the scattered light is examined in the plane of polarisation of the incident light, but appears with about twice the intensity of the other two when observed in a direction at right angles to it.

The only explanation of this phenomenon which suggests itself, couched in terms of the classical theory, would seem to be that the oscillation giving rise to the modified line at 4447 A. is linear, whereas the other two are not. If one assumes that a polarised quantum can only interact with a linear oscillator if the plane of polarisation is perpendicular to the line in which oscillation occurs and that it is re-radiated polarised parallel to this line, it is clear that the above result would be observed.

This explanation is of course only tentative. The exact intensity ratios are being determined, and work on other liquids with unsymmetrical molecules as well as on crystals is proceeding which will, it is hoped, throw further light on this interesting phenomenon.

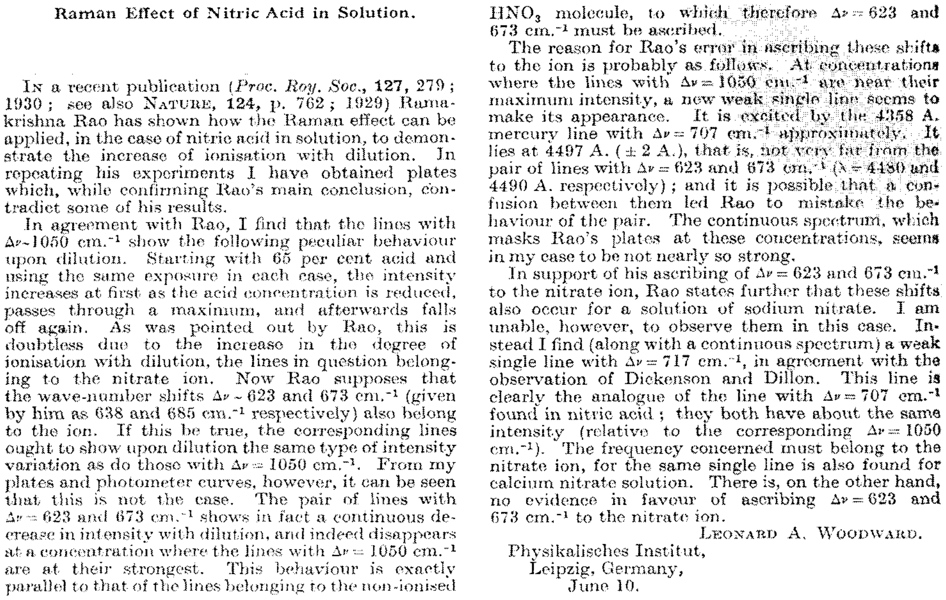
F. A. LINDEMANN.
T. C. KEELEY.
N. R. HALL.

Clarendon Laboratory, Oxford.
Nov. 28.

Figure 22. From *Nature*, **122,** 921, 1928.

Figure 23. F. A. Lindemann (Lord Cherwell).

Figure 24. L. A. Woodward.



Raman Effect of Nitric Acid in Solution.

In a recent publication (*Proc. Roy. Soc.*, **127**, 279; 1930; see also Nature, **124**, p. 762; 1929) Ramakrishna Rao has shown how the Raman effect can be applied, in the case of nitric acid in solution, to demonstrate the increase of ionisation with dilution. In repeating his experiments I have obtained plates which, while confirming Rao's main conclusion, contradict some of his results.

In agreement with Rao, I find that the lines with $\Delta\nu \sim 1050$ cm.$^{-1}$ show the following peculiar behaviour upon dilution. Starting with 65 per cent acid and using the same exposure in each case, the intensity increases at first as the acid concentration is reduced, passes through a maximum, and afterwards falls off again. As was pointed out by Rao, this is doubtless due to the increase in the degree of ionisation with dilution, the lines in question belonging to the nitrate ion. Now Rao supposes that the wave-number shifts $\Delta\nu \sim 623$ and 673 cm.$^{-1}$ (given by him as 638 and 685 cm.$^{-1}$ respectively) also belong to the ion. If this be true, the corresponding lines ought to show upon dilution the same type of intensity variation as do those with $\Delta\nu = 1050$ cm.$^{-1}$. From my plates and photometer curves, however, it can be seen that this is not the case. The pair of lines with $\Delta\nu = 623$ and 673 cm.$^{-1}$ shows in fact a continuous decrease in intensity with dilution, and indeed disappears at a concentration where the lines with $\Delta\nu = 1050$ cm.$^{-1}$ are at their strongest. This behaviour is exactly parallel to that of the lines belonging to the non-ionised HNO_3 molecule, to which therefore $\Delta\nu = 623$ and 673 cm.$^{-1}$ must be ascribed.

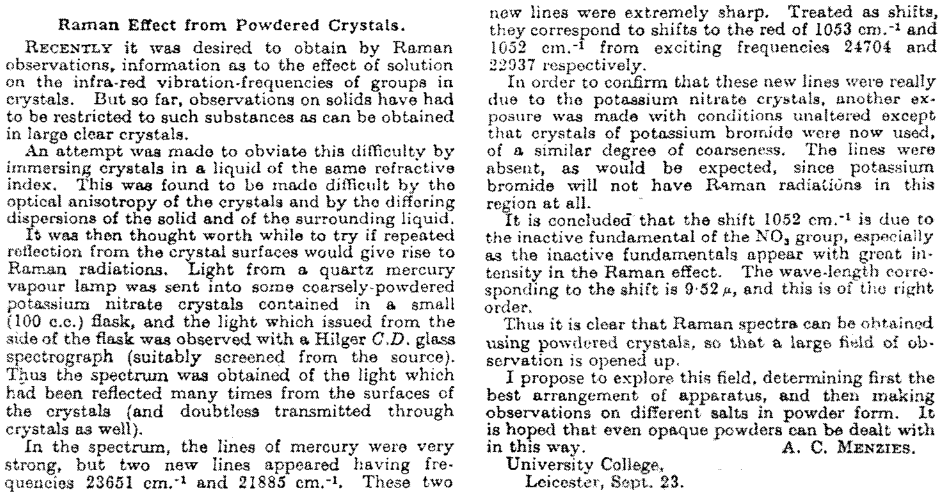
The reason for Rao's error in ascribing these shifts to the ion is probably as follows. At concentrations where the lines with $\Delta\nu = 1050$ cm.$^{-1}$ are near their maximum intensity, a new weak single line seems to make its appearance. It is excited by the 4358 A. mercury line with $\Delta\nu = 707$ cm.$^{-1}$ approximately. It lies at 4497 A. (± 2 A.), that is, not very far from the pair of lines with $\Delta\nu = 623$ and 673 cm.$^{-1}$ ($\lambda = 4480$ and 4490 A. respectively); and it is possible that a confusion between them led Rao to mistake the behaviour of the pair. The continuous spectrum, which masks Rao's plates at these concentrations, seems in my case to be not nearly so strong.

In support of his ascribing of $\Delta\nu = 623$ and 673 cm.$^{-1}$ to the nitrate ion, Rao states further that these shifts also occur for a solution of sodium nitrate. I am unable, however, to observe them in this case. Instead I find (along with a continuous spectrum) a weak single line with $\Delta\nu = 717$ cm.$^{-1}$, in agreement with the observation of Dickenson and Dillon. This line is clearly the analogue of the line with $\Delta\nu = 707$ cm.$^{-1}$ found in nitric acid; they both have about the same intensity (relative to the corresponding $\Delta\nu = 1050$ cm.$^{-1}$). The frequency concerned must belong to the nitrate ion, for the same single line is also found for calcium nitrate solution. There is, on the other hand, no evidence in favour of ascribing $\Delta\nu = 623$ and 673 cm.$^{-1}$ to the nitrate ion.

Leonard A. Woodward.

Physikalisches Institut,
Leipzig, Germany,
June 10.

Figure 25. From *Nature*, **126**, 58, 1930.



Raman Effect from Powdered Crystals.

Recently it was desired to obtain by Raman observations, information as to the effect of solution on the infra-red vibration-frequencies of groups in crystals. But so far, observations on solids have had to be restricted to such substances as can be obtained in large clear crystals.

An attempt was made to obviate this difficulty by immersing crystals in a liquid of the same refractive index. This was found to be made difficult by the optical anisotropy of the crystals and by the differing dispersions of the solid and of the surrounding liquid.

It was then thought worth while to try if repeated reflection from the crystal surfaces would give rise to Raman radiations. Light from a quartz mercury vapour lamp was sent into some coarsely-powdered potassium nitrate crystals contained in a small (100 c.c.) flask, and the light which issued from the side of the flask was observed with a Hilger *C.D.* glass spectrograph (suitably screened from the source). Thus the spectrum was obtained of the light which had been reflected many times from the surfaces of the crystals (and doubtless transmitted through crystals as well).

