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The Polarisation of Resonance Radiation and the Duration of Excited State.[1]

By

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Introduction.

According to Bohr, the emission of radiation from an atom is preceded by the transference of an electron from its normal stationary orbit to an orbit of higher energy and the radiation takes place during the return of the electron to its normal orbit. From his correspondence principle, the polarisation and intensity of light of a definite frequency emitted during any transition process can be co-ordinated with the configuration of the orbits and the amplitudes of the appropriate components of vibration in different directions. In the case of resonance radiation, the exciting agency is the electric vector in the incident light-wave, and, if the incident light is plane-polarised, we may expect that when just excited, the component of vibration corresponding to the transition would be greatest in the direction of the electric vector in the incident light. The polarisation of the emitted radiation would depend on the orientation of the plane of motion of the electron at the time of its return to the original orbit. When secondary radiation can be neglected, the circumstances that might alter the orientation and form of the orbits are (1) Perturbations due to internal or external fields of force and (2) Collisions with other atoms or molecules. If by reason of one or more of these causes, the orientations of the electron orbits have been rendered random before the quantum-jump takes place, the radiation would be unpolarised.

[1] Read before the Indian Science Congress—January, 1924. Revised August, 1924.

Proc. Ind. Assn. Cult. Sci. 9, 93–102, 1925–26.

The recent experimental results of Professor R. W. Wood and Mr. A. Ellett[1] on the polarisation of the resonance radiation of the vapours of mercury and sodium in weak magnetic fields are of considerable interest in this connection. In the case of the resonance radiation 2537A° in mercury vapour at a pressure of the order of ·0002 mm., a field of 1·5 gauss applied in the direction of the magnetic vector of the incident light was sufficient to reduce the polarisation of the light emitted in that direction from 90 per cent. to about 10 per cent. Various interesting features of polarisation as the direction of the magnetic field was altered are recorded. A simple general explanation of the observed phenomena can be given by taking into account the Larmor precession of the approximately elliptic orbit of the electron round the direction of the magnetic field and the finite duration of the excited condition of the atom.

For convenience of reference, it is useful to summarise in a tabular form Wood's detailed observations which were made on sodium vapour at about 180°C. OX denotes the direction of the incident beam of plane polarised light and OY the direction of observation. When the direction of the electric vector of the incident light was parallel to OZ, the polarisation of the resonant light was 5 per cent. in zero field and it required a field of about 100 gauss parallel to OY to destroy the initial polarisation.

TABLE I.

Direction of Electric Vector in incident light.	Direction of magnetic field (100 gauss).	Polarisation.
OZ	OY	Nil
OZ	OX	Strong (about 30 p. c.) with el. vector II OZ.
OZ	OZ	Strong with el. vector II OZ.
OZ	45° with OZ in XZ plane	Nil
OY	zero field	Nil
OY	OX	Strong with el. vector II OZ.
OY	OZ	Strong with el. vector II OX.
OY	45° with OZ in XZ plane	Strong with el. vector $\perp^{r}$ field.

[1] Proc. Roy. Soc. A, Vol. 103, p. 396 (1923).

Results of the same general character were obtained with mercury vapour also, with the difference that the polarisation was much more pronounced and the various features came out with a much weaker field of about 2 gauss.

Simple Theory of the Changes of Polarisation in a Magnetic Field.

The effect of a magnetic field is to superpose on the motion of the electron a uniform rotation round the direction of the field, the frequency of rotation being $\pm$ He/4πmc.[1] We shall take the simple case when the resonance radiation is completely polarised in the absence of the field, as is nearly the case in mercury vapour. When the incident light is plane-polarised with the electric vector parallel to OZ and the light is observed along OY, the application of a magnetic field either along OX or OZ would cause the light to be polarised along OZ, because the rotation round OX or OZ cannot contribute anything to the X-component. As the magnetic field is gradually turned from OX to OZ, the axis round which precession takes place would also turn round and it is easily seen by decomposing the vibrations parallel and perpendicular to the field that the percentage of polarisation would first diminish to zero and again increase. The minimum of polarisation can easily be shown to occur when the magnetic field makes an angle θ with OX where $\tan^2\theta = 1/2$. This angle, which is nearly 35° differs appreciably from the 45° which Wood obtained with sodium vapour. When the electric vector is applied parallel to OY and the magnetic field is applied parallel to OX or OZ, the rotation of the orbits round the field would lead to strong polarisation, the stronger components being along OZ and OX respectively, and this will also be accompanied by an *increase* of intensity. All these results are in general agreement with Wood's observations.

[1] J. Larmor, Phil. Mag., 44, 503 (1897).

