

REMINISCENCES RELATING TO THE DISCOVERY OF THE RAMAN EFFECT

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WHEN the discovery of Raman Effect was published in the *Indian Journal of Physics* in March 1928, I was learning spectroscopy at King's College, London, in Prof. O. W. Richardson's Laboratory with R. C. Johnson. In those days, news took a long time to travel from place to place. There was no Airmail Service and a full fortnight was needed for the mail from India to reach London.

The discovery did not evoke much interest, nor did it make any impression when the news of it came to be known in London. It was casually dismissed as a possible fluorescence phenomenon. This was partly due to the fact that very few people were actively working in London on problems of light scattering; also the way in which it was attempted to prove that it was a universal effect, did not carry much conviction that it was a fundamental discovery, to those who were working in other fields of physics or chemistry.

In November 1928, S. Ramachandra Rao, who had previously worked in Raman's Laboratory at Calcutta, joined us. He joined Richardson's group, and worked on critical potentials of single crystal metals by the electron impact method. From him we gathered some more details of how the phenomenon had really been observed for a number of years and how the effect finally came to be published only after the discovery of Compton Effect. Later I. Ramakrishna Rao, who held a doctorate from Calcutta University and who was also from Raman's Laboratory, came to London. He was interested at that time in investigating the phenomenon of progressive dissociation with dilution of strong electrolytes in solution by Raman Effect techniques.

The reason why serious attention was not paid to the numerous Indian publications, dealing with the effect was perhaps that these concerned with large molecules like benzene, chloroform, glycerine, carbon tetrachloride, etc., in the liquid state. Molecular spectroscopy was just taking shape then. The first and the only report on the subject 'Molecular Spectra on Gases' was published by NRC of USA as its Bulletin, Vol. II, Part 3, No. 57 in December 1926. Beyond a few simple diatomic and triatomic molecules, we had no information of the vibrations or rotations of such large molecules. The technique of infrared spectroscopy which held the key to vibration and rotation frequencies of molecules was laborious and difficult. There were not more than four or five laboratories and the world, engaged in infrared spectroscopy and the few that were working in the field were not interested in large molecules. Scattered radiation from large molecules in the liquid state on the other hand contained, apart from the exciting line, several new lines which were different for different liquids. This proved beyond doubt that the molecules exhibit characteristic scattering; but because of the lack of information of the vibration frequencies of such molecules, it was not possible to prove convincingly what information the Effect actually provided in terms of properties of molecules.

It was towards the end of 1928 that matters became clearer. Wood, Rasetti and McLennan were among the first to select simple diatomic molecules whose frequencies of vibration and rotation could just then be established spectroscopically and they were able to show that the Raman displacements actually represent the vibration or rotation frequencies of the molecules concerned. McLennan for example,

wanting to see if the Raman Effect could be observed with homopolar molecules was able to prove that the Raman displacements which he observed in liquid oxygen and nitrogen, using for excitation, the Hg lines 4046.6 and 4358 Å coincided with the 'primary' and 'two-quantum' vibration states of the two molecules as calculated from Band electronic spectral data (Table I).

TABLE I

	Observed cm ⁻¹	Calculated cm ⁻¹
Oxygen	1551.5 3049	1554 Primary vibration 3085 Two quantum vibration
Nitrogen	2328.5 4632	2331 Primary vibration 4633 Two quantum vibration

Using the same lines for excitation in liquid hydrogen, McLennan observed Raman displacements of 354, 588 and 4149 cm⁻¹. He showed that the first two displacements corresponded to the 0 → 2 and 1 → 3 rotational transitions in the zero vibrational state, and the third to the 0 → 1 vibrational transition, his calculated values being 347, 578 and 4159 cm⁻¹ respectively. At that time it was known that homopolar molecules did not absorb in the infrared so that the vibration and rotation frequencies of oxygen, nitrogen and hydrogen had to be indirectly derived from their electronic spectra which were better known for oxygen and nitrogen than for hydrogen. The case of the hydrogen molecule was different. Its spectrum was styled as the secondary or many-line spectrum, as opposed to the primary or visible line-spectrum, consisting of the well-known Balmer lines of

the hydrogen atom. The many-line spectrum was so unlike, the band spectra due to molecules that it took some time to believe that in spite of its structure, the secondary or many-line spectrum of hydrogen is really due to the diatomic nature of hydrogen molecule. Lack of accurate wavelengths of these enormous number of lines added to the difficulty of analysis. Richardson was one of the early workers on this spectrum. Progress was very slow until Gale Monk and Lee published in 1928, their exhaustive measurements of the entire many-line spectrum in the visible and ultra-violet regions, obtained under high resolution and dispersion. Since then, though the analysis of the H₂ spectrum proceeded rapidly, yet much of the data were contained mostly in original papers. McLennan could correctly calculate the required rotation and vibration frequencies of H₂ from available data.

Similarly Wood, due to whom were several improvements in the technique, investigated the Raman Effect in HCl gas in collaboration with Dieke and showed that the Raman displacement actually represented the fundamental vibration frequency of HCl. His value 2886.0 cm⁻¹ coincided with 2885.9, a value well established by its infrared spectrum for this frequency and left no doubt as to its origin. Wood, like McLennan, used mercury arc lines in the visible region for excitation.

Then came the still more valuable experiments of Rasetti. It was he who for the first time employed the resonance line 2537 Å of Hg for excitation. In the scattered beam this radiation was absorbed by a column of cold Hg vapour, so that the masking of the Raman lines by the over-exposed intense resonance line of Hg used as the exciting line, was considerably reduced and allowed investigation of small displacements characteristic of rotation frequencies. This method was usefully employed later by R. S. Krishnan in his studies on the Raman Effect in Crystals.