In the spectrum, the lines of mercury were very strong, but two new lines appeared having frequencies 23651 cm.$^{-1}$ and 21885 cm.$^{-1}$. These two new lines were extremely sharp. Treated as shifts, they correspond to shifts to the red of 1053 cm.$^{-1}$ and 1052 cm.$^{-1}$ from exciting frequencies 24704 and 22937 respectively.

In order to confirm that these new lines were really due to the potassium nitrate crystals, another exposure was made with conditions unaltered except that crystals of potassium bromide were now used, of a similar degree of coarseness. The lines were absent, as would be expected, since potassium bromide will not have Raman radiations in this region at all.

It is concluded that the shift 1052 cm.$^{-1}$ is due to the inactive fundamental of the NO_3 group, especially as the inactive fundamentals appear with great intensity in the Raman effect. The wave-length corresponding to the shift is 9·52 μ, and this is of the right order.

Thus it is clear that Raman spectra can be obtained using powdered crystals, so that a large field of observation is opened up.

I propose to explore this field, determining first the best arrangement of apparatus, and then making observations on different salts in powder form. It is hoped that even opaque powders can be dealt with in this way.

A. C. Menzies.

University College,
Leicester, Sept. 23.

Figure 26. From *Nature*, **124**, 511, 1929.

Figure 27. A. C. Menzies (left) with Raman and Kastler.

Austria

Experimental studies of the Raman effect were begun by K. W. F. Kohlrausch (figure 28) in Graz in December 1928. In the next 15 years, in association with his co-workers, A. Dadieu, L. Kahovec, A. Pongratz, A. W. Reitz, R. Seka, J. Wagner and others he made extensive studies of the Raman spectra of an extraordinarily wide range of compounds. The results of these painstaking and valuable studies were published in three classic works on 'Der Smekal Raman-effekt' which appeared in 1931, 1938 and 1943.

His first collaborator, A. Dadieu has described the early days of Raman spectroscopy at Graz.

> First news of the discovery of the Raman effect reached us early in December 1928 through a paper by R. W. Wood... I referred to it at the weekly colloquium held at our Institute by physicists and chemists for the purpose of discussing new trends... Immediately after the colloquium I therefore suggested to Kohlrausch that we should abandon ultra-violet spectroscopy and devote our entire energies to the far more promising Raman effect.
>
> I vividly remember Kohlrausch's characteristic look of ironic scepticism and his reply: 'You want to achieve that with our teaching spectrometer?' As our Institute was quite inadequately endowed, it was obvious that it would be far beyond our financial resources to acquire within a short space of time an instrument with higher light intensity. So I said: 'Well, we have also got a Zeiss instrument with a Rutherford prism. True, it isn't an actual giant as to its light intensity, nevertheless I should like to have a crack at it'.
>
> I took our old mercury lamp, fitted it with the largest lens at my disposal, inserted it into a round bottomed flask filled with freshly distilled carbon tetrachloride and pointed the spectrograph at the scattered light. After an exposure of 30 minutes, I developed the plate and placed it in a fixing solution. Kohlrausch who had followed me to the darkroom, pushed up his glasses and smiled maliciously: he saw no Raman line! I 'divined' one and predicted that it would become visible on the dry plate. And that is exactly what happened.
>
> From then on, the Raman lamp burned day and night. We slept in turns in the Institute, I myself distilled and cleaned until midnight the liquids we meant to analyse, made more exposures and measured the spectra. Kohlrausch saw to the marking of the lines, worked out the resulting Raman spectra and tried to interpret their structure. After two months we sent our first paper to the Austrian Academy of Science (Studien zum Ramaneffekt: Das Ramanspektrum organischer Substanzen (Fettsauren und ihre Ester) A. Dadieu and K. W. F. Kohlrausch, *Sitzungsberichte der Akademie der Wissenschaften Wien*, **138,** 41, 1929). Another five papers right across organic chemistry followed up to the end of 1929.

In 1923 A. Smekal (figure 29), in Vienna, had predicted that the frequency of light could be changed on scattering, in a note entitled 'Zur Quantentheorie der Dispersion' (*Die Naturwissenschaften*, **11,** 873, 1923). When Raman's discovery was announced, Smekal was not slow to draw attention to the theoretical predictions he had made. A note from him entitled 'Zur Quantentheorie der Streuung und Dispersion' appeared in *Die Naturwissenschaften* for 3 August 1928. This also referred to the classic theoretical paper by Kramers and Heisenberg (*Zeitschrift für Physik*, **31,** 681, 1925).

Figure 28. K. W. F. Kohlrausch.

Figure 29. A. G. Smekal.

K. W. F. Kohlrausch was born in 1884 in Austria, and educated at the University of Vienna. In 1920 he was appointed Professor of Physics at the Technische Hochschule, Graz, where he remained until his retirement. He died in 1943.

A. G. Smekal was born in Vienna in 1895. He studied at the Universities of Graz (1913–1917) and Berlin (1917–1919). From 1920–1927 he taught in Vienna, first at the University and then at the Technical University. Subsequently he was Professor at Halle (1928–1945), Darmstadt (1946–1949) and Graz (1949–1959). Smekal was the author of several important books, including *Allgemeine Grundlagen der Quantenstatistik und Quantentheorie* and *Atomphysik.* He was the founder of the Austrian Physical Society and a member of the Austrian Academy of Sciences. Smekal died in Graz in 1959.

Canada

On 20 December 1928 J. C. McLennan and J. H. McLeod sent a letter to *Nature* entitled 'The Raman effect with liquid Oxygen, Nitrogen and Hydrogen' (figure 30). This was published on 2 February 1929. This work was also reported early in 1929 in two short papers in the *Transactions of the Royal Society of Canada.*

The results of McLennan and McLeod were of very great significance. They gave direct experimental evidence that: (i) the vibrations of homopolar molecules which are infra-red inactive can be observed in the Raman effect; (ii) two quantum rotational transitions occur in Raman scattering; (iii) hydrogen at low temperatures must be regarded as a mixture of two effectively distinct sets of molecules, symmetrical and antisymmetrical. This work formed one part of the Ph.D thesis of J. H. McLeod (figure 32) submitted to the University of Toronto in November 1929. The other part was concerned with the nature of the auroral green spectral line, to which McLeod also made a significant contribution. His outstanding Ph.D thesis is further remarkable for its brevity, consisting of *just 21 pages*! Pages 13–21 deal with the Raman work including detailed suggestions for further work.

J. C. McLennan (1867–1935) (figure 33) was a very notable Canadian scientist. He graduated from the University of Toronto in 1892 and from 1898–1900 was a graduate student in the Cavendish Laboratory, Cambridge under J. J. Thomson. A fellow graduate student at Cambridge was E. Rutherford. In 1907 he became Professor and Head of the Department of Physics at Toronto (figure 31) where he stayed until his retirement in 1932.

He achieved great distinction as a physicist. He was a Fellow of the Royal Society of London and was awarded the Society's Gold Medal in 1927. He was knighted in 1935. He also contributed greatly to the development of physics in Toronto and the Physics Department of the University of Toronto is housed appropriately in the McLennan Laboratories.

It is intriguing to recall that as a boy in the small Ontario town of Ingersoll, McLennan's ambition was to work for the Grand Trunk Railway. Failing to obtain a position he decided on further education!

