

LASER RAMAN SPECTROSCOPY OF ORGANIC COMPOUNDS

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THE weakness of the Raman scattering and the experimental difficulties in obtaining good Raman spectra had, in the past, prevented extensive application of Raman spectroscopy in the study of organic compounds although its potentialities are at least as great as those of IR spectroscopy. The advent of continuous wave gas lasers in recent years has brought about a radical change in this situation. The difficulties and inadequacies of earlier experimental techniques have now been overcome and a great spurt of activity in the applications of Raman spectroscopy may be expected in the near future.

As compared with IR, Raman spectroscopy has a number of advantages. Glass cells and aqueous solutions may be employed. Solids may be studied directly without mulling. Unlike in IR spectroscopy, it is possible to make suitable choice of incident radiation so that the scattered radiation falls in a region which is readily observable. Moreover, depolarization measurements give additional information. However, in actual practice, it has not been possible to avail of these advantages because of the low intensity of Raman lines. In conventional Raman spectroscopy, the intense blue line of the mercury arc is generally used as the exciting radiation. As a consequence, observation of spectra is often rendered difficult by fluorescence and photo-decomposition. The photographic method has been the most widely employed for recording spectra, and with the prolonged exposures that are generally required, the large intensity of the central part of the scattered radiation, representing Rayleigh scattering, tends to smudge out Raman lines in the neighbourhood because of scattering from the photographic plate. Very often these lines are of considerable interest. For materials which absorb over very wide ranges, it is practically impossible to obtain Raman spectra in the conventional manner. These difficulties have now been overcome with the extremely high intensities obtained in laser beams. Laser beams are readily focussed on to small samples. There is no difficulty any more in recording small Raman shifts. It is now possible to study Raman spectra of even materials like graphite. Also, the line widths ob-

tainable with lasers are about an order of magnitude smaller than for the mercury line. Spectra of very high resolution can, therefore, be obtained. A number of laser Raman spectrometers have been marketed by instrument manufacturers (Cary, Perkin-Elmer, etc.).

This revolution in instrumental technique has not yet affected organic chemistry in a big way. Nevertheless, some interesting laser Raman studies have appeared. Several unsaturated acyclic monoterpenes have been investigated and Raman intensities and depolarization ratios of C=C stretching vibrations have been discussed in terms of structural features.¹ It has been shown that 4-methyl-isochroman exhibits two conformations in the liquid state while only one is shown in the solid state.² It has been recognised³ that Raman scattering of steroid derivatives is dominated by skeletal vibrations involving carbon-carbon bonds, and it has been found that polar functional groups of these molecules scatter relatively poorly. If substituent effects on the skeletal modes are small and they are analyzable as electronic and mass effects then Raman spectral data may be empirically used for recognition of ring systems. Exploratory work done in this context has already yielded useful results. Examination of a series of cedranes has shown that a set of five intense Raman bands between 500 and 900 cm^{-1} is characteristic of the cedrane skeleton.⁴ Similarly, a set of seven Raman bands in the region 350 to 1100 cm^{-1} has been found to characterise a pinane ring system.⁵ It has been shown⁶ from laser Raman study of the longitudinal accordion motion in polymethylene liquids that the abundance of *trans* conformation falls as chain length increases. The abundance is vanishingly small for $n \geq 9$. A temperature study of laser Raman effect on chlorocyclopentane has shown that the barrier to pseudo-rotation in the system is at least an order of magnitude higher than previous estimates.⁷ Laser Raman studies on polymers have also appeared.⁸

More active pursuit of applications of laser Raman spectroscopy in the study of structure and conformation of organic molecules may be expected very soon. Effort in this area is apparently limited at present by poor access

to instruments. But this situation is bound to change with time.

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STUDIES OF THE STRUCTURE AND PROPERTIES OF DIAMOND

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SIR C. V. RAMAN's interest in the beauty of the diamond and its remarkable structure and properties was a life-long involvement although in later years it was overshadowed by his love of flowers and his search for an explanation of the origin of their colours and an understanding of the physiology of vision. "Opportunities for observing the luminescence of diamond in an impressive fashion first presented themselves.....in the year 1930 in connection with spectroscopic studies on the scattering of light in crystals.....It was then found that the luminescence spectrum of diamond recorded itself on the spectrograms simultaneously with the scattering of light in the crystal, its leading feature being a band at 4155 Å.U. and its intensity varying enormously from specimen to specimen.....The difficulty of obtaining suitable material discouraged the pursuit of the subject" (Raman, 1944). Later on, noting that "cleavage plates of diamonds of excellent quality and good size could be obtained at very modest prices and that diamond in this form was more suitable for physical investigations than the high-priced brilliants of the jeweller's trade" Sir C. V. Raman acquired a few specimens, which led to a very fruitful series of investigations on the scattering and absorption of light in diamond and its photoluminescence at various temperatures by Dr. P. G. N. Nayar (1941, 1942).

The researches of Dr. Nayar in 1941 and 1942 on the luminescence and absorption spectra of diamonds demonstrated the existence of many more vibrations of the diamond structure with discrete frequencies than the single line with a frequency shift of 1332 cm^{-1} which appears in the Raman spectrum of diamond (Ramaswami, 1930; Bhagavantam, 1930). The main results of the early investigations were

summarised by Sir C. V. Raman in his Presidential Address to the Eighth Annual Meeting of the Indian Academy of Sciences at Bangalore in 1942 and published as a supplement to *Current Science* in January 1943.

In 1942, Sir C. V. Raman purchased a representative collection of diamonds mined in Panna in Central India and enlarged his collection of polished cleavage plates. The diamonds in his personal collection in 1944 numbered 310, consisting of crystals in their natural condition, polished cleavage plates and cut brilliants of both Indian and South African origin, a unique collection, probably unparalleled anywhere in a scientist's laboratory or museum. Then followed a period of intense activity when almost every student in the Physics Department was working on one aspect or other of the properties of diamond and two symposia on the structure and properties of diamond were published; again unequalled in the scope and range of the aspects studied and the results obtained.

The first symposium on diamond published in 1944 consisted of 17 papers. The first two papers on the crystal symmetry and structure of diamond, and the nature and origin of the luminescence of diamond were by Sir C. V. Raman himself. These were followed by 15 papers by his associates and pupils on the Raman spectrum of diamond, the fluorescence and absorption spectra of diamond in the visible region, the ultraviolet absorption spectrum of diamond, luminescence and birefringent patterns in diamond, the intensity of X-ray reflection by diamond, X-ray topographs of diamond, X-ray reflection and the structure of diamond, ultraviolet transparency patterns in diamond, the lattice spectrum and specific heat of diamond, the magnetic susceptibility of