M. N. SAHA, D. S. KOTHARI AND G. R. TOSHNIWAL

IN a paper published in 1923, Einstein and Ehrenfest discussed the general problem of thermodynamical equilibrium in an assembly traversed by light, which is subjected to scattering by the particles of the assembly. They deduced, in a way (which is quite analogous to Einstein's famous deduction of the laws of black body radiation by consideration of thermodynamical equilibrium in the presence of Bohr type of vibrators), that the excited particles of the system would give rise to a type of modified scattering analogous to Einstein's negative absorption. Smekal pointed out in a letter to *Naturwissenschaften* (1923) that if light of frequency $\nu$ is scattered by the particles of the assembly, then in addition to unmodified scattering of frequency $\nu$, scattered light should also consist of light of frequency $\nu + \nu_k$, $\nu - \nu_k$, where $h\nu_k$ is the energy difference between the excited state and the normal state of the scattering particles ("Handbuch der Physik," Bd. 23, pp. 93-99).

This last prediction has been very brilliantly confirmed by Raman and Krishnan, who exposed liquid benzene to the monochromatic mercury radiation $\lambda 4358$, and on examining the spectrum of the scattered light found modified scattered light of frequencies $\nu + \nu_k$ where $\nu_k$ is any one of the fundamental frequencies of liquid benzene. We wish to point out that Raman and Krishnan's experiment is not, strictly speaking, a confirmation of Einstein's negative or stimulated emission, as mentioned by these authors (NATURE, June 30, 1928), but of the analogous case of negatively modified scattering (that is, scattering of light of frequency $\nu + \nu_k$) discussed by Smekal.

We wish further to point out that the theory of modified scattering affords a very simple and convincing explanation of the phenomena of resonance spectra of vapours of sodium, potassium, and the halogens discovered and so elaborately described by R. W. Wood in his numerous papers. He found that when vapour of these substances is illuminated by monochromatic light (lithium, cadmium, bismuth, or zinc arc), then the vapour emits laterally a partially polarised spectrum consisting of the original line, and a number of fine lines spaced at equal frequency intervals (of about 145 in the case of Na). The position of these excited lines in the spectrum depends upon that of the exciting light, though the frequency interval between the exciting line and its adjacent excited light is independent

of the exciting frequency for the same substance. The remarkable fact is that there are also a number of lines on the shorter wavelength side of the exciting light, which have been styled by the German authors (Pringsheim and his students) the 'anti-Stokes' 'lines. These 'anti-Stokes' lines also show equal spacing, and they can be explained as being due to negatively modified scattering.

Pringsheim and his students have shown that the sodium vapour contains temporary $Na_2$ molecules and gives rise to banded spectra on excitation. One of the strongest vibration frequency intervals is $\triangle\nu = 145$, which may be identified with the frequency of one of the fundamental modes of vibration of the component atoms. So the explanation of Wood's resonance spectra becomes evident now. When the exciting light traverses $Na_2$ molecules, the light is scattered by them, the scattered light having the frequencies $\nu \pm \nu_k$ where $h\nu_k$ is the energy difference between any excited state and the normal state of the $Na_2$ molecule; the excitation not involving the electron displacement, but being due only to the vibration of the component atoms which are easily produced under moderate heating. The plus sign refers to the negatively modified scattered light and accounts for the anti-Stokes' lines. Similar explanations hold good for the resonance spectra of $K_2$ and the halogens. These substances alone have been shown to be capable of giving rise to resonance radiation, as the molecules can be easily excited to higher vibration frequencies. But it can presumably be proved to be a general phenomenon in the case of all molecules.

We wish further to point out that though the phenomenon has been described as one of 'scattering', it seems to be intermediate between pure scattering (as by fog-particles in which the agent responsible for scattering does suffer no physical change) and pure absorption (as, for example, the absorption of the sodium line by the sodium atom, resulting in the utilisation of the total energy of the energy-particle in lifting the electron to the higher orbit and production of a new system). This phenomenon is just intermediate between the two, as the incident light reacts on the particle, and robs it of its internal energy and is re-emitted as a new radiation of increased frequency.