Rasetti obtained rotation Raman spectra of NO, O₂, and N₂ in the gaseous state. The oxygen spectrum showed that alternate lines are absent. This conclusively proved that the ¹⁶O molecule has zero spin. In the case of N₂, all the lines were present but their intensities were alternating, the even rotational lines being stronger than the odd ones. This led to the fundamental discovery that the nucleus of nitrogen obeys Bose-Einstein statistics and must have an even number of particles. Incidentally, Rasetti's Raman spectrum of NO also contained a line of displacement 120 cm⁻¹ which is the doublet separation in the ground state of the molecule. It was till recently, one of the very few examples of an electronic Raman Effect.

McLennan's work in liquid H₂, O₂, N₂ and the work of Rasetti on gaseous O₂ and N₂ brought to light, several important facts regarding the principles governing Raman Effect. They showed that Raman spectra gave information regarding the vibration and rotation frequencies of homonuclear molecules which infrared or microwave spectra could not give. This was very important because in the absence of this method the molecular constants of homonuclear species relating to vibration and rotation could only be indirectly derived from their electronic spectra. They also showed that the vibration frequencies of molecules which, in general lie in the infrared region, could be investigated in the more convenient visible region. Very little work on infrared spectra of molecules and their interpretation was available due to the experimental difficulties and the absence of any fairly well-established theory. Raman Effect was thus discovered at a time when spectroscopists were in need of a convenient method which would enable the vibration and rotation frequencies of molecules to be determined in the more convenient visible region. This became possible by studies on Raman Effect, using the Hg arc lines for excitation,

In addition to these advantages and gains of Raman Effect to spectroscopic methods, the following important discoveries due to Raman Effect were fundamental to the progress of Physics and Chemistry.

1. The absence of alternate lines in the Raman spectrum of O₂ proved that the nuclear spin of ¹⁶O is zero.

2. Even rotational lines are stronger than odd rotational lines in the rotational spectrum of N₂ which therefore proved that the nitrogen nucleus was governed by Bose-Einstein statistics, and not by Fermi Dirac statistics, as till then believed, and contained not an odd but even number of particles. This and the discovery of neutron led to a revision of the theory of nuclear structure. Both these results followed from the experiments of Rasetti.

3. Another important contribution resulting from McLennan's work on the Raman Effect in liquid hydrogen was equally fundamental. Dennison in his work on the specific heat of hydrogen at low temperatures found indirect evidence that molecular hydrogen at low temperatures consisted of two effectively distinct species now known as the ortho and para forms. McLennan's work gave direct experimental evidence for the correctness of Dennison's view. Incidentally McLennan's work on liquid O₂ and H₂ showed that quantised rotation of these molecules took place even in the liquid state.

Essentially, it is these discoveries which proved the fundamental nature of Raman Effect worthy of the much covered Nobel Prize which was consequently awarded in 1930. I think I have said enough to bring home the importance of the Raman Effect as a special, convenient and valuable tool to investigations of molecular spectra and structure, and, that its utility can never be overestimated.

I shall not deal with the later impact of the discovery on the development of the theory of vibration-rotation and rotation

spectra of molecules and their structure, nor is this the place to dwell upon the more recent developments consequent on the use of highly coherent monochromatic, intense radiations afforded by lasers for excitation of Raman spectra.* But I must mention one event, for which the very contribution of the initial fundamental discoveries may be deemed responsible. The new knowledge that the nuclei of nitrogen obey Bose-Einstein statistics and have even number of particles stimulated the search for new particles in the nuclei leading to the discovery of the neutron and other nuclear particles. These and the discoveries of deuterium and a host of isotopes of carbon, oxygen, nitrogen, etc., by molecular spectroscopy diverted the interest of physicists to the infant branch of nuclear physics, leaving the yet unexplored region of extra-nuclear physics, to less than a handful of physicists. Chemists and the physicists still in the line, on the other hand, utilised the opportunity and collected a vast amount of knowledge regarding the vibration frequencies of typical molecules and the laws governing different types of spectra using both Raman and infrared techniques, which had even considerably improved in course of time. Unfortunately, this led some to believe wrongly that spectroscopy was a chemist's job. The fact that the progress thus achieved in our knowledge of the spectra and the structure of molecules brought several disciplines together, seems to have escaped the attention of several scientists.

* See article by R. S. Krishnan in this number p. 196.

I suppose it will not be out of place if I make some remarks on the aftermath of Raman's discovery. There were some scientists who suggested that the Effect had already been predicted earlier by Smekal and by the quantum theory of dispersion by Kramers and Heissenberg. Then there was also the experiment of Landsberg and Mandelstam which dealt with a similar anomalous scattering in crystals. This work, apart from the fact that it was not the same as Raman's discovery, could not even claim priority as it was published three months after Raman's paper.

In 1931 J. Springer the well-known publishing company of treatises and the advanced Research topics in the physical sciences, published a book by K. W. F. Kohlrausch entitled "Der Smekal-Raman Effect". Unfortunately all this upset Raman very much. There is however little doubt in my mind that a certain amount of prejudice did exist. The second edition of Kohlrausch's book appeared again under the same title in 1938, although the entire scientific community was unanimous in calling the discovery just the Raman Effect.

When the 1928 Nobel Prize was awarded to Richardson, it was expected by several scientists that the 1929 prize would probably be awarded to Raman. Instead, it was de Broglie who got it. Raman had to wait till 1930 to get his. In my view the delay in recognition of Raman's work was not so much due to the scientific conservatism (as is usually thought) as to the fact that the fundamental importance of the Effect was appreciated fully only after the experiments of Wood, Rasetti and McLennan.