We cannot, however, expect quantitative agreement with the theory outlined above except in the case where the atom shows normal Zeeman effect. With atoms like sodium which exhibit an anomalous Zeeman effect, the effect of the magnetic field would not be a simple rotation round the direction of the field.[1] The 2,537 line of mercury also does not show a normal effect, but its Zeeman separation is of the normal triplet type with a separation $\frac{3}{2}$ times the normal value.

Period of Precessional Rotation and Duration of Excited State.

One interesting feature observed with mercury vapour was the gradual decrease of polarisation from 90 per cent. to 10 per cent. as the magnetic field along OY was increased from 0 to 1·3 gauss. The phenomenon admits of a simple explanation on the above theory. When the precessional rotation is very slow, most of the radiation would have taken place before the corresponding vibrations in the excited atoms have been deflected through an appreciable angle from OZ and the radiation would retain most of its initial polarisation. As the intensity of the field increases, the component of vibration along the original direction would diminish and that in a perpendicular direction would increase, until with large speeds of rotation the light would be completely unpolarised. Putting in numerical values, the period of precessional rotation $4\pi mc/eH$ round the direction of the magnetic field is $7\times10^{-7}/H$ sec, and according to the measurements of Wien[2] on the gradual decrease of intensity of the 2,537 line of mercury when positive rays are allowed to stream into a

[1] G. Breit (Phil. Mag., May, 1924) has succeeded in explaining the leading features of the polarisation of resonance radiation in sodium vapour on the lines of the quantum-theory of anomalous Zeeman Effect.

"Molrefraction von Ionen und Molekülen in Lichte der Atomstructur" by K. Fajan and G. Joos—Zeitschrift Für Physik, April, 1924, p. 1.

[2] Wien; Ann der Physik, 73, p. 483, 1924.

high vacuum, the intensity diminishes with time in the ratio[1] e^{-2at} where $2a=1\cdot02\times10^7$ sec.$^{-1}$ Let us consider a large number of atoms excited to resonance with vibrations parallel to OZ and rotated round the direction of the magnetic field OY with angular velocity ω. The intensity of radiation from the atoms whose corresponding vibration directions make an angle θ with OZ would be, on the average, a^2e^{-2at} and the average amplitude would be ae^{-at} where t is the time required to turn through an angle θ under the precessional rotation, and a is the amplitude of the corresponding vibration when $t=0$. Resolving along OZ and OX, squaring, and integrating over all atoms at different stages of radiation from $t=0$ to $t=\infty$, we get

$$\frac{Z}{X}=\frac{\int_0^\infty e^{-2at}\cos^2\omega t\,dt}{\int_0^\infty e^{-2at}\sin^2\omega t\,dt}$$

where Z and X are the components of intensity with vibrations along OZ and OX respectively. The integrals are easily evaluated and give

$$\frac{Z}{X}=\frac{\omega^2+2a^2}{\omega^2}$$

Hence, the polarisation as observed along the Y axis is measured by

$$\frac{Z-X}{Z+X}=\frac{a^2}{\omega^2+a^2}$$

[1] It does not matter for our present purpose whether this exponential decrease in intensity is due to the rate of decrease in the number of quantum-jumps or whether it is due to an exponential decrease with time of each elementary process of radiation. For a discussion, see G. Mie; Ann. der Physik, 73, p. 195, 1924.

This shows a gradually decreasing polarisation as ω is increased.

Substituting Wien's value of 2α in our expression, we obtain a series of values for the polarisation for different intensities of the magnetic field. These have been plotted in Figure I. Wood's experimental values have also been plotted for comparison. The *course* of experimental values of the polarisation is well reproduced by the theoretical curve. It should be remembered that we have assumed perfect polarisation for zero field, while the experimental value was 90 per cent.

Mean Interval between Molecular Collisions and Duration of Excited State.

There is yet another direction from which we can get some information regarding the duration of emission. Wood has observed that the intensity and polarisation of resonance radiation in mercury vapour are affected by admixture with other gases.[1] The addition of helium or argon increases the intensity while the addition of air or hydrogen diminishes it, but in all cases, the effect of the addition is to diminish the polarisation. It is obvious that the effect of some of the collisions of an excited mercury atom with a molecule of hydrogen or of air is to prevent the radiation taking place. But not all collisions are deadly, as is shown by the increasing imperfection of polarisation on increase of pressure. We may take it that a collision would disturb the electron-orbit of the excited atom; when the disturbance is mild, the effect will only be to change the configuration of the orbit thus disturbing the polarisation and to give it a slow rotation which would slightly affect the frequency of the emitted radiation, and when the disturbance is intense, the radiation

[1] Phil. Mag., Vol. 44, p. 1107 (1922).

of the proper frequency will altogether be prevented.[1] From the chemical behaviour of the molecules and their behaviour towards free electrons, we may expect that collisions with helium and argon would on the whole be mild and that they would get more and more intense in the order nitrogen, hydrogen and oxygen.