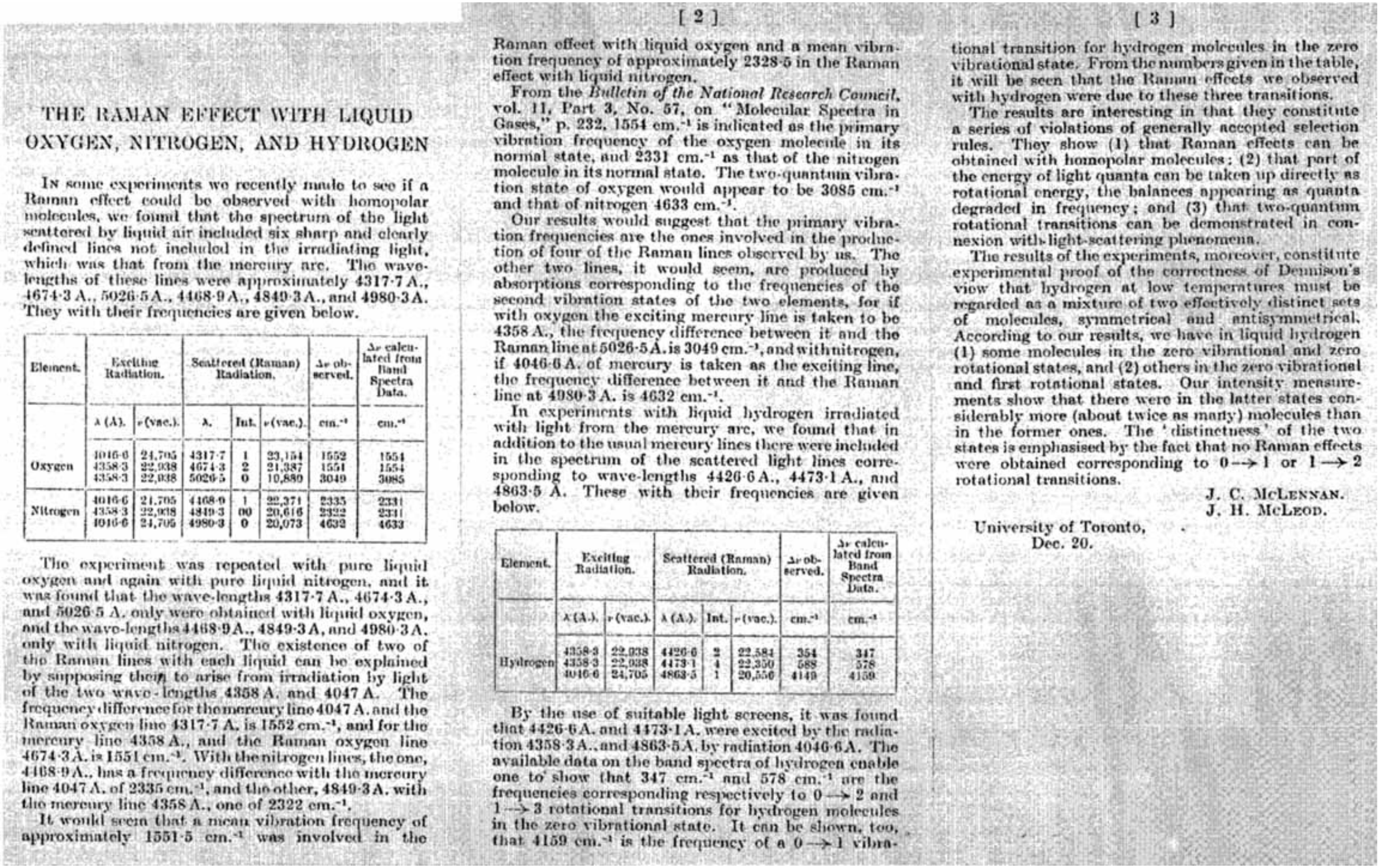
Italy

There were a number of notable contributions from Italy in this period.

F. Rasetti (figure 34) published a series of classical papers dealing with the rotational Raman spectra of gases (for example see figure 37) and the associated selection rules. He also made the first observation of an electronic transition in a Raman spectrum. Doublets in the Raman spectrum of NO with a separation of 124 cm^{-1} were assigned to transitions between the two electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ (*Nature*, **124,** 93, 1929).

Contributions to the theory of the Raman effect were made by E. Amaldi (figure 35) A. Carelli, E. Fermi and E. Segré.

In Bologna G. B. Bonino (figure 36) appreciated that the Raman effect was a valuable tool for research relating to organic molecules. He has recalled the excitement he felt when one day in 1928 he found Raman and Krishnan's paper in his university library. He quickly realised that a Raman spectrum would be easier to obtain than an infra-red spectrum using the techniques then available.



THE RAMAN EFFECT WITH LIQUID OXYGEN, NITROGEN, AND HYDROGEN

In some experiments we recently made to see if a Raman effect could be observed with homopolar molecules, we found that the spectrum of the light scattered by liquid air included six sharp and clearly defined lines not included in the irradiating light, which was that from the mercury arc. The wave-lengths of these lines were approximately 4317·7 A., 4674·3 A., 5026·5 A., 4468·9 A., 4849·3 A., and 4980·3 A. They with their frequencies are given below.

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			$\Delta\nu$ observed.	$\Delta\nu$ calculated from Band Spectra Data.
	λ (A).	ν (vac.).	λ.	Int.	ν (vac.).	cm.$^{-1}$	cm.$^{-1}$
Oxygen	4046·6	24,705	4317·7	1	23,154	1552	1554
	4358·3	22,938	4674·3	2	21,387	1551	1554
	4358·3	22,938	5026·5	0	10,889	3049	3085
Nitrogen	4046·6	21,705	4468·9	1	22,371	2335	2331
	4358·3	22,938	4849·3	00	20,616	2322	2331
	4046·6	24,705	4980·3	0	20,073	4632	4633

The experiment was repeated with pure liquid oxygen and again with pure liquid nitrogen, and it was found that the wave-lengths 4317·7 A., 4674·3 A., and 5026·5 A. only were obtained with liquid oxygen, and the wave-lengths 4468·9 A., 4849·3 A, and 4980·3 A. only with liquid nitrogen. The existence of two of the Raman lines with each liquid can be explained by supposing them to arise from irradiation by light of the two wave-lengths 4358 A. and 4047 A. The frequency difference for the mercury line 4047 A. and the Raman oxygen line 4317·7 A. is 1552 cm.$^{-1}$, and for the mercury line 4358 A., and the Raman oxygen line 4674·3 Å. is 1551 cm.$^{-1}$. With the nitrogen lines, the one, 4468·9 A., has a frequency difference with the mercury line 4047 A. of 2335 cm.$^{-1}$, and the other, 4849·3 A. with the mercury line 4358 A., one of 2322 cm.$^{-1}$.

It would seem that a mean vibration frequency of approximately 1551·5 cm.$^{-1}$ was involved in the

[2]

Raman effect with liquid oxygen and a mean vibration frequency of approximately 2328·5 in the Raman effect with liquid nitrogen.

From the *Bulletin of the National Research Council*, vol. 11, Part 3, No. 57, on "Molecular Spectra in Gases," p. 232, 1554 cm.$^{-1}$ is indicated as the primary vibration frequency of the oxygen molecule in its normal state, and 2331 cm.$^{-1}$ as that of the nitrogen molecule in its normal state. The two-quantum vibration state of oxygen would appear to be 3085 cm.$^{-1}$ and that of nitrogen 4633 cm.$^{-1}$.

Our results would suggest that the primary vibration frequencies are the ones involved in the production of four of the Raman lines observed by us. The other two lines, it would seem, are produced by absorptions corresponding to the frequencies of the second vibration states of the two elements, for if with oxygen the exciting mercury line is taken to be 4358 A., the frequency difference between it and the Raman line at 5026·5 Å. is 3049 cm.$^{-1}$, and with nitrogen, if 4046·6 A. of mercury is taken as the exciting line, the frequency difference between it and the Raman line at 4980·3 A. is 4632 cm.$^{-1}$.

In experiments with liquid hydrogen irradiated with light from the mercury arc, we found that in addition to the usual mercury lines there were included in the spectrum of the scattered light lines corresponding to wave-lengths 4426·6 A., 4473·1 A., and 4863·5 Å. These with their frequencies are given below.

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			$\Delta\nu$ observed.	$\Delta\nu$ calculated from Band Spectra Data.
	λ (A.).	ν (vac.).	λ (A.).	Int.	ν (vac.).	cm.$^{-1}$	cm.$^{-1}$
Hydrogen	4358·3	22,938	4426·6	2	22,584	354	347
	4358·3	22,938	4473·1	4	22,350	588	578
	4046·6	24,705	4863·5	1	20,556	4149	4159

By the use of suitable light screens, it was found that 4426·6 A. and 4473·1 A. were excited by the radiation 4358·3 A., and 4863·5 A. by radiation 4046·6 A. The available data on the band spectra of hydrogen enable one to show that 347 cm.$^{-1}$ and 578 cm.$^{-1}$ are the frequencies corresponding respectively to 0 → 2 and 1 → 3 rotational transitions for hydrogen molecules in the zero vibrational state. It can be shown, too, that 4159 cm.$^{-1}$ is the frequency of a 0 → 1 vibra-

[3]

tional transition for hydrogen molecules in the zero vibrational state. From the numbers given in the table, it will be seen that the Raman effects we observed with hydrogen were due to these three transitions.

