# The Raman Effect.

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### Introductory.

IT is now just two years since the effect known by his name was discovered by Sir Chandrasakara Raman,[1] but the phenomenon has aroused so much interest that even in this short time a tremendous amount of work has been done. A summary, therefore, at this stage may serve a useful purpose.

In brief, the effect may be thus described : When a beam of monochromatic light is directed into some transparent substance, some of the light is scattered, and this light has the same frequency as the incident light (unmodified scattering). In addition, a much smaller quantity of the light suffers a change of frequency, usually a diminution (modified scattering), and it is this which constitutes the Raman effect. The magnitude of the change is found to depend upon the nature of the scattering material and is independent of the frequency of the incident light. In general each exciting line evokes several modified lines, some of which may be plane polarised.

On account of their superficial resemblance, it would be well to make clear the respects in which this effect differs from fluorescence.

(a) In fluorescence, the frequencies of the fluorescent spectrum are independent of those of the exciting radiation, provided the latter are able to excite fluorescence at all. On the other hand, the frequencies of the radiations modified by Raman scattering are directly related to the incident frequencies $\nu_i$, being ($\nu_i \pm \nu_R$). These shifts, $\nu_R$, are either actual infra-red frequencies in the absorption spectrum of the scattering material, or differences in such frequencies.[2,3] For example, measuring wave numbers in cm.$^{-1}$, the frequencies 27354, 27290, 24704, and 22939 emitted by a mercury vapour lamp are scattered by benzene molecules and give rise to the Raman lines (among others) 24294, 24231, 21646, and 19877 respectively. These, it will be seen, are lines shifted to the red by an amount 3060 cm.$^{-1}$ approximately, and correspond to an infra-red wave-length $3.27 \mu$, while the infra-red absorption spectrum of benzene includes a strong band at $3.25 \mu$.

(b) The intensities of the Raman lines are of a different order of magnitude.

(c) Many of the Raman lines are strongly polarised.

### Technique.

The first observations were made with complementary light filters, but this was abandoned in favour of spectroscopic methods. The light from a mercury vapour lamp is directed by a large condensing lens into a flask and the light scattered at right-angles is focused on to the slit of a spectrograph (flask method). This has been modified by R. W. Wood,[4] who uses a long tube, water-cooled, placed parallel to a long tubular mercury arc and almost touching it. Observation is made axially along the tube, and portions of the spectrum of the incident light may be filtered out by the addition of suitable colouring matter to the cooling water (tube method).

As a source for Raman scattering experiments, the mercury vapour lamp has the disadvantage that it cannot be arranged to give really monochromatic radiation. For this reason, helium excitation is sometimes used,[5] since the strong line λ3888 A.U. can be isolated by ultra-violet glass and the results are then unambiguous.

Although most observations have been made in the visible region, the ultra-violet region has been used as well, entailing the use of quartz throughout. This region has the advantage that the Raman lines are considerably stronger. It must be borne in mind, however, that chemical action may easily be induced by the use of such short-wave exciting light, and the experiment thereby vitiated.

When gases are to be investigated, the tube method is used, and the exposure may be shortened by having the gas under pressure.

In the case of solids, a block is treated as in the flask method. Recently, it has been shown by me[6] and independently by Bär[7] that the Raman spectra of solids in powder form may be obtained, since the incident radiation is much weakened by repeated reflections. Thus the field for investigation is considerably greater, since only a few solids are obtainable in large pieces.

### Width of Lines.

The scattered lines differ greatly in respect of width.[8,9] When scattered by crystals, the lines are particularly sharp, less sharp for amorphous solids, and some lines scattered from liquids are more diffuse still. The change in sharpness in the transition from solid to liquid is well shown in the liquefaction of ice.[10] In this case the lines become much broader when the ice melts, but with little alteration of frequency. This, as pointed out by C. P. Snow (private communication), means that ice is a molecular lattice and not an ionic one. In some liquids the lines are very sharp indeed, but quite frequently a continuous spectrum[11] is obtained, especially in very viscous liquids. The unmodified lines are often diffusely broadened ; this is perhaps to be accounted for as a Raman scattering where the incident radiation has been modified by the abstraction of energy required to produce changes in the rotational frequencies of the molecules.[12]