For the same mean interval between two collisions of a mercury atom with a gas molecule the effect on the polarisation of the resonance radiation would be less and less marked (and the destructive effect on the intensity more and more marked) as we proceed in the same order, for in the latter gases, only a smaller fraction of the excited atoms can stand the shock of a collision and yet retain the power to radiate.

The following table shows the changes of intensity and polarisation as the mean interval between two collisions is altered. The experimental data have been taken from Wood's paper. The mean interval between two collisions of a mercury atom with a gas molecule has been calculated from the formula

$$\frac{1}{t} = 2v_2 s_{12}^2 \sqrt{\frac{\pi}{h}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}$$

(Jeans, Dynamical Theory of Gases, Second Edition, page 268) where v_2 is the number of molecules of the gas per c.c, s_{12} the sum of the radii of a mercury atom and of a gas molecule assuming them to be spherical, and m_1 and m_2 are the masses of a mercury atom and of a gas molecule respectively. The diameter of a mercury atom has been assumed to be $3 \cdot 2 \times 10^{-8}$cm. as calculated from the atomic volume (Sommerfeld : Atombau und spectral linien, p. 122, 3rd edition). The diameter of the excited atom is probably greater than that of

[1] Klein and Rosseland's impact of the "second kind," Zeit. fur Physik, 4, 46, 1921.

the normal one and the mean intervals given below too large on that account. The collisions of two mercury atoms with each other have been neglected as the vapour pressure of mercury was very small compared with the pressure of the added gases.

TABLE II

Gas.	Pressure.	Mean interval between two collisions of a mercury atom with a gas molecule.	Intensity on an arbitrary scale.	Polarisation.
Argon	3 mm.	6×10^{-8} sec	5	Faint
	5 mm.	$3{\cdot}6 \times 10^{-8}$ sec	10	Gone
Helium	2 mm.	5×10^{-8} sec	4	Faint
	6 mm.	$1{\cdot}7 \times 10^{-8}$ sec	10	Gone
Air ($0{\cdot}8\ N_2 + 0{\cdot}2\ O_2$)	0·65 mm.	$2{\cdot}4 \times 10^{-7}$ sec	2·5	Strong
	4 mm.	4×10^{-8} sec	1·	Nearly Gone
	1 cm.	$1{\cdot}6 \times 10^{-8}$ sec	0·5	Gone
Hydrogen	0·65 mm.	9×10^{-8} sec	1·	Strong
	4 mm	$1{\cdot}5 \times 10^{-8}$ sec	0·5	Faint
	1 cm.	$0{\cdot}6 \times 10^{-8}$ sec	0·2	A trace

When the added gas is helium or argon, the interpretation of polarisation is not simple inasmuch as Wood has found that when mixed with these gases, the mercury atom can be excited over a small range of frequencies lying on either side of the proper resonating frequency, and we cannot *assume* that this resonant radiation would be as polarised as that excited by the core of the line. The case of air also is not simple, because we have here two kinds of collisions, collisions with nitrogen molecules and collisions with oxygen molecules. Of these, the former may be expected to give rise to some unpolarised light while the latter will be more effective in

causing a radiationless transfer of the electron. In hydrogen, which causes the most marked change in intensity, we have, I think, the least complicated case.[1] When the mean interval between two collisions of a mercury atom with a hydrogen molecule is 9×10^{-8} sec, the polarisation is strong, but when the interval has come down to $0\cdot6\times10^{-8}$ sec, it has become a mere trace. From this, we can infer that a considerable part of the radiation has taken place between two collisions in the first case and that only a small part has taken place in the second. Assuming an exponential decrease of radiation with time, it is easy to calculate the average amount of radiation in the interval between two collisions. We have to remember that the time during which radiation can take place may be anything from o to t as the atom may be excited at any instant between two collisions. We thus get for the average fraction of energy radiated in the interval between two collisions [2]

$$R=1-\frac{1}{2at}\left(1-e^{-2at}\right)$$

Adopting Wien's value of $2a$ for 2,536 line of mercury, we get the following values of R for various values of t.

TABLE III.

$t\times10^8$ sec.	R.
20	·57
10	·37
5	·22
2	·10
1	·05

[1] It is of interest to note that Franck and Cario have found that collisions of excited mercury atoms with hydrogen molecules cause them to dissociate. Such a collision will certainly be radiationless. (Zeit. fur Physik, 11, 161, 1922.)

[2] Cario, Zeit. fur Physik 10, 185, 1922. Also Mie, loc. cit.

Of the unradiated part 1—R, most of it would disappear on collision (being convert into other forms of energy) with the exception of a small fraction which would appear as unpolarised radiation. As T decreases, this fraction would increase and the polarised part R decrease, both causes tending to reduce the polarisation. Comparison of Table III with the figures for hydrogen in Table II show that this is sufficient to account for the leading features of the phenomenon.