The results are interesting in that they constitute a series of violations of generally accepted selection rules. They show (1) that Raman effects can be obtained with homopolar molecules; (2) that part of the energy of light quanta can be taken up directly as rotational energy, the balances appearing as quanta degraded in frequency; and (3) that two-quantum rotational transitions can be demonstrated in connexion with light-scattering phenomena.

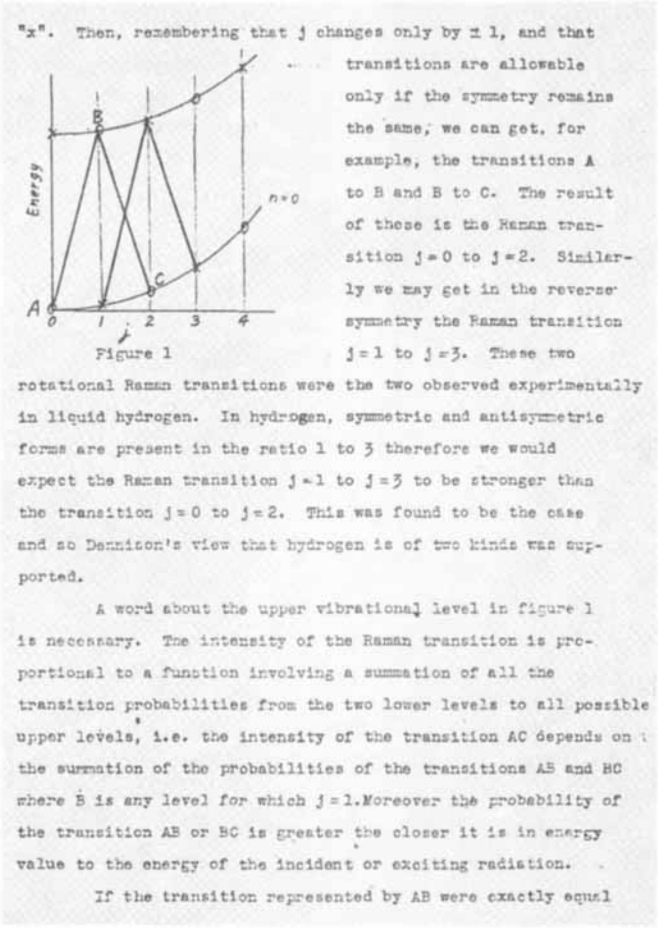
The results of the experiments, moreover, constitute experimental proof of the correctness of Dennison's view that hydrogen at low temperatures must be regarded as a mixture of two effectively distinct sets of molecules, symmetrical and antisymmetrical. According to our results, we have in liquid hydrogen (1) some molecules in the zero vibrational and zero rotational states, and (2) others in the zero vibrational and first rotational states. Our intensity measurements show that there were in the latter states considerably more (about twice as many) molecules than in the former ones. The 'distinctness' of the two states is emphasised by the fact that no Raman effects were obtained corresponding to 0 → 1 or 1 → 2 rotational transitions.

J. C. McLennan.
J. H. McLeod.

University of Toronto,
Dec. 20.

Figure 30. From *Nature*, **123**, 160, 1929.

Figure 31. Physics Laboratories, Toronto, in the 1920s.



"x". Then, remembering that j changes only by ± 1, and that transitions are allowable only if the symmetry remains the same, we can get, for example, the transitions A to B and B to C. The result of these is the Raman transition j = 0 to j = 2. Similarly we may get in the reverse symmetry the Raman transition j = 1 to j = 3. These two rotational Raman transitions were the two observed experimentally in liquid hydrogen. In hydrogen, symmetric and antisymmetric forms are present in the ratio 1 to 3 therefore we would expect the Raman transition j = 1 to j = 3 to be stronger than the transition j = 0 to j = 2. This was found to be the case and so Dennison's view that hydrogen is of two kinds was supported.

Figure 1

A word about the upper vibrational level in figure 1 is necessary. The intensity of the Raman transition is proportional to a function involving a summation of all the transition probabilities from the two lower levels to all possible upper levels, i.e. the intensity of the transition AC depends on the summation of the probabilities of the transitions AB and BC where B is any level for which j = 1. Moreover the probability of the transition AB or BC is greater the closer it is in energy value to the energy of the incident or exciting radiation.

If the transition represented by AB were exactly equal

Figure 32. From the Ph. D. thesis of J. H. McLeod submitted to the University of Toronto, November 1929.

Figure 33. J. C. McLennan.

Figure 34. F. Rasetti.

Figure 35. E. Amaldi, spring 1931, on the road between Dresden and Leipzig.

Figure 36. G. B. Bonino.

It is interesting to note that Rasetti, who was born in 1901, is now the most senior Fellow of the Lincei Academy of Rome, and Amaldi who was born in 1908, is now the President of the Lincei. The photograph of Amaldi on a motorcycle was taken near Leipzig in 1931 when he was working with Debye.

Über die Rotations-Ramanspektren von Stickstoff und Sauerstoff.

Von F. Rasetti in Rom.

Mit 2 Abbildungen. (Eingegangen am 10. März 1930.)

Die Rotations-Ramanspektren von Stickstoff und Sauerstoff wurden mit großer Dispersion (3 Å/mm) photographiert. Die früheren Angaben des Verf. über die Intensität der gerad- und ungeradzahligen Rotationslinien werden bestätigt.

Die Rotations-Ramanbanden von einigen zweiatomigen Molekülen wurden vom Verfasser bei Anregung mit der Quecksilberlinie λ 2536

Fig. 1. Rotations-Ramanspektren von Sauerstoff und Stickstoff (8-fach vergrößert).

Figure 37. From *Zeitschrift für Physik*, **61**, 598, 1930.

Japan

The first Japanese paper on Raman spectroscopy came from M. Kimura and Y. Uchida (figures 38 and 39). It was submitted for publication on 5 December 1928 and appeared later that month in the *Japanese Journal of Physics* (figure 40).

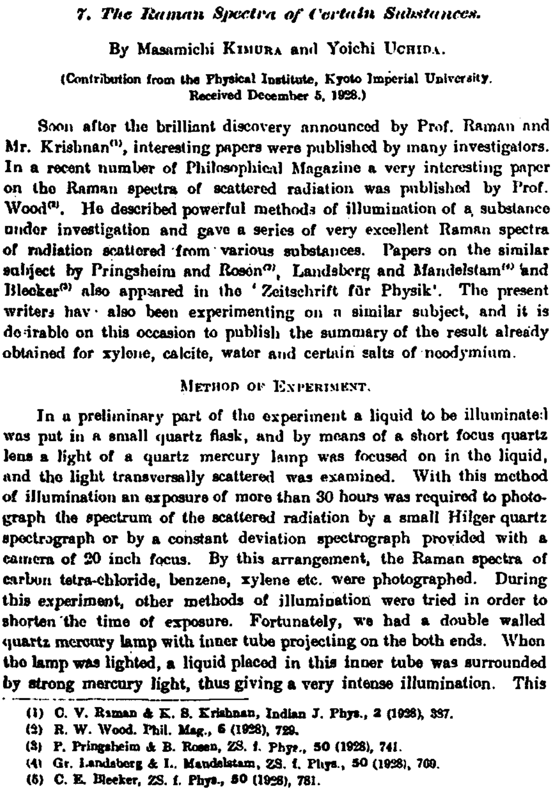
From 1929–31 S. Mizushima was in Debye's Laboratory at Leipzig. On his return to Japan he established a strong school of Molecular Spectroscopy at Tokyo. His many distinguished pupils included Y. Morino, T. Shimanouchi (figure 41) and M. Tsuboi, who was Chairman of ICORS IX.

Professor M. Kimura, the senior author, was born in 1883. He studied under R. W. Wood at Johns Hopkins University, Baltimore, USA from 1915 to 1917. He was professor of physics at the then Imperial University of Kyoto (now the University of Kyoto) until his retirement. He died in 1962.

Professor Y. Uchida was born in 1903 and graduated from Kyoto in 1926. He did spectroscopic research with Kimura and became professor of physics at Kyoto in 1946.

Figure 38. M. Kimura.

Figure 39. Y. Uchida.



7. *The Raman Spectra of Certain Substances.*

By Masamichi **Kimura** and Yoichi **Uchida**.

(Contribution from the Physical Institute, Kyoto Imperial University.
Received December 5, 1928.)

Soon after the brilliant discovery announced by Prof. Raman and Mr. Krishnan(1), interesting papers were published by many investigators. In a recent number of Philosophical Magazine a very interesting paper on the Raman spectra of scattered radiation was published by Prof. Wood(2). He described powerful methods of illumination of a substance under investigation and gave a series of very excellent Raman spectra of radiation scattered from various substances. Papers on the similar subject by Pringsheim and Rosen(3), Landsberg and Mandelstam(4) and Blecker(5) also appeared in the 'Zeitschrift für Physik'. The present writers have also been experimenting on a similar subject, and it is desirable on this occasion to publish the summary of the result already obtained for xylene, calcite, water and certain salts of neodymium.

METHOD OF EXPERIMENT.

In a preliminary part of the experiment a liquid to be illuminated was put in a small quartz flask, and by means of a short focus quartz lens a light of a quartz mercury lamp was focused on in the liquid, and the light transversally scattered was examined. With this method of illumination an exposure of more than 30 hours was required to photograph the spectrum of the scattered radiation by a small Hilger quartz spectrograph or by a constant deviation spectrograph provided with a camera of 20 inch focus. By this arrangement, the Raman spectra of carbon tetra-chloride, benzene, xylene etc. were photographed. During this experiment, other methods of illumination were tried in order to shorten the time of exposure. Fortunately, we had a double walled quartz mercury lamp with inner tube projecting on the both ends. When the lamp was lighted, a liquid placed in this inner tube was surrounded by strong mercury light, thus giving a very intense illumination. This

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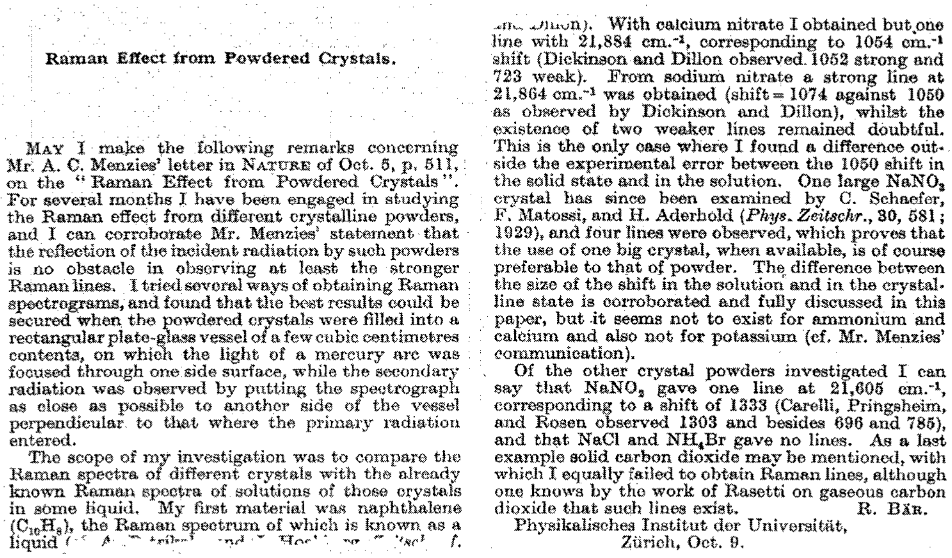
(1) C. V. Raman & K. S. Krishnan, Indian J. Phys., 2 (1928), 387.
(2) R. W. Wood. Phil. Mag., 6 (1928), 729.
(3) P. Pringsheim & B. Rosen, ZS. f. Phys., 50 (1928), 741.
(4) Gr. Landsberg & L. Mandelstam, ZS. f. Phys., 50 (1928), 769.
(5) C. E. Bleeker, ZS. f. Phys., 50 (1928), 781.

Figure 40. From *Japanese Journal of Physics*, **5**, 97, 1928.

Figure 41. T. Shimanouchi in jovial mood.



Raman Effect from Powdered Crystals.

MAY I make the following remarks concerning Mr. A. C. Menzies' letter in NATURE of Oct. 5, p. 511, on the "Raman Effect from Powdered Crystals". For several months I have been engaged in studying the Raman effect from different crystalline powders, and I can corroborate Mr. Menzies' statement that the reflection of the incident radiation by such powders is no obstacle in observing at least the stronger Raman lines. I tried several ways of obtaining Raman spectrograms, and found that the best results could be secured when the powdered crystals were filled into a rectangular plate-glass vessel of a few cubic centimetres contents, on which the light of a mercury arc was focused through one side surface, while the secondary radiation was observed by putting the spectrograph as close as possible to another side of the vessel perpendicular to that where the primary radiation entered.

The scope of my investigation was to compare the Raman spectra of different crystals with the already known Raman spectra of solutions of those crystals in some liquid. My first material was naphthalene ($C_{10}H_8$), the Raman spectrum of which is known as a liquid [illegible] on). With calcium nitrate I obtained but one line with 21,884 cm.$^{-1}$, corresponding to 1054 cm.$^{-1}$ shift (Dickinson and Dillon observed 1052 strong and 723 weak). From sodium nitrate a strong line at 21,864 cm.$^{-1}$ was obtained (shift = 1074 against 1050 as observed by Dickinson and Dillon), whilst the existence of two weaker lines remained doubtful. This is the only case where I found a difference outside the experimental error between the 1050 shift in the solid state and in the solution. One large $NaNO_3$ crystal has since been examined by C. Schaefer, F. Matossi, and H. Aderhold (*Phys. Zeitschr.*, 30, 581; 1929), and four lines were observed, which proves that the use of one big crystal, when available, is of course preferable to that of powder. The difference between the size of the shift in the solution and in the crystalline state is corroborated and fully discussed in this paper, but it seems not to exist for ammonium and calcium and also not for potassium (cf. Mr. Menzies' communication).

Of the other crystal powders investigated I can say that $NaNO_2$ gave one line at 21,605 cm.$^{-1}$, corresponding to a shift of 1333 (Carelli, Pringsheim, and Rosen observed 1303 and besides 696 and 785), and that NaCl and NH_4Br gave no lines. As a last example solid carbon dioxide may be mentioned, with which I equally failed to obtain Raman lines, although one knows by the work of Rasetti on gaseous carbon dioxide that such lines exist.

R. BÄR.

Physikalisches Institut der Universität,
Zürich, Oct. 9.

Figure 42. From a letter to *Nature*, **124**, 692, 1929.

Switzerland

The first contributions from Switzerland came from Zurich. In 1929 R. Bär described a method for obtaining the Raman spectrum of a powdered crystal (figure 42), and Victor Henri (at that time professor of physical chemistry at Zurich) and Owen Howell (University of Manchester) (figure 43) published a short paper on The Structure and Activation of the Phosgene Molecule Part II—The Raman Spectrum of Phosgene, in the *Proceedings of the Royal Society*. The paper was submitted in November 1929 and appeared early in 1930 (*Proc. Roy. Soc. London*, **128,** 190, 1930).

Victor Henri played quite an important role in the development of Raman spectroscopy in Europe. He encouraged Langseth from Copenhagen, Denmark, who spent a period at Zürich as a Rockefeller Foundation Fellow, to interest himself in Raman spectroscopy; and later when Henri went to Liège, Belgium, he continued to promote the study of Raman spectroscopy there.

Denmark

In Denmark, Raman spectroscopy was pioneered by A. W. Langseth (figure 44). When the Raman effect was discovered in 1928 he was in Zurich with V. Henri studying visible and ultra-violet absorption spectra. He was very skilled with his hands. As soon as he came to Copenhagen in 1929 he built a Raman spectrograph. The result of his first study, entitled 'A Relation between Raman Spectra and Ultra-Violet Absorption' (figure 45) was published in *Nature* in 1929. The Langseth spectrograph apparently had better resolution than any other at the time and a little later Langseth observed the fine structure of vibration lines due to isotopes of chlorine.

Later pupils and associates included J. Rud Nielsen, R. C. Lord, B. Bak, H. J. Bernstein and S. Brodersen.

H. J. Bernstein was the initiator of ICORS and Chairman of ICORS I.

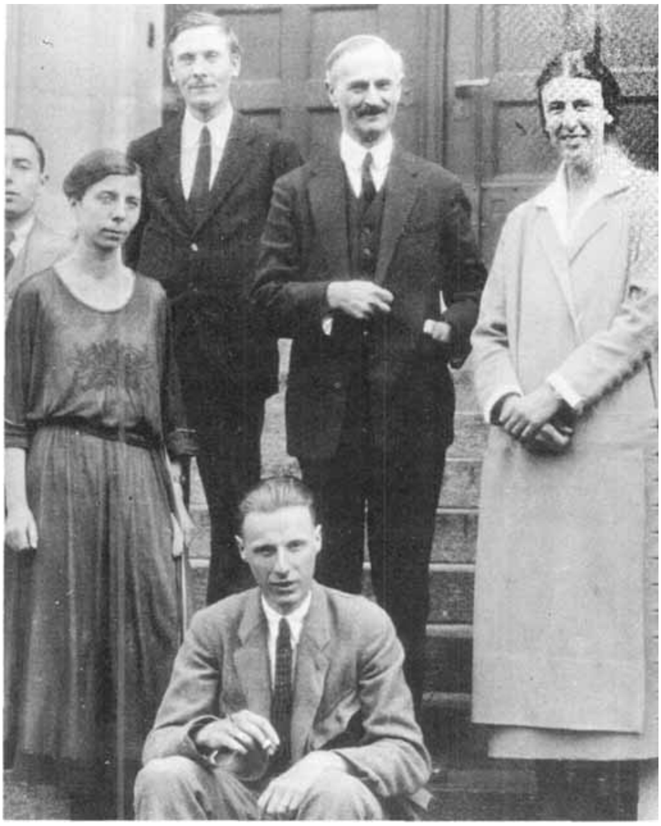
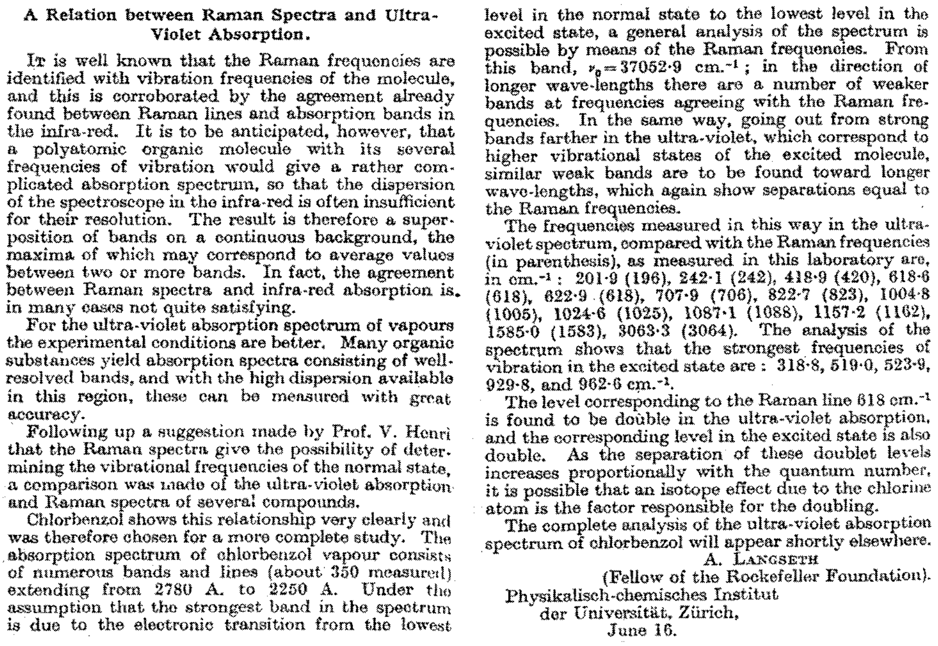


Figure 43. Victor Henri and some of his collaborators at Zürich in the late 1920s. Owen Howell is to the left of Victor Henri in the centre.

Figure 44. A. W. Langseth (1895–1961).



A Relation between Raman Spectra and Ultra-Violet Absorption.

It is well known that the Raman frequencies are identified with vibration frequencies of the molecule, and this is corroborated by the agreement already found between Raman lines and absorption bands in the infra-red. It is to be anticipated, however, that a polyatomic organic molecule with its several frequencies of vibration would give a rather complicated absorption spectrum, so that the dispersion of the spectroscope in the infra-red is often insufficient for their resolution. The result is therefore a superposition of bands on a continuous background, the maxima of which may correspond to average values between two or more bands. In fact, the agreement between Raman spectra and infra-red absorption is in many cases not quite satisfying.

For the ultra-violet absorption spectrum of vapours the experimental conditions are better. Many organic substances yield absorption spectra consisting of well-resolved bands, and with the high dispersion available in this region, these can be measured with great accuracy.

Following up a suggestion made by Prof. V. Henri that the Raman spectra give the possibility of determining the vibrational frequencies of the normal state, a comparison was made of the ultra-violet absorption and Raman spectra of several compounds.

Chlorbenzol shows this relationship very clearly and was therefore chosen for a more complete study. The absorption spectrum of chlorbenzol vapour consists of numerous bands and lines (about 350 measured) extending from 2780 A. to 2250 A. Under the assumption that the strongest band in the spectrum is due to the electronic transition from the lowest level in the normal state to the lowest level in the excited state, a general analysis of the spectrum is possible by means of the Raman frequencies. From this band, $\nu_0 = 37052{\cdot}9$ cm.$^{-1}$; in the direction of longer wave-lengths there are a number of weaker bands at frequencies agreeing with the Raman frequencies. In the same way, going out from strong bands farther in the ultra-violet, which correspond to higher vibrational states of the excited molecule, similar weak bands are to be found toward longer wave-lengths, which again show separations equal to the Raman frequencies.

The frequencies measured in this way in the ultra-violet spectrum, compared with the Raman frequencies (in parenthesis), as measured in this laboratory are, in cm.$^{-1}$: 201·9 (196), 242·1 (242), 418·9 (420), 618·6 (618), 622·9 (618), 707·9 (706), 822·7 (823), 1004·8 (1005), 1024·6 (1025), 1087·1 (1088), 1157·2 (1162), 1585·0 (1583), 3063·3 (3064). The analysis of the spectrum shows that the strongest frequencies of vibration in the excited state are: 318·8, 519·0, 523·9, 929·8, and 962·6 cm.$^{-1}$.

The level corresponding to the Raman line 618 cm.$^{-1}$ is found to be double in the ultra-violet absorption, and the corresponding level in the excited state is also double. As the separation of these doublet levels increases proportionally with the quantum number, it is possible that an isotope effect due to the chlorine atom is the factor responsible for the doubling.

The complete analysis of the ultra-violet absorption spectrum of chlorbenzol will appear shortly elsewhere.

A. Langseth
(Fellow of the Rockefeller Foundation).
Physikalisch-chemisches Institut
der Universität, Zürich,
June 16.

Figure 45. From *Nature*, **124,** 92, 1929.

Poland

Polish scientists were quick to follow up Raman's discovery. A paper by W. Czapska on the Raman spectra of *para*, *ortho* and *meta*-xylenes appeared in *Comptes Rendus* for 1 July 1929 (Spectres de Raman des para, ortho, métaxylenes. Note de Mlle W. Czapska, transmise par M. M. de Broglie. *Comptes Rendus*, **189,** 32, 1929); and this was followed later in the year by a paper by S. Ziemecki and K. Jodko-Narkiewicz (*Naturwissenschaften*, **17,** 876, 1929).

Belgium

The first paper on the Raman effect from Belgium was published by C. Manneback (figure 46), of the University of Louvain, in 1929 (Die Intensität der sekundären Streustrahlung ('Raman-Linien'), C. Manneback. *Die Naturwissenschaften*, **17,** 364, 1929).

Victor Henri came to Liège from Zurich in 1931 (figure 47), and the Department of Chemistry at Liège contains a number of early photographic plates of Raman spectra taken by him and his collaborators. One of these is the Raman spectrum of chlorobenzene (figure 48), taken on 13 February 1929 by A. Langseth, which formed the basis of his note in *Nature* later that year.

Norway

In Norway from late 1929 Bjorn Trumpy (figure 49) was active in the determination of the Raman spectra of a number of molecules and his first paper on Raman spectroscopy was published in 1930 (Ramaneffekt und Konstitution der Moleküle, I., B. Trumpy, *Zeitschrift für Physik*, **62,** 806, 1930). Over the next five years he determined

Figure 46. Charles Manneback, Secretaire Perpetuel de l'Academie royale de Belgique.

Figure 47. V. Henri and Raman at Liège.