### Intensities.

If corresponding Raman lines (that is, lines having the same frequency shift from the different exciting lines) be considered, the intensity is augmented considerably as the frequency of the exciting line is increased. It does not, however, follow the fourth power law.[13] The Stokes lines (shifts to the red) are very much more intense than the corresponding anti-Stokes lines.[14,15] The ratio of the intensities of corresponding Stokes and

anti-Stokes lines has provided an interesting criterion for the quantum theory of dispersion. Schrödinger's original dispersion theory implies an intensity-ratio equal to one.[16] Statistical mechanics, however, yields intensity-ratios in accordance with those observed.[17, 18]

### EFFECT OF TEMPERATURE.

Intimately connected with the consideration of the intensity-ratio just mentioned is the effect of change of temperature. Whatever the true explanation of the Raman effect may be, jumps between quantised states must be involved and intensities will be affected by the molecular populations of these states. So increase of temperature, which favours an increase in population in the higher states, is bound to augment the intensities of the anti-Stokes lines, and this is found to occur.[19] In quartz, for example, a particular Stokes line has an intensity about two-fifths of that of the corresponding unmodified line. As the temperature is increased, the unmodified line increases in intensity, the anti-Stokes line increases more rapidly and the Stokes line decreases slightly in intensity.[20, 21] At the same time, the lines become more diffuse; this has been attributed to an increase in the molecular rotation.[22]

### CRITICAL STATE.

Ordinary unmodified scattering increases very considerably in intensity as the critical state is approached, but there is little corresponding increase in the intensity of the modified radiations. This is taken as a proof that the modified radiations are incoherent.[23, 24]

### POLARISATION.

In scattering by liquids, the modified lines may be plane polarised parallel to the direction of polarisation of the unmodified lines, partially polarised in this direction, or unpolarised.[1, 25] In scattering by solids, it is possible in addition for modified lines to be plane polarised in a direction perpendicular to that of the unmodified lines. This has been shown to occur in quartz, and is related to the direction of the optic axis with regard to the directions of the incident and scattered beams. A new orientation of the crystal produces a change in the direction of the plane of polarisation for some of the lines, but not for others.[26, 27]

### SCATTERING IN GASES.

It has been suggested that many of the weak lines listed in spectrum tables may be Raman lines excited by strong lines of the element involved. For example, H. S. Allen suggests that some of the secondary lines of hydrogen may be Raman lines excited in the molecules by Balmer lines.[28]

Hydrogen chloride gas gives a sharp Raman line corresponding to the 'missing' line in its absorption spectrum, together with some lines corresponding to molecular rotations.[29] It is interesting that the changes in the rotational quantum number $m$ for the Raman spectrum of HCl gas are given by

$$\Delta m = 0 \text{ or } \pm 2,$$

while in the infra-red absorption spectrum they are given by

$$\Delta m = \pm 1.$$

This fits in with the 'three-level' theory discussed later.

Carbon monoxide gives a line corresponding to the infra-red absorption band, while carbon dioxide gives two lines which correspond to the *differences* in frequency of the components of the doublet infra-red absorption bands.[2]

Oxygen, hydrogen, and nitrogen scatter the exciting line with several equally spaced lines on either side; these are found to be due to changes in molecular rotational energy, with alternate rotational levels missing or relatively weak. In oxygen the lines are due to transitions between odd levels only; in hydrogen the lines due to transitions between odd levels are strong, while those between even levels are weak; and in nitrogen the intensities are reversed.[30] The difference between the three gases in this respect may be made clearer by the use of heavier type to indicate larger intensities:

| | | |
|---|---|---|
| Oxygen | **odd** | |
| Hydrogen | **odd** | even |
| Nitrogen | odd | **even** |

It is remarkable that in this respect nitrogen should be unlike hydrogen, for from the point of view of nuclear states one would expect them to be similar.

In nitrogen monoxide a Raman line has been photographed corresponding to a change in the direction of electronic spin.[31]

Oxygen, hydrogen, and nitrogen were first examined in the liquid state,[32] and in the case of hydrogen two-quantum transitions in the molecular rotation were observed, and a one-quantum vibrational transition. The rotational transitions are $0 \longrightarrow 2$ and $1 \longrightarrow 3$, the molecules being in the zero vibrational state. This is evidence of the existence of both the $a$- and $\beta$-forms in liquid hydrogen.

### SCATTERING IN LIQUIDS.

The effect was first discovered with liquids, and it is with the scattering material in this state that most of the work has been done. With the exception of the work on liquefied gases just mentioned, the results obtained with liquids have been important more with regard to the infra-red spectra and chemical constitution of the material than to the elucidation of the effect itself. It would be impossible here to refer to many of the papers dealing with liquids; a comprehensive memoir has lately been published by Ganesan and Venkateswaran.[33]

As an example of the use of the effect for the study of chemical constitution we may consider the C-H bond. This bond is found to involve a Raman shift corresponding to 3·35 $\mu$ in tetrachlorethane for example, but when the carbon has a double bond, the C-H line is displaced towards the shorter wave-lengths, for example, 3·25 $\mu$ in trichlorethylene.[34, 35] In a similar way other Raman shifts are connected with chemical linkages. In

the instance just quoted, Raman effect measurements are supported by infra-red observations; unsupported evidence should be treated with caution, since Raman shifts correspond so frequently to the difference between frequencies rather than to the frequencies themselves.

Solutions of salts in water show Raman lines characteristic of the salts in addition to those due to the water. As an example of work on solutions may be quoted the recent interesting experiments of I. R. Rao with nitric acid at different concentrations.[36] Lines were found with the concentrated acid, due to the $NO_3$ ion, as well as lines attributed to $HNO_3$. On dilution, the $NO_3$ lines intensified up to a maximum and thereafter diminished in intensity, while the $HNO_3$ lines progressively grew weaker and faded out altogether. The dilution at which the $HNO_3$ lines disappeared was the same as that at which the intensity of the $NO_3$ lines was a maximum. Thus, literally an ocular demonstration is provided of the increase of ionisation in a solution when it is made more dilute.

### Scattering in Solids.

Quartz and iceland spar were investigated by Landsberg and Mandelstam,[37] who claim to have discovered the effect independently of Raman; one of the shifts found by them in Iceland spar corresponds to the optically inactive fundamental frequency of the $CO_3$ ion. Such inactive frequencies occur with great strength in the Raman effect in crystals; they may be observed easily using the crystals as a coarse powder, or in solution.

When water of crystallisation is present, the water Raman lines are found, and are considerably sharper than in water itself.

Raman lines corresponding to the residual ray frequency of rock-salt are *not* found, nor do the residual ray frequencies appear in the Raman effect investigation of lithium or sodium fluoride. Schaefer[38] suggests that the Raman effect implies an asymmetrical vibration, while the lattice vibration of NaCl is essentially a symmetrical vibration.

### Theory.

The original theory as put forward by Raman was that the modified lines were displaced by an energy amount equal to that required to raise a molecule from the normal state to some higher energy state. If this were so, all Raman lines would correspond to infra-red absorption lines, and this is certainly not the case. The modified lines are implicit in the Kramers-Heisenberg[39] dispersion formula, which was developed from the theory of Smekal.[40] The existence of the effect was nevertheless not sought for, and remained to be discovered quite independently.

The modified lines differ in frequency from the exciting lines by an amount equal to a difference in frequency between infra-red absorption lines. The absorption lines themselves may appear, but they are usually very weak. Three levels are involved in the production of a single Raman line, say $k$, $l$, and $n$. If transitions may take place be-

tween $k$ and $n$, and between $l$ and $n$, then a Raman line may be expected corresponding to the transition between $k$ and $l$, even though this may be a forbidden transition in the infra-red.[3, 41] Thus it is at once explained why Raman lines exist having no counterpart in the infra-red, and vice versa. As the energy of the exciting quantum approaches the value $(E_n - E_k)$, the Raman scattering becomes increasingly intense, and when it reaches it, fluorescence occurs.[42]

The theoretical explanation of the polarisation of the lines is not yet fully understood. Raman has sought to explain it in terms of the optical anisotropy of the molecule,[12] while I have endeavoured to picture it in terms of the energy transitions between directions of vibration which have different orientations in the molecule.[27]

### Future Progress.

Although a great deal has been done, much remains for investigation. The polarisations of the lines, the relative intensities of the Stokes and anti-Stokes lines, and the energy-levels of molecules deduced from the Raman effect observations combined with infra-red work, are a few of the lines of investigation which will provide work for many investigators. There is little doubt that when its usefulness is appreciated, it will be constantly employed by the research chemist.

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