The importance of obtaining further quantitative data in this field is obvious.

Summary.

1. The changes of polarisation of the resonance radiation of the vapour of mercury in weak magnetic fields which have been studied by Wood and Ellett can be explained by taking into account the Larmor precession of the orbit of the electron round the direction of the magnetic field and the finite duration of the excited condition of the atom.

2. The duration of excited state required to explain the decrease of polarisation in mercury vapour resonance when a magnetic field is applied parallel to the direction of observation and perpendicular to the incident beam of light is consistent with Wien's determination of the same quantity.

The changes of intensity and polarisation of the resonance radiation when mercury vapour is mixed with other gases can also be explained by assuming that there is a finite time during which the atom remains in the excited state, and that the effect of a collision is either to destroy the radiation, or to disturb the polarisation so as to make its direction random.

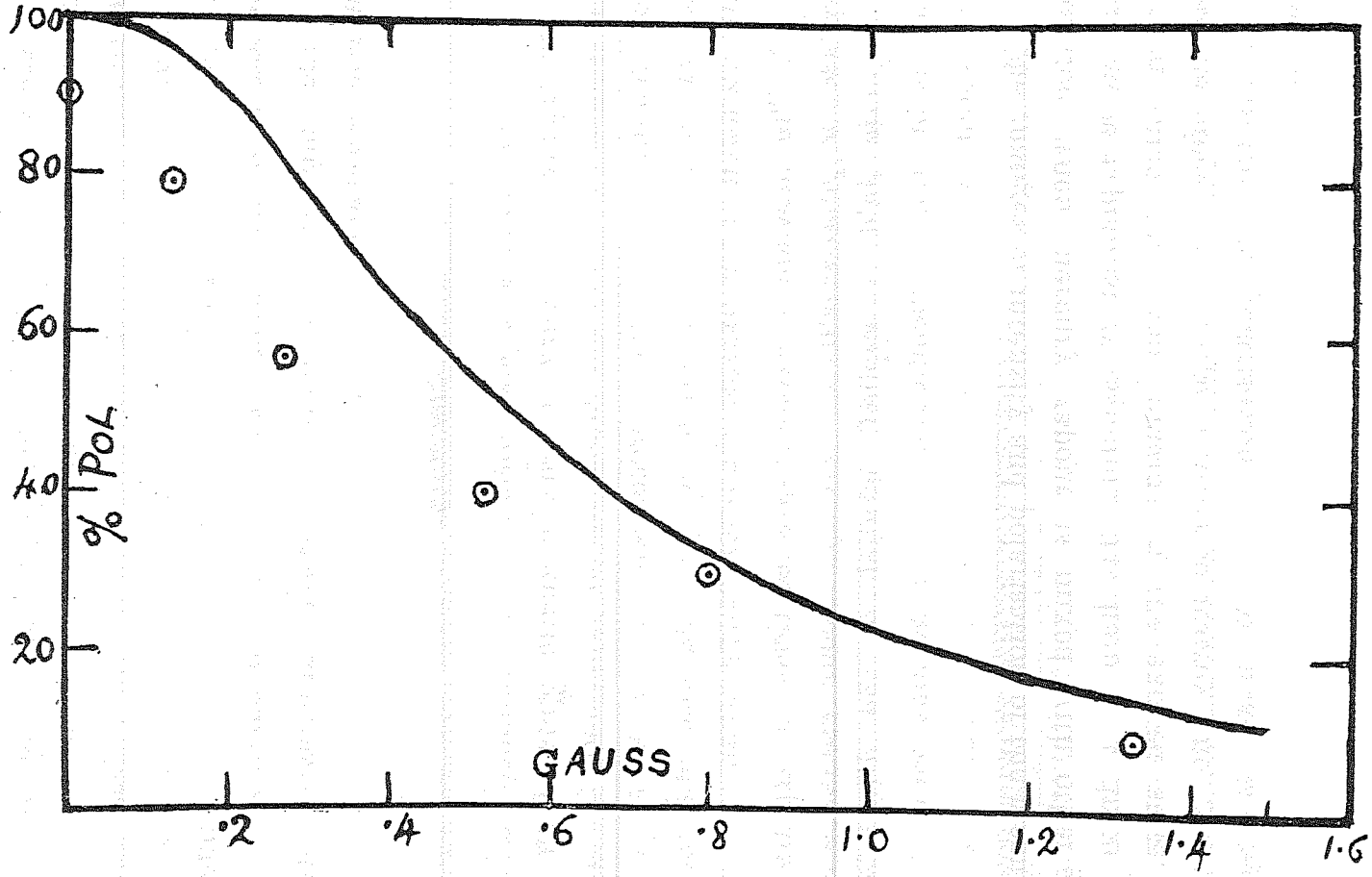

FIG. I.