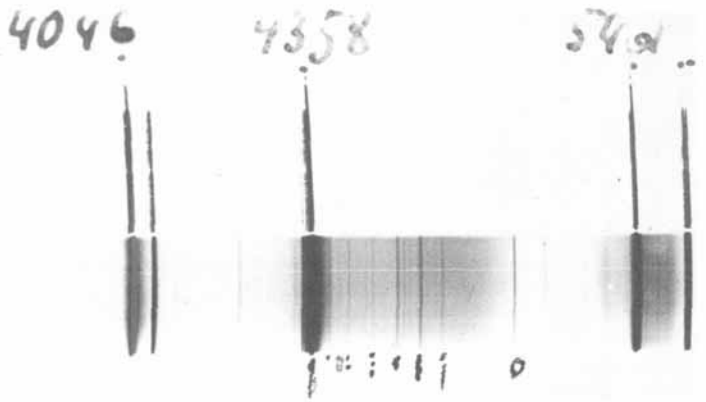


Figure 48. Raman spectrum of chlorobenzene, taken by A. Langseth on 13 February 1929.

molecular energy levels, measured the degree of polarization of the scattered light and deduced symmetry properties. He also used the technique of substituting deuterium for hydrogen in molecules, to assist in the interpretation of their Raman spectra. He developed a method for the calculation of intramolecular forces from Raman spectra, and employed the Raman effect for the analysis of kinetics of chemical reactions. Trumpy also made a number of studies of Rayleigh scattering.

Bjorn Trumpy was born in Bergen, Norway in 1904. His research in physics was mainly carried out at the Technical University in Trondheim and at the University in Bergen, and consisted of numerous experimental studies in atomic and molecular physics, cosmic radiation and nuclear physics. During the years 1925–30 he made extensive studies of the shape and width of spectral lines. In 1928 and 1930 Trumpy stayed for periods at the universities in Göttingen and Copenhagen, where he made further studies of atomic physics. With this background it was natural that the newly discovered Raman effect caught his interest.

Figure 49. Bjorn Trumpy.

Netherlands

Harm Gerding (figure 50) was one of the first to work on Raman spectroscopy in The Netherlands. His first paper was on sulphur trioxide in the liquid state, in solution in sulphur dioxide, and in the gaseous state (Das RAMAN-Spektrum des Schwefeltrioxyds. H. Gerding, W. J. Nijveld and G. J. Muller. *Zeitschrift für Physikalische Chemie*, **35,** 193, 1937).

Amongst the many other compounds he and his collaborators investigated over the years were many so-called addition compounds which were found to be ionic compounds involving cations like PCl_4^+, $SeCl_3^+$, $AsCl_4^+$, etc. often in combination with complex anions like $AsCl_6^-$, $SeCl_5^-$, PCl_6^-, etc. Other studies included the conformations of organic molecules.

Harm Gerding was born in Meppel, The Netherlands, in 1899. He studied at the University of Amsterdam where he subsequently joined the staff, progressing from

Figure 50. Harm Gerding.

'Privaat-docent' to Professor. He retired as Emeritus Professor in 1970. Amongst his many pupils was J. A. Koningstein, now Professor at Carleton University, Ottawa, Canada and Chairman of ICORS VII.

Bristol 1929

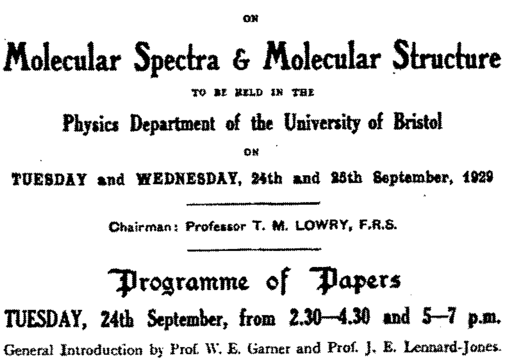
This General Discussion of the Faraday Society (figure 51) was held on 24 and 25 September 1929 in the Physics Department of the University of Bristol. The cost, including full board, was £1·25 for members and £1·50 for non-members! It was attended by many eminent spectroscopists. Raman presented a paper entitled 'Investigation of molecular structure by light scattering' (figure 52), to open the section devoted to the Raman effect; and other contributors to this section included J. Cabannes, R. W. Wood, P. Daure, A. C. Menzies and J. C. McLennan.

Dr G. Herzberg has provided the following reminiscences of this meeting:

> I met Raman for the first time in 1929 at the General Discussion of the Faraday Society on Molecular Spectra and Molecular Structure. It was a very memorable meeting largely because of the presence of Raman. For me it was the first time that I attended a meeting held in the English language. The first speaker was O. W. Richardson, who unfortunately mumbled and made it quite impossible for me to understand him. The second speaker was Raman. He spoke clearly and lucidly in beautiful English that even I could understand and his enthusiasm was certainly infectious. Just shortly preceding this meeting Heitler and I had discussed the importance of Rasetti's result about the intensity alternation in the Raman spectrum of nitrogen for nuclear theory and Raman showed considerable interest in and understanding of our result.

Dr A. C. Menzies has recalled that Raman, during his stay in Bristol, regularly enquired of the hotel porter if there was a cable for him from Stockholm! In fact Raman had to wait until 1930 for his Nobel Prize.

Amongst the younger contributors to this Meeting was Menzies' first research student, C. P. Snow (figures 53 and 54), who later acquired considerable distinction as a novelist. His 'Lewis Elliot' sequence of novels published over the period 1940–1960



The Faraday Society

A GENERAL DISCUSSION

ON

Molecular Spectra & Molecular Structure

TO BE HELD IN THE

Physics Department of the University of Bristol

ON

TUESDAY and WEDNESDAY, 24th and 25th September, 1929

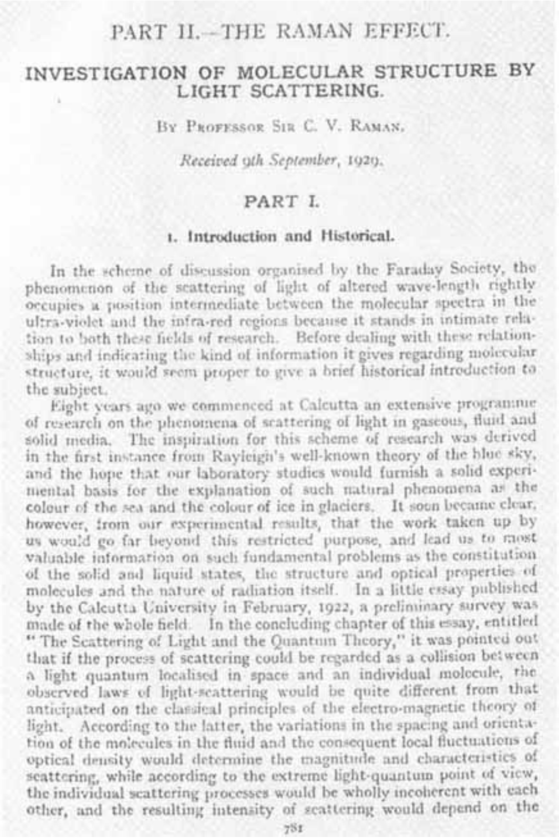
Chairman: Professor T. M. LOWRY, F.R.S.

Programme of Papers

TUESDAY, 24th September, from 2.30—4.30 and 5—7 p.m.

General Introduction by Prof. W. E. Garner and Prof. J. E. Lennard-Jones.

Figure 51.



PART II.—THE RAMAN EFFECT.

INVESTIGATION OF MOLECULAR STRUCTURE BY LIGHT SCATTERING.

BY PROFESSOR SIR C. V. RAMAN.

Received 9th September, 1929.

PART I.

1. Introduction and Historical.

In the scheme of discussion organised by the Faraday Society, the phenomenon of the scattering of light of altered wave-length rightly occupies a position intermediate between the molecular spectra in the ultra-violet and the infra-red regions because it stands in intimate relation to both these fields of research. Before dealing with these relationships and indicating the kind of information it gives regarding molecular structure, it would seem proper to give a brief historical introduction to the subject.