It seems that the polarisation of the secondary rays is probably only a time effect, depending upon the intimacy

of the reactions taking place between the incident light and the scattering particle. Therefore in pure scattering, the scattered light should be completely polarised in pure absorption and in re-emission unpolarised; and in phenomena intermediate between these two it should be partially polarised, as has been proved by Wood.

The phenomena of negative scattering should also be capable of extension to free electrons, and will thus probably afford an easy explanation of the origin of bright and broad bands in the spectra of Novae, and of winged lines in the solar spectrum.

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# 46. ON THE METHOD OF HORIZONTAL COMPARISON IN THE LOCATION OF SPECTRA OF ELEMENTS

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For sometime past workers in spectroscopy in this laboratory are using a new principle in the location of spectra of elements, which, in the absence of a better name, may be styled the method of Horizontal Comparison. To explain the method, we start with Table I, where, in the first row, we have taken the successive elements, B, C, N, O, F, Ne, and Na (atomic numbers 5 to 11). The K- and $L_1$-rings of these elements are complete but the number of electrons in the $L_2$-orbit in the normal state varies from 1 to 6 from B up to Ne; in Na there is one more electron in $M_1$ besides the full quota of 6 in $L_2$. The optically excited states are obtained by allowing one electron to run through the higher orbits. If $x$ denotes the number of electrons in the $L_2$-orbit, the different optically excited states can be represented by

$xL_2M_1$, $xL_2M_2$, $xL_2M_3$, $xL_2M_1$, $xL_2M_2$, etc.

It is apparent that in the elements B to Na, $x$ varies from 1 to 6.

In the second row, we have put the elements $C^+$, $N^+$,....... $Mg^+$, and in the third row the elements $N^{++}$, $O^{++}$,...$Al^{++}$, so that elements in the same vertical column have the same electronic configurations, the nuclear charge increasing by one in each step.

### TABLE I

| x→ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|----|---|---|---|---|---|---|---|
| I | B | C | N | O | F | Ne | Na |
| II | $C^+$ | $N^+$ | $O^+$ | $F^+$ | $Ne^+$ | $Na^+$ | $Mg^+$ |
| III | $N^{++}$ | $O^{++}$ | $F^{++}$ | $Ne^{++}$ | $Na^{++}$ | $Mg^{++}$ | $Al^{++}$ |

The elements in the same vertical column, *e.g.*, C, $N^+$, $O^{++}$, follow the arithmetic progression law, when the transition is along the same horizontal level, that is, when the transition takes place between orbits having the same total quantum number, *e.g.*, $M_1 \leftarrow M_2$. Recently this case has been exhaustively discussed by Prof. M. N. Saha and Dr. P. K. Kichlu[1] who have shown the validity of the law to higher valence elements. The purpose of the present paper is to compare the corresponding lines of the elements in the same horizontal row in table I. We shall at present confine our attention to the transition $xL_2$ ($M_1 \leftarrow M_2$).

Owing to the variety of the electronic configurations of these elements, the nature of the lines involved is widely different. We shall, therefore, for the sake of simplicity, chose lines which arise from terms of the highest multiplicity. As for example, according to the Hund's theory, we expect the following terms in oxygen,—

$$3L^2M_1 \left\{ \begin{array}{llll} {}^5S & {}^3S & {}^3D & {}^3P \\ & {}^1D & {}^1P \end{array} \right.$$

$$3L_2M_2 \left\{ \begin{array}{llllllll} {}^5P & {}^3P & {}^3F & {}^3D & {}^3P & {}^3D & {}^3P & {}^3S \\ & {}^1F & {}^1D & {}^1P & {}^1D & {}^1P & {}^1S \end{array} \right.$$

which will give rise to a very large number of lines. As it is not possible to compare all the lines due to the above transition,—most of them have yet to be discovered,—we have taken only the quintet lines ${}^5S$—${}^5P$, which are also the strongest in the transition. In Chart I are collected the lines (of the highest multiplicity) of the corresponding elements given in Table I, due to the transition $M_1 \leftarrow M_2$. We have chosen from a multiplet only one line which has the average of the frequencies forming the multiplet. In the case where the average frequency does not much differ from the frequency of the strongest line in the multiplet, the latter frequency has been taken.

[1] Saha and Kichlu, *Ind. Jour. Phys.*, 2, (1928).