Eight years ago we commenced at Calcutta an extensive programme of research on the phenomena of scattering of light in gaseous, fluid and solid media. The inspiration for this scheme of research was derived in the first instance from Rayleigh's well-known theory of the blue sky, and the hope that our laboratory studies would furnish a solid experimental basis for the explanation of such natural phenomena as the colour of the sea and the colour of ice in glaciers. It soon became clear, however, from our experimental results, that the work taken up by us would go far beyond this restricted purpose, and lead us to most valuable information on such fundamental problems as the constitution of the solid and liquid states, the structure and optical properties of molecules and the nature of radiation itself. In a little essay published by the Calcutta University in February, 1922, a preliminary survey was made of the whole field. In the concluding chapter of this essay, entitled " The Scattering of Light and the Quantum Theory," it was pointed out that if the process of scattering could be regarded as a collision between a light quantum localised in space and an individual molecule, the observed laws of light-scattering would be quite different from that anticipated on the classical principles of the electro-magnetic theory of light. According to the latter, the variations in the spacing and orientation of the molecules in the fluid and the consequent local fluctuations of optical density would determine the magnitude and characteristics of scattering, while according to the extreme light-quantum point of view, the individual scattering processes would be wholly incoherent with each other, and the resulting intensity of scattering would depend on the

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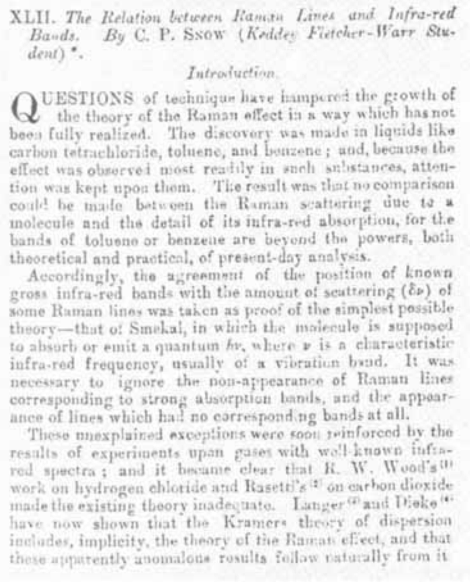
Figure 52.

Figure 53. C. P. Snow as a young Fellow of Christ's College, Cambridge.



XLII. *The Relation between Raman Lines and Infra-red Bands.* *By* C. P. SNOW (*Keddey Fletcher-Warr Student*) *.

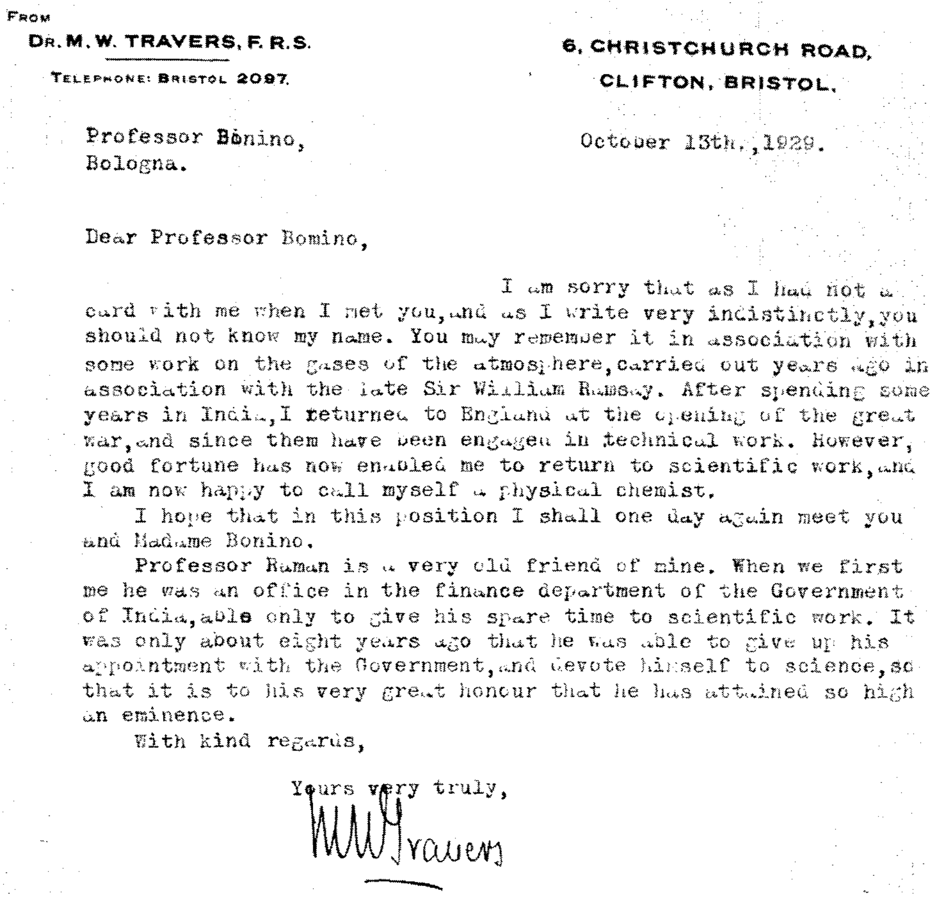
Introduction.

QUESTIONS of technique have hampered the growth of the theory of the Raman effect in a way which has not been fully realized. The discovery was made in liquids like carbon tetrachloride, toluene, and benzene; and, because the effect was observed most readily in such substances, attention was kept upon them. The result was that no comparison could be made between the Raman scattering due to a molecule and the detail of its infra-red absorption, for the bands of toluene or benzene are beyond the powers, both theoretical and practical, of present-day analysis.

Accordingly, the agreement of the position of known gross infra-red bands with the amount of scattering ($\delta\nu$) of some Raman lines was taken as proof of the simplest possible theory—that of Smekal, in which the molecule is supposed to absorb or emit a quantum $h\nu$, where ν is a characteristic infra-red frequency, usually of a vibration band. It was necessary to ignore the non-appearance of Raman lines corresponding to strong absorption bands, and the appearance of lines which had no corresponding bands at all.

These unexplained exceptions were soon reinforced by the results of experiments upon gases with well-known infra-red spectra; and it became clear that R. W. Wood's(1) work on hydrogen chloride and Rasetti's(2) on carbon dioxide made the existing theory inadequate. Langer(3) and Dieke(4) have now shown that the Kramers theory of dispersion includes, implicity, the theory of the Raman effect, and that these apparently anomalous results follow naturally from it

Figure 54.



FROM
DR. M. W. TRAVERS, F. R. S.
TELEPHONE: BRISTOL 2097.

6, CHRISTCHURCH ROAD,
CLIFTON, BRISTOL,

Professor Bonino,
Bologna.

October 13th.,1929.

Dear Professor Bomino,

I am sorry that as I had not a card with me when I met you,and as I write very indistinctly,you should not know my name. You may remember it in association with some work on the gases of the atmosphere,carried out years ago in association with the late Sir William Ramsay. After spending some years in India,I returned to England at the opening of the great war,and since them have been engaged in technical work. However, good fortune has now enabled me to return to scientific work,and I am now happy to call myself a physical chemist.

I hope that in this position I shall one day again meet you and Madame Bonino.

Professor Raman is a very old friend of mine. When we first me he was an office in the finance department of the Government of India,able only to give his spare time to scientific work. It was only about eight years ago that he was able to give up his appointment with the Government,and devote himself to science,so that it is to his very great honour that he has attained so high an eminence.

With kind regards,

Yours very truly,

MWTravers

Figure 55.

concerned with science and scientists is particularly well-known. It is perhaps not surprising that his scientific papers are particularly well written!

The Faraday Society is now the Faraday Division of the Royal Society of Chemistry. The Faraday Discussions are still a regular and valued feature of the Society's scientific programme. The present President of the Faraday Division is A. D. Buckingham, who was a member of the Executive Committee of ICORS XI.

As is usual with International Conferences, the Faraday Discussion Meeting at Bristol led to new friendships as illustrated by the letter from M. W. Travers to G. B. Bonino reproduced here (figure 55).

Conclusion

The Raman effect continued to justify its early promise. In the first decade after its discovery nearly 2000 papers on the Raman effect were published and the Raman spectra of more than 2500 compounds reported.

The advent of the laser in the early 1960s not only revolutionized the practice of linear Raman spectroscopy but also led to the discovery of a variety of non-linear Raman effects which have been much investigated.

By the end of 1978, the 50th anniversary of Raman's discovery, nearly 24 000 original papers dealing with the various kinds of Raman effect had been published; for the year 1987 *Chemical Abstracts* listed over 2700 papers relating to Raman spectroscopy; and some 500 original papers were presented at the XIth International Conference on Raman Spectroscopy held in London in September 1988 (*Eleventh International Conference on Raman Spectroscopy*, editors R. J. H. Clark and D. A. Long, John Wiley and Sons, Chichester, 1988).

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Permission to reproduce copyright material has been kindly granted by Dover Publications Inc., New York (figure 20), the Governing Body of Jesus College, Oxford (figure 24), Aster Publishing Corporation, Oregon (Dadieu diary quotation on p. 333 from JONES, R. N., 1987, *European Spectroscopy News*, **72,** 10), Mr Philip Snow (figure 53), the Indian Academy of Sciences (Krishnan diary quotation on pp. 321 and 322 from VENKATARAMAN, G., *Journey into Light, Life and Science of C. V. Raman*) and Lady W. Harrod (figure 23 from HARROD, R., *The Prof